

# **PNCS16**

## **CANTERBURY 2022**

### **PROGRAMME AND ABSTRACTS**

**16th International Conference on the  
Physics of Non-Crystalline Solids**

**University of Kent, Canterbury**

**10–15 July 2022**



# **16th International Conference on the Physics of Non-Crystalline Solids**

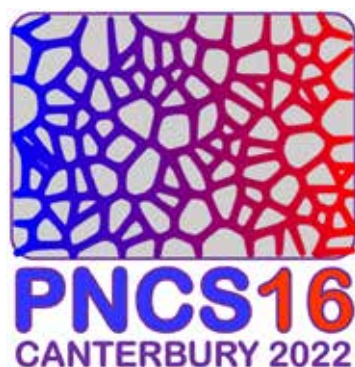
**University of Kent, Canterbury**

**10–15 July 2022**

**Programme**

**and**

**Abstracts**



**Sponsors**

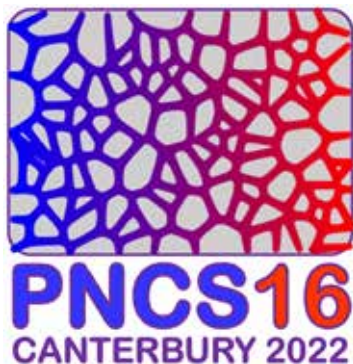


**ISIS Neutron and  
Muon Source**



**16th International Conference on the Physics of Non-Crystalline Solids**  
University of Kent, Canterbury, UK. 10–15 July 2022. Programme and Abstracts

Conference co-chairs Alex C. Hannon and Gavin Mountjoy



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2022 is the United Nations International Year of Glass  
[www.iyog2022.org](http://www.iyog2022.org)

# PNCS16 Honorary Sessions

At the 16<sup>th</sup> International Conference on the Physics of Non-Crystalline Solids in Canterbury, there will be two special sessions in honour of two recently deceased exceptional scientists, who made major contributions to the study of non-crystalline solids, and who were both members of the PNCS International Advisory Board.

## C. Austen Angell, 1933–2021

*Session to be held on Monday 11th July afternoon*

Austen Angell was an internationally recognised luminary in the fields of glasses, water and ionic liquids. He introduced the strong/fragile classification of liquids, and the “Angell plot” of glass-forming liquids is probably his most celebrated emblem. You are encouraged to refer to his autobiography,<sup>(1)</sup> an online biography,<sup>(2)</sup> obituaries,<sup>(3,4)</sup> or a recent journal issue in his honour.<sup>(5)</sup>

## G. Neville Greaves 1945–2019

*Session to be held on Tuesday 12<sup>th</sup> July afternoon*

Neville Greaves was a key figure in the early development of techniques and instrumentation for the exploitation of synchrotron radiation. His research interests were very wide, but he has become known above all for proposing the Modified Random Network model of glasses. You are encouraged to refer to an online obituary,<sup>(6)</sup> a recent journal issue in his honour,<sup>(7)</sup> or an account of his work with synchrotron radiation.<sup>(8)</sup>



Austen Angell



Neville Greaves

1. Angell, C. A. Charles Austen Angell biography. *J. Phys. Chem B*, 1999, **103**, 3977–3978.
2. [https://en.wikipedia.org/wiki/Austen\\_Angell](https://en.wikipedia.org/wiki/Austen_Angell)
3. Lucas, P., Martin, S. W., Kieffer, J., Poole, P. H. & Wei, S. Charles Austen Angell, 1933–2021. *J. Non-Cryst. Solids*, 2021, **568**, 120869.
4. Debenedetti, P. G., Poole, P. H., Sastry, S. & Sclortino, F. Obituary C. Austen Angell (1933–2021), *Nature*, 2021, **593**, 336.
5. Lucas, P., Alba-Simionesco, C., Yue, Y., Kieffer, J. & Martin, S. W. “Glass is frozen beauty” - A Memorial Issue in Honor of C. Austen Angell (1933–2021). *J. Non-Cryst. Solids*, 2022, **X14**, 100096.
6. <https://www.aber.ac.uk/en/development/alumni/obituaries/obituary-profiles/neville-greaves/>
7. Bras, W., Catlow, R., Chadwick, A., Millan, P. M., Sankar, G., Sen, S. & Takada, A. The physics and chemistry of disordered materials. *J. Non-Cryst. Solids*, 2016, **451**, 1.
8. Chadwick, A. V. & Catlow, C. R. A. A tribute to the scientific career of Neville Greaves: The Daresbury years. *J. Phys.: Condens. Matter*, 2021, **33**, 320401.

Speaker names are underlined. Invited speakers \*.

All talks and posters will be presented in the Sibson Building, University of Kent.

Talks will be presented in the main lecture theatre (*LT3*), or lecture theatre 1 where indicated: *LT1*

The poster session will take place in Sibson Seminar Room 1.

At 13:15 on Monday, Tuesday, Wednesday and Thursday, a two-course lunch will be provided at Rutherford College, University of Kent

### PNCS16 : MONDAY 11 JULY : OPENING

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**Session chair: Alex Hannon**

- 09.00 Opening  
Alex Hannon & Gavin Mountjoy
- 09.15 Controlled crystallization of amorphous chalcogenide thin films for solar energy harvesting  
Xianghua Zhang,\* Guangxing Liang, Ping Fan, Shuo Chen, Donglou Ren, Michel Cathelinaud & Hongli Ma
- 09.45 NMR and atomistic simulation reveal structural relaxation and crystallization in supercooled liquids and glasses  
Andrea de Camargo,\* Hellmut Eckert & Edgar Dutra Zanotto\*

### PNCS16 : MONDAY 11 JULY : THEORY & SIMULATION 1

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**Session chair: Alastair Cormack**

- 10.15 Modern computer simulations of simple models for supercooled liquids and glasses  
Ludovic Berthier\*
- 10.45 **Coffee**

### PNCS16 : MONDAY 11 JULY : THEORY & SIMULATION 2

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**Session chair: Alastair Cormack**

- 11.15 Hyperbonding in glassy tellurides: the case of phase-change memory materials  
Tae Hoon Lee & Stephen Elliott
- 11.30 Phase separation and structural evolution of oxyfluoride glasses from molecular dynamics simulations  
Jincheng Du
- 11.45 Study of ultra-stable thin films using swapping in molecular dynamics simulations  
Richard B. Stephens
- 12.00 Engineered structural relaxation of amorphous phase-change memory materials via the application of electric fields  
Konstantinos Konstantinou, Felix C. Mocanu, Jaakko Akola & Stephen R. Elliott
- 12.15 Energy landscapes and structure in ion conducting solids  
Karl-Michael Weitzel
- 12.30 Structure factor of a phase segregating binary mixture affected by natural and forceful molecular interconversion  
Thomas J. Longo, Nikolay A. Shumovskyi, Salim M. Asadov, Sergey V. Buldryev
- 12.45 Atomic-scale modeling of tellurium oxide glass: network topology and third-order non-linear properties  
Raghvender Assil Bouzid, Philippe Thomas & Olivier Masson
- 13.00 **Lunch**

### PNCS16 : MONDAY 11 JULY : ANGELL SESSION 1

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**Session chair: Yuangzheng Yue**

- 14.30 A perspective on the fragility of glass-forming liquids  
Christiane Alba-Simionesco\* & Gilles Tarjus
- 15.00 The glass transition of water, insight from phase change materials  
Pierre Lucas, Julian Pries, Shuai Wei & Matthias Wuttig
- 15.15 Anomalous liquids on a new landscape: from water to phase-change materials  
Shuai Wei
- 15.30 Fragility and the rate of change of the energy landscape topography  
M. Cameran Beg & John Kieffer

15.45 **Coffee**

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**PNCS16 : MONDAY 11 JULY : ANGELL SESSION 2**

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**Session chair: Christiane Alba-Simionesco**

- 16.15 How much do we know about the fragility of glass-forming liquids? In honour of Austen Angell  
Yuanzheng Yue\*
- 16.45 Characterisation of the dynamics and structure of the boson peak in a supercooled and vitrified small-molecule liquid  
Mario González-Jiménez, Trent Barnard, Ben A. Russell, Nikita V. Tukachev, Laure-Anne Hayes, Andrew J. Farrell, Sarah Guinane, Hans M. Senn, Andrew J. Smith, Martin Wilding, Paul McMillan, Gabriele C. Sosso, & Klaas Wynne
- 17.00 A heart of glass – two-level systems in a fragile glass model  
Felix-Cosmin Mocanu, Camille Scalliet, Dmytro Khomenko, Simone Ciarella, Ludovic Berthier, David R. Reichman & Francesco Zamponi
- 17.15 Neodymium titanate: exploring structure, viscosity and density for the fragile liquid of an octahedral network glass  
Stephen K. Wilke, Richard Weber, Vrishank Menon, Jared Rafferty, Chihiro Koyama, Takehiko Ishikawa, Hirohisa Oda, Shinji Kohara, Michael SanSoucie, Chris J. Benmore, Oliver L.G. Alderman & Jörg Neuefeind

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**PNCS16 : MONDAY 11 JULY : THEORY & SIMULATION 3**

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**Session chair: Gavin Mountjoy**

- 17.30 Graphitization of amorphous carbon  
D. A. Drabold, R. Thapa, C. Ugwumadu, Kishor Nepal & J. Trembly
- 17.45 Effect of Ca/K replacement on the atomic structure of  $P_2O_5$ - $K_2O$ -CaO glasses – A molecular dynamics study  
Bushra Al Hasni
- 18.00 **End**

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**PNCS16 : TUESDAY 12 JULY : GLASS FORMATION**

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**Session chair: Chris Benmore**

- 09.00 Connecting coordination change to configurational properties in glass-forming liquids  
Oliver L. G. Alderman,\* Chris J. Benmore, Steve Feller & Rick Weber
- 09.30 Atomistic simulations of melting silicates  
Alastair N. Cormack
- 09.45 New understanding of liquid thermodynamics, viscosity and its lower bounds  
Kostya Trachenko
- 10.00 Relaxation dynamics of glass forming metals: Study of aging, delayed elasticity and supercooled liquid behaviors in a ZrTiCuNiBe alloy  
Mehran Nabahat & Eloi Pineda

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**PNCS16 : TUESDAY 12 JULY : PHYSICAL PROPERTIES LT1**

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**Session chair: Paul Bingham**

- 09.30 The influence of  $ZrO_2$  addition on thermal behavior and mechanical properties of  $Al_2O_3$ - $Y_2O_3$ - $ZrO_2$  ceramics  
Jana Valúchová, Anna Prnová, Beáta Pecušová, Milan Parchovianský, Monika Michálková, Róbert Klement & Dušan Galusek
- 09.45 Enhanced mobility of lithium and sodium ions in phosphate glasses obtained by  $WO_3$  and  $MoO_3$  addition  
Sanja Renka, Luka Pavić, Grégory Tricot, Tomáš Hostinský, Petr Kalenda, Petr Mošner, Ladislav Koudelka, Andrea Moguš-Milanković & Ana Šantić
- 10.00 Thermal, chemical and phase property changes in Hanford analogue glasses with varying  $Fe_2O_3$  contents  
I. D. Eales, K. M. Fox, A. A. Kruger, A. Goel, D. P. Guillen, J. S. McCloy, J. D. Vienna, S. Aminorroaya-Yamini & P. A. Bingham

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## PNCS16 : TUESDAY 12 JULY : DENSIFICATION & PHASE CHANGES 1

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**Session chair: Chris Benmore**

- 10.15 Structure and dynamics in densified silica glass  
Shinji Kohara\*

10.45 **Coffee**

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## PNCS16 : TUESDAY 12 JULY : DENSIFICATION & PHASE CHANGES 2

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**Session chair: Chris Benmore**

- 11.15 Thermal relaxation of electron irradiated densified silica phases  
M. Mobasher, M. Lancry, D. Neuville & N. Ollier
- 11.30 Structural approach and relaxation processes according to thermo-mechanical histories of densified silicate glasses  
Antoine Cornet, Christine Martinet, Dominique De Ligny, Thierry Deschamps & Valérie Martinez
- 11.45 Tomographic spectroscopic of densification process of silicate glasses under micro-indentation  
Alice Berthelot, Elodie Romeo & Christine Martinet
- 12.00 Pressure induced fast atomic motion in metallic glasses at extreme conditions  
Antoine Cornet, Shubin Li, Thierry Deschamps, Christine Martinet, Yuriy Chushkin, Federico Zontone, Gaston Garbarino, Mohamed Mezouar & Beatrice Ruta
- 12.15 Structural transformation and phase change properties of Se substituted GeTe  
Roopali Shekhawat, Shweta Chahal, Haritha Pamuluri, Vinod Erkkara Madhavan & K. Ramesh
- 12.30 Co-sputtered Ga–Sb–Te thin films: phase change material characterization  
M. Kotrla, J. Přikryl, P. Janíček, J. Gutwirth, T. Halenkovič, F. Cheviré, V. Nazabal & P. Němec
- 12.45 Phase relations in heat treated sodium borosilicate glasses – investigations by thermal analysis and scanning electron microscopy  
Hans Roggendorf, Stephan A. H. Sander & Dirk Enke

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## PNCS16 : TUESDAY 12 JULY : NUCLEAR WASTE STORAGE LT1

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**Session chair: Georges Calas**

- 11.15 Characterisation of crystalline material in simulated UK vitrified high-level waste using Raman spectroscopy  
Mike Harrison, Mark Sarsfield & Josh Holt
- 11.30 Characterization, structure refinement and durability of sodium iron phosphate glass ceramic materials for immobilization of spent fuel  
Liam Harnett, Martin Stennett, Ewan Maddrell, Neil Hyatt & Russell Hand
- 11.45 Solubility of uranium oxide in aluminosilicate glass melts  
Olivier Podda, Laurent Tissandier, Annabelle Laplace & Etienne Deloule
- 12.00 Volatilisation from borosilicate radioactive waste glasses  
Alex H. Stone, Aleksey Nabok, Alan Holloway, Sean P. Morgan, Donna McKendrick & Paul A. Bingham
- 12.15 Radiation induced diffusion in UK-nuclear waste glasses  
P. Sanchez-Morillas, Aine Black, J. Sanchez-Prieto, Alex Scrimshire,
- 12.30 Alternative foam reductants for the vitrification of high-iron Hanford High Level Waste (HLW) feeds  
I. C. Rigby, D. R. Dixon, J. Kloužek, R. Pokorný, P. B. J. Thompson, A. A. Kruger, A. M. T. Bell & P. A. Bingham
- 13.00 **Lunch**



## PNCS16 : TUESDAY 12 JULY : GREAVES SESSION 1

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**Session chair: Martin Wilding**

- 14.30 Structural versus chemical disorder in modified random networks  
Sabyasachi Sen\*
- 15.00 Investigation of the properties and structure of fragile metal oxide liquids  
Richard Weber, Stephen K. Wilke, Chris J. Benmore, Michael SanSoucie, Vrishank Menon, Jared Rafferty, Shinji Kohara, Hirohisa Oda, Chihiro Koyama & Takehiko Ishikawa
- 15.15 Combined X-ray diffraction and X-ray absorption spectroscopy: a valuable tool to determine atomic architecture of reacting solids  
Gopinathan Sankar
- 15.30 Sodium silicate glasses: the structural roles of sodium and oxygen  
Alex C. Hannon, Shuchi Vaishnav, Oliver L. G. Alderman & Paul A. Bingham
- 15.45 **Coffee**

## PNCS16 : TUESDAY 12 JULY : GREAVES SESSION 2

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**Session chair: Sebyasachi Sen**

- 16.15 The influence of nitrogen on the structure and properties of lithium and sodium metaphosphate glass electrolytes  
Martin C. Wilding\*, Steve Kmiec, Steve. W. Martin, Mark Wilson & Alex C. Hannon
- 16.45 A critical evaluation of barium silicate glass network polymerization  
B. J. A. Moulton, A. Picinin, L. D. Silva, C. Doerenkamp, H. Lozano, D. Sampaio, E. D. Zanutto, J. Due, H. Eckert & P. S. Pizani
- 17.00 Computer modelling of pressure-induced structural disorder in  $\text{ZrW}_2\text{O}_8$  to explore paradigms for solid state amorphization  
Gavin Mountjoy & Finnian Stanford
- 17.15 Electric transport and crystallization in  $\text{V}_2\text{O}_5\text{-TeO}_2$  glass and glass-ceramics  
Piotr Okoczek, Natalia Wójcik, Marcin Łapiński, Piotr Winiarz, Leon Murawski, Leszek Wicikowski & Barbara Kościelska

## PNCS16 : TUESDAY 12 JULY : CRYSTALLISATION

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**Session chair: Sebyasachi Sen**

- 17.30 Characterisation of metastable phase formation in binary AuGe via correlated flash differential scanning calorimetry and electron microscopy  
Štefan Stanko, Jürgen E. K. Schawe & Jörg F. Löffler
- 17.45 **End**
- 18.30 **Poster Session and Buffet – Seminar Room 1**
- 20.00 **End**

## PNCS16 : WEDNESDAY 13 JULY : STRUCTURE - NMR

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**Session chair: Richard Brow**

- 09.00 NMR studies of glass structure: current issues  
Josef W. Zwanziger\*
- 09.30 Multinuclear NMR investigation of the composition-dependent structural role of  $\text{Pb}^{2+}$  in lead borogallate and boroaluminate glasses  
S. Kroeker, A. Krishnamurthy, J. E. C. Wren & V. K. Michaelis
- 09.45 Study of the short- and medium-range structural order in  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$  glasses doped with  $\text{P}_2\text{O}_5$   
Katrina Skerratt-Love, Ulrike Werner-Zwanziger, Josef Zwanziger, Francis Sweeney, Anthony M. T. Bell, Jaime George, Albert A. Kruger & Paul A. Bingham
- 10.00 Extent of structural disorder in  $\text{SrO-Ga}_2\text{O}_3\text{-2SiO}_2$  glass and  $\text{SrGa}_2\text{Si}_2\text{O}_8$  transparent ceramic from advanced solid-state NMR spectroscopy  
Amandine Ridouard, Cécile Genevois,<sup>1\*</sup> Michael J. Pitcher, Mathieu Allix, Dominique Massiot & Franck Fayon



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## PNCS16 : WEDNESDAY 13 JULY : OPTICAL PROPERTIES 1 LT1

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### Session chair: Laurence Galois

- 09.30 Development of glass optical fibers 1978–2021 providing us the digitalized communication world  
Tarja T. Volotinen & C. Bertil Arvidsson
- 09.45 Erbium fluorescence by energy transfer from defects states in As–Se thin films  
Y. N. Colmenares, Maria José Bell, Sandra Helena Messaddeq & Younès Messaddeq
- 10.00 Photo-thermal precipitation of PbS quantum dots in glass using Co<sup>2+</sup> light absorption  
Jong Heo, Hojeong Lee, Tihitnaw Fentahun Degu & Yong K. Kwon
- 10.15 Carbon dots in mesoporous silica matrices: promoting green emission  
ChiaraOlla, Luigi Stagi, Maria Francesca Casula, Marzia Fantauzzi, Francesca Mocci, Pier Carlo Ricci & Carlo Maria Carbonaro

### 10.45 Coffee

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## PNCS16 : WEDNESDAY 13 JULY : STRUCTURE - DIFFRACTION 1

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### Session chair: Uwe Hoppe

- 11.00 Automated development of machine learning inter-atomic potentials driven by diffraction experiments  
Chris J. Benmore\* & Ganesh Sivaraman
- 11.30 Interpolation method for calculation of disorder in PDF and XAS  
Lucy Haddad, Ying Liu, Lei Tan, Martin Dove, David Dunstan, Stanislav O. Yurchenko, Nikita Kruchkov, Lukia Mistryukova & Andrei Sapelkin

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## PNCS16 : WEDNESDAY 13 JULY : METALLIC GLASSES

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### Session chair: Uwe Hoppe

- 11.45 Diffusion in metallic and in oxide glasses – an overview  
H. Mehrer
- 12.00 The Invar effect of Fe-based bulk metallic glasses at the atomic scale  
Alexander Firlus, Mihai Stoica, Stefan Michalik, Robin E. Schäublin & Jörg F. Löffler
- 12.15 Viscoelastic behavior of high-entropy metallic glasses  
Y. J. Duan, E. Pineda, D. Crespo & J. C. Qiao

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## PNCS16 : WEDNESDAY 13 JULY : OPTICAL PROPERTIES 2 LT1

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### Session chair: Jeong Heo

- 11.30 Color–structure relationships in transition element bearing borate glasses  
Laurence Galois, Georges Calas, Myrtille Hunault, Laurent Cormier & Gerald Lelong
- 11.45 Controlling glass properties through surface mediated equilibration  
Zahra Fakrhaai, Aixi Zhang, Peng Luo, Shivajee Govind, Richard Stephens, Yi Jin & Sarah Wolf
- 12.00 Impact of glass composition on electro-magnetic radiation effects observed in phosphate optical and photonic glass materials  
Owen McGann, Hanna Profeta & Adam Jackson
- 12.15 Effect of batch content and preparation conditions on the colour of glass: iron–manganese coloured soda–lime–silica glasses  
David B. Hollis & Tarja Volotinen
- 13.00 **Lunch**
- 14.15 **Excursion to Leeds Castle**
- 19.00 **for Conference Banquet**
- 19.30 The Conference Banquet will be held at the Darwin Conference Centre, Darwin College, University of Kent

## PNCS16 : THURSDAY 14 JULY : HEAVY METAL IONS

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### Session chair: Phil Salmon

- 09.00 Network-forming oxides with non-centrosymmetric structural groups – diffraction results of molybdate and antimonite glasses  
Uwe Hoppe,\* Aswini Ghosh & Dörte Stachel
- 09.30 Novel insights into the roles of WO<sub>3</sub> and MoO<sub>3</sub> in the electrical conductivity of phosphate glasses  
Ana Šantić, Sanja Renka, Juraj Nikolić, Luka Pavić, Ladislav Koudelka, Petr Mošner, Petr Kalenda & Andrea Moguš-Milanković
- 09.45 Structural role of lanthanum and yttrium onto heavy metal oxide (HMO) gallo–germanate glass network for infrared optical fiber applications  
Florian Calzavara, Pierre Florian, Vincent Sarou-Kanian, Frank Fayon, Sylvain Danto, Marc Dussauze, Véronique Jubera, Thierry Cardinal & Evelyne Fargin
- 10.00 Structure and properties of potassium niobato-phosphate glasses  
Ladislav Koudelka, Petr Mošner & Lionel Montagne
- 10.15 Insights on the relationship between structural and electrical properties in sodium vanadium niobium phosphate glasses  
Sara Marijan, Marta Razum, Teodoro Klaser, Željko Skoko, Jana Pisk & Luka Pavić

## PNCS16 : THURSDAY 14 JULY : APPLIED GLASS SCIENCE *LT1*

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### Session chair: Angela Seddon

- 09.30 The use of controlled dissolution glasses for the consolidation and strengthening of loose rock soil and sediments  
Marlin Magallanes, Chris Holcroft, Arne Stavland, Nils Harald Giske, Ragni Hatlebakk, Max Olsen & Martyn Marshall
- 09.45 An approach to using biomass ashes as glass batch materials: towards net zero glass production  
W. Deng, D. J. Backhouse, F. Kabir, R. Janani, C. Holcroft, M. Marshall, M. Magallanes, C. M. Jackson & P. A. Bingham
- 10.00 The use of secondary raw materials derived from industrial wastes in glass manufacture enabling increasing recycled content beyond cullet  
Martyn Marshall, Adam Jackson, Marlin Magallanes, Chris Holcroft, Robert Werner, Daniel J. Backhouse, Wei Deng, Hywel Jones, Feroz Kabir & Paul A. Bingham
- 10.30 **Coffee**

## PNCS16 : THURSDAY 14 JULY : DIFFRACTION 2

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### Session chair: Shinji Kohara

- 11.00 Nanotectonic effect, viscosity anomaly, transient immiscibility and semiconductor-metal transition in Ga–Te liquids and glasses  
Daniele Fontanari, Anton Sokolov, Mohammad Kassem, Maria Bokova, Eugene Bychkov,\* Alex C. Hannon, Chris J. Benmore, Takeshi Usuki & Koji Ohara
- 11.30 Short range order in glassy KSb<sub>5</sub>S<sub>8</sub>  
Pál Jóvári, Ivan Kaban, Ildikó Pethes, Shinji Kohara, Brigitte Beuneu & Spyros Yannopoulos
- 11.45 Short range order in binary Ge–S glasses  
I. Pethes, P. Jóvári, S. Michalik, T. Wagner, V. Prokop, I. Kaban, A. C. Hannon & M. Krbal
- 12.00 Structure of magnesium aluminosilicate glass  
Hesameddin Mohammadi, Lawrence V. D. Gammond, Rita Mendes Da Silva, Anita Zeidler, Randall E. Youngman, Bruce G. Aitken & Philip S. Salmon

## PNCS16 : THURSDAY 14 JULY : FUNDAMENTAL STUDIES

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### Session chair: Eugene Bychkov

- 12.15 Amorphous chalcogenide thin films: tailoring of multisource sputtering conditions towards required chemical composition  
Jan Gutwirth, Magdaléna Kotrla, Tomáš Halenkovič, Virginie Nazabal & Petr Němec
- 12.30 Phosphate glasses – chemical point of view  
Jana Holubová, Zdeněk Černošek & Monika Chládková
- 12.45 The structure of glasses – as seen through their behaviour in a magnetic field and now under a simple microscope  
Giancarlo Jug

## PNCS16 : THURSDAY 14 JULY : IONS IN GLASS LT1

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### Session chair: Mike Harrison

- 11.30 Structure–property relationships of ferrous and ferric iron containing glasses  
Georges Calas, Laurence Galois, Gérald Lelong & Laurent Cormier
- 11.45 Charge transfer transitions in glasses  
Doris Möncke & Doris Ehrt
- 12.00 Functionalisation of hydrated phosphate glasses with tungsten oxide nanoparticles for optical applications  
S. Kaser, M. Duttine, S.H. Santagneli, Y. Badour, T. Guérineau, M. Gaudon, T. Cardinal, Y. Messaddeq
- 12.15 X-ray beam as a source and probe of defects nucleation  
Erica Alfinelli, Alessandro Martinelli, Giulio Monaco, Marco Zanatta & Giacomo Baldi
- 12.30 3D localization beyond diffraction limit of near-IR emission excited by resonant energy transfers from silver clusters in phosphate glasses  
Fouad Alassani, Gustavo Galleani, Guillaume Raffy, Joëlle Harb, Andrea Simone Stucchi de Camargo, Véronique Jubera, Lionel Canioni, Thierry Cardinal & Yannick Petit
- 12.45 Photoluminescence studies of transition metal doped soda–lime–silica glasses  
Tarja T. Volotinen, Ilknur Bayrak Pehlivan & David B Hollis
- 13.00 **Lunch**

## PNCS16 : THURSDAY 14 JULY : CHALCOGENIDES

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### Session chair: Xianghua Zhang

- 14.30 Structure–property relationships in Ge–Sb–Se chalcogenide glasses  
Emma Barney,\* Mohammad Al Hammouri, James Towey, Jessica Butterworth, Harriet Parnell, Boyu Xiao, David Furniss, Trevor M. Benson & Angela B. Seddon
- 15.00 Mercury iodide containing chalcogenide glasses: structural, macroscopic and electric properties  
Maria Bokova, Mohammad Kassem, Alex C. Hannon & Eugene Bychkov
- 15.15 Thermal and optical properties of Ge–Te–Se glasses for infrared transmitting glasses  
Shweta Chahal, Roopali Shekawat & K. Ramesh
- 15.30 Structural insight into sodium thiogermanate Na<sub>2</sub>S–GeS<sub>2</sub> glasses and relation to properties  
M. Kassem, T. Bounazef, D. Fontanari, A. Sokolov, M. Bokova, A. Hannon & E. Bychkov

## PNCS16 : THURSDAY 14 JULY : SILICATE GLASSES

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### Session chair: Josef Zwanziger

- 16.15 Structural model for amorphous aluminosilicates  
Lawrence V. D. Gammond, Rita Mendes Da Silva, Hesameddin Mohammadi, Anita Zeidler, Randall E. Youngman, Bruce G. Aitken, Henry E. Fischer, Alex C. Hannon, Chris J. Benmore & Philip S. Salmon\*
- 16.45 Misconceptions and flawed assumptions, with regard to silicate glasses: the high frequency bands of vitreous SiO<sub>2</sub>  
Grant S. Henderson, G. M. Bancroft, H. W. Nesbitt & P. A. Dean

- 17.00 Two-point bend studies of the inert failure characteristics of pristine glasses  
Richard K. Brow

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**PNCS16 : THURSDAY 14 JULY : THEORY & SIMULATION 4**

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**Session chair: Stephen Elliott**

- 17.15 Dynamical relaxations in a model metallic glass investigated by atomistic simulations  
Guo-Jian Lyu, Ji-Chao Qiao, Yao Yao, Jean-Marc Pelletier, David Rodney, Julien Morthomas & Claudio Fusco
- 17.30 Atomistic simulation study of lithium aluminosilicate glass scintillators  
E. M. Ghardi, P. Rautiyal, F. Pearce, A. Crompton, L. J. Evitts, S. C. Middleburgh, W. E. Lee & M. J. D. Rushton
- 17.45 Evolution of local structures in alkali-borate glasses  
Richard Kerner

**18.00 End**

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**PNCS16 : FRIDAY 14 JULY : BIOACTIVE**

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**Session chair: Oliver Alderman**

- 09.00 Tuning bioactive glass properties via their phosphate/silicate ratio: imaging using TEM and nano-CT  
Gloria Kirste, Araceli de Pablos Martín, Altair T. Contreras Jaimes, Juliana Martins de Souza e Silva, Natalia Karpukhina & Delia S. Brauer\*
- 09.30 Reactive molecular dynamics simulation of ternary phosphate-based bioactive glasses  
Zohreh Fallah & Jamieson K. Christie
- 09.45 Ultra-low network connectivity fluoride containing bioactive glasses: glass structure, design, crystallization and bioactive properties  
Melissa Tiskaya, Saroash Sahid & Robert Hill
- 10.00 Nano scale amorphous phase separation and its role in subsequent crystal nucleation  
Robert Hill, Saroash Shahid, Roweina Mansouri, Ralf Schweins & Slobodan Sirovica

**10.15 Coffee**

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**PNCS16 : FRIDAY 14 JULY : APPLICATIONS**

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**Session chair: Delia Brauer**

- 10.45 Into the light of a dark black night: glasses for mid-infrared applications  
A. B. Seddon\*
- 11.15 A comparative evaluation of “House of Cards” and “Cabbage Head” fluormica glass-cramics  
Maher Rashwan, Alexander Creswell-Boyes, Natalia Karpurkhina & Robert Hill
- 11.30 Two-dimensional wide angle x-ray diffraction on a radioactive borosilicate glass in a beryllium container  
Olivier Bouty, L. Ramond, K. Dardenne & J. Röthe
- 11.45 Surface engineering of silica and silicate glasses using femtosecond laser induced plasma  
Gin Jose, Robert Mathieson & Eric Kumi-Barimah
- 12.00 Hydrophobic silica aerogels containing magnetic nanoparticles  
Eleanor G. Sutherland, Patrycja E. Rose & Anna Corrias
- 12.15 Towards low-cost radiation-resistant silicate and borosilicate glasses  
G. Gupta, T.-Y. Chen, P. Rautiyal, A. G. Williams, A. H. Jones, J. A. Johnson, C. E. Johnson, A. Scrimshire, R. Edge, M. K. Patel & P. A. Bingham

**Session chair: Gavin Mountjoy**

- 12.30 Closing  
Alex Hannon & Gavin Mountjoy
- 13.00 Packed Lunch**

Synthesis, structure and luminescence properties of  $\text{Eu}^{3+}$  doped  $50\text{ZnO}-40\text{B}_2\text{O}_3-5\text{WO}_3-5\text{Nb}_2\text{O}_5$  glass  
Lyubomir Aleksandrov, Margarita Milanova, Reni Iordanova, Nikolay Nedyalkov & Petia Petrova

The effect of lithium concentration on the radiation damage in UK nuclear waste glasses  
Aine G. Black, Laura Leay, Mike Harrison, Frédéric Blanc & Maulik Patel

New pair distribution function analysis of International Simple Glass (ISG) from neutron and x-ray diffraction  
Natasha Brown, Aine Black, Paul A. Bingham, Frederic Blanc, Alex C. Hannon, Gavin Mountjoy, Maulik Patel, Mike Harrison & Laura Leay

Synthesis and characterisation of novel metal-organic framework-inorganic glass blends  
Ashleigh Chester, Celia Castillo-Blas, Bruno P. Rodrigues, Lothar Wondraczek, David A. Keen & Thomas D. Bennett

Quasi-elastic neutron scattering investigation of intermediate range order dynamics in supercooled liquids and glass-formers  
Peter Falus, Antonio Faraone, Victoria García Sakai, Monika Hartl, Yukinobu Kawakita, Paul Kienzle, Tatsuya Kikuchi, Maiko Kofu, Juscelino B. Leão, Peng Luo, Michihiro Nagao, Kenji Nakajima & Yanqin Zhai

The viscosity in supersaturated aqueous sugar solutions and applications in cryopreservation  
Soledad Ruiz Matus & Patricia Goldstein

Amorphous silica coating of phosphorescent nanoparticles  
Md Towhidul Islam, Patrycja Rose, Anna Corrias & Gavin Mountjoy

A TEM study into helium bubble behaviour in  $\text{Gd}_2\text{Ti}_2\text{O}_7$  glass-ceramic composites  
Menghan Jiang, Anamul H. Mir, Yingjie Zhang & Maulik Patel

Features of formation of perovskite quantum dots  $\text{CsPbX}_3$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) in fluorophosphate glasses  
Elena Kolobkova, Nikolay Nikonov & Maria Kuznetsova

Thermophysical property measurements of liquid lanthanoid sesquioxides by the electrostatic levitation furnace onboard the ISS  
Chihiro Koyama, Takehiko Ishikawa, Hirohisa Oda & Rina Shimonishi

The influence of fluorides on the luminescence of  $\text{Eu}^{3+}$  doped phosphate glasses  
Michał Maciejewski, Karolina Milewska, Anna Synak, Wojciech Sadowski & Barbara Kościelska

Combination of neutron techniques for mosaic glasses analysis  
Giulia Marcucci, Antonella Scherillo, Zsolt Kasztovszky, Ildikó Harsányi, Massimiliano Clemenza & Daniela Di Martino

Structural study of  $\text{ZnO}-\text{B}_2\text{O}_3-\text{WO}_3$  glasses modified with  $\text{Nb}_2\text{O}_5$   
Margarita Milanova, Reni Iordanova, Lyubomir Aleksandrov, Dimitrios Palles & Efstratios I. Kamitsos

Structure and luminescent properties of borate-bismuth glass and glass-ceramics doped with Ag nanoparticles  
Karolina Milewska, Michał Maciejewski, Marcin Łapiński, Michał Žitňan, José Joaquín Velázquez García, Wojciech Sadowski & Barbara Kościelska

Structure and properties of boron oxide-doped sodium niobate-phosphate glasses  
Petr Mošner, Ladislav Koudelka, Tomáš Hostinský, Lionel Montagne & Bertrand Revel

Similarities and differences between homo- and hetero-connectivity in crystals and glasses of the  $\text{BaO}-\text{SiO}_2$  system  
Benjamin J. A. Moulton

Silver photochemical reactivity under electronic irradiation analysis of gallo-phosphate glasses  
Fouad Alassani, Yannick Petit, Thierry Cardinal & Nadège Ollier

Use of glass from smartphone touch screen for radiological accident dosimetry by EPR spectroscopy  
Mahinour Mobasher, Damien Giovanelli, Chuanhao Li, Nadège Ollier & Francois Trompier

Unveiling the depolymerization of densified lead metasilicate glass: an in-situ high-pressure vibrational spectroscopy investigation  
Rafaella B. Pena, Thierry Deschamps, Christine Martinet & Paulo S. Pizani

Microstructure and characterization of coloured zirconia ceramics

R. Rada, D. Manea, R. Erhan, V. Bodnarchuk & S. Rada

Polaronic transport in vanadium phosphate glasses containing transition metal oxides

M. Razum, L. Pavić, D. Pajić, J. Pisk, P. Mošner, L. Koudelka & A. Šantić

Synthesis and characterisation of magnetic iron oxide nanoparticles coated in a silica shell

Patrycja E. Rose, Md Towhidul Islam, Gavin Mountjoy & Anna Corrias

Effects of thermal history on UK radioactive waste glasses

A. Scrimshire, A. Black, R. Edge, M. K. Patel & P. A. Bingham

Effect of sulfur on the structure of silicate-phosphate glasses

Iustyna Sułowska, Magdalena Szumera & Anna Berezicka

Ultrafast pulsed lasers – shining light on bone and dental tissue scaffold engineering

Neelam Iqbal, Emaan Alshubhe, Lemiha Yildizbakan, Sarath K. Loganathan, Geeta Sharma, Eric K-Barimah, Simon Strafford, Payal Ganguly, El Mostafa Raif, Elena Jones, Brian Nattress, Peter V. Giannoudis & Animesh Jha





## Practical information

### Security

999 is the phone number of national emergency response service in the UK. (112 is the pan-European equivalent and can be used in the UK.)

Campus Security staff are on duty 24 hours per day, 365 days per year. Their office is at campus map position “J4”, close to the central pedestrian crossing. They can be contacted as follows:

Emergency phone: (+44) 01227 823333

Non-Emergency phone: 823300

Email: [security@kent.ac.uk](mailto:security@kent.ac.uk)

### Shops on campus

There is a Co-op supermarket, a Café Nero coffee shop, and a Blackwell’s book shop, all located at campus map position “J14”. These are independent businesses which are not operated by University of Kent. Opening hours may vary.

Note that University of Kent operates a “cashless campus” policy and payments are expected to be made using credit or debit cards.

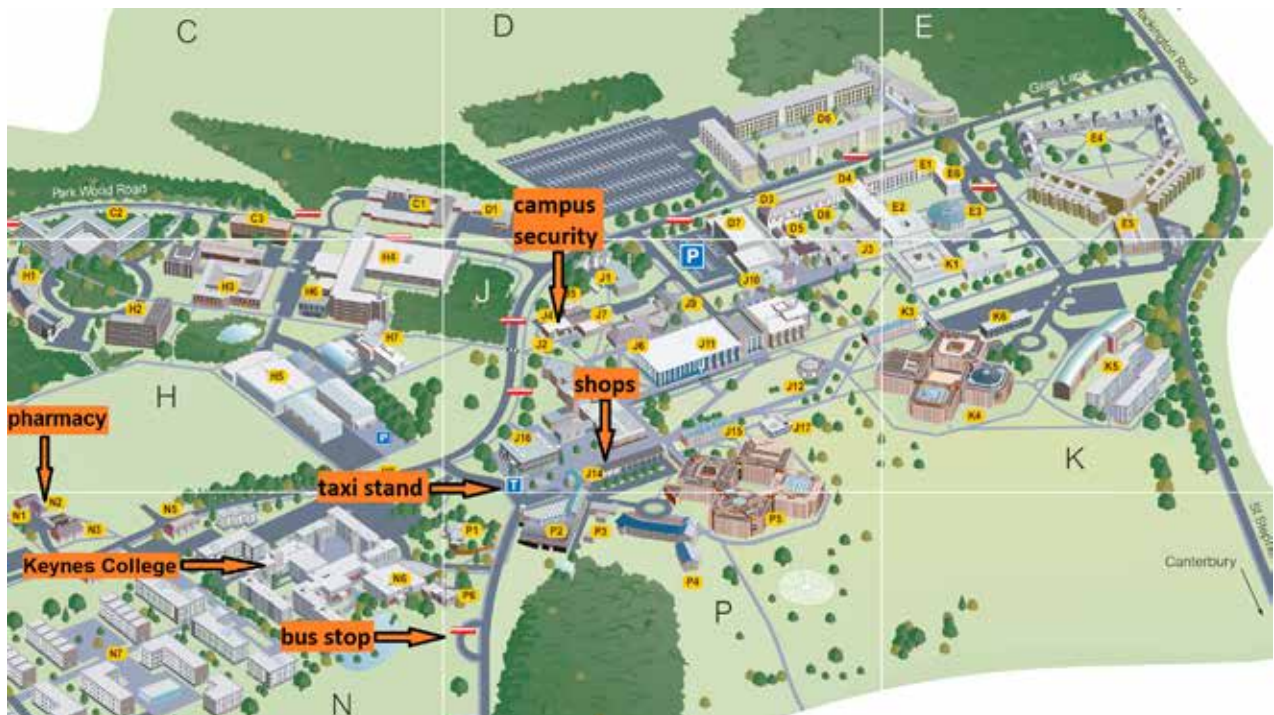
### Taxis

There is a taxi stand close to campus map position “J14”. Like all cities in the UK, there are many different taxi companies serving Canterbury.

### Buses to Canterbury

The local and regional bus company is called Stagecoach. All Stagecoach buses that come to the campus stop at the main bus stop, which is just southeast of Keynes College, close to campus map position “P6”. Tickets can be bought from the driver.

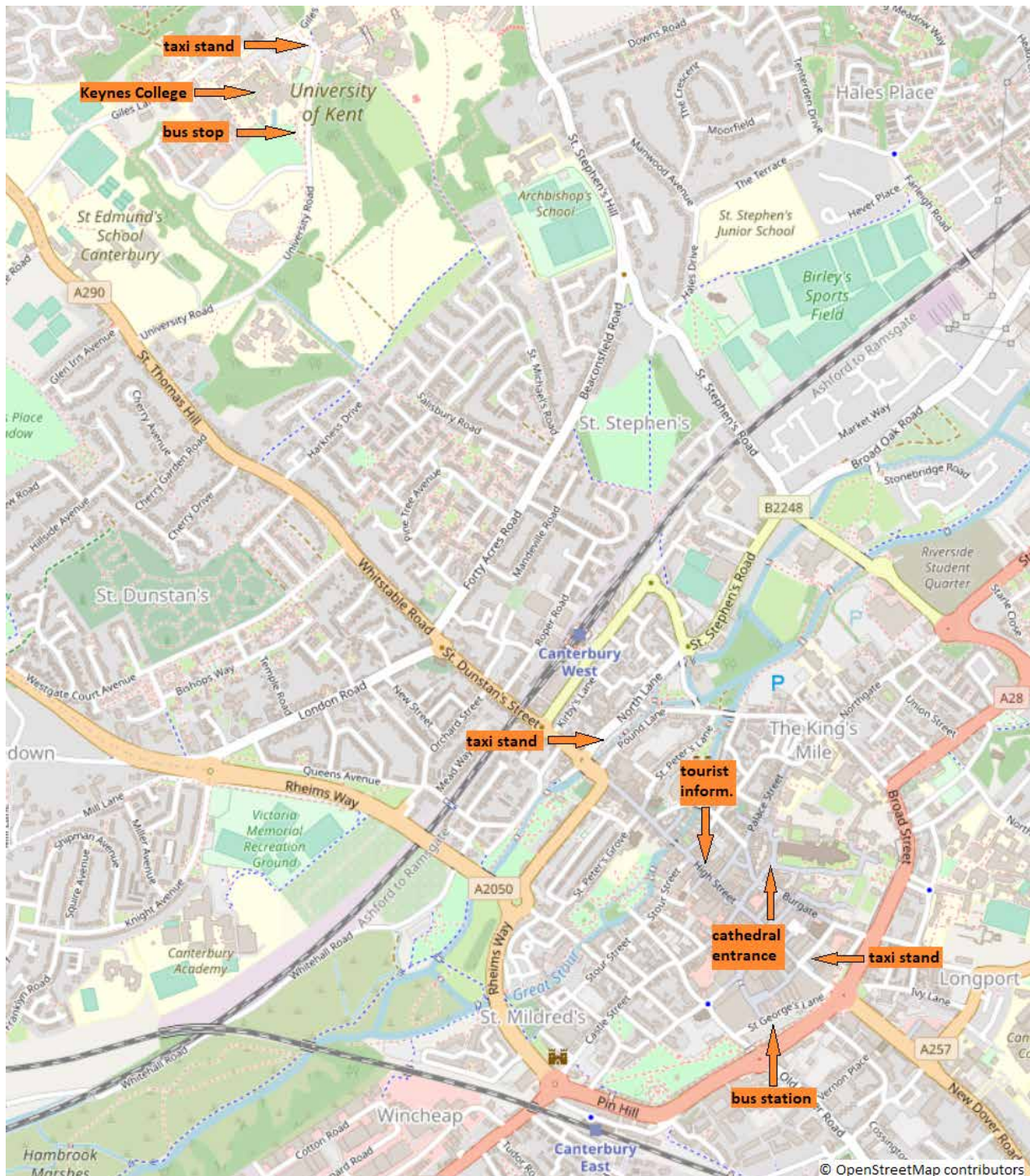
Up-to-date bus timetables and route maps can be found here: <https://www.stagecoachbus.com/timetables>



## Map of Canterbury City Centre

The walking distance from Keynes College to the Canterbury tourist information centre is 1.5 miles (2.5 km) and takes 30 mins (according to Google Maps).

Visitor information guides and maps can be found here: [https://www.canterbury.co.uk/info/27/getting\\_around\\_the\\_district/14/visitor\\_information\\_centres/2](https://www.canterbury.co.uk/info/27/getting_around_the_district/14/visitor_information_centres/2)





# Controlled crystallization of amorphous chalcogenide thin films for solar energy harvesting

Xianghua Zhang,<sup>1</sup> Guangxing Liang,<sup>2</sup> Ping Fan,<sup>2</sup> Shuo Chen,<sup>2</sup> Donglou Ren,<sup>1</sup>  
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Thin film photovoltaic (PV) solar cell has many advantages including lightweight, less material consumption, flexibility, simple and low cost production process. However, its market share is in constant decrease since the last decade when the cumulated PV capacity has been multiplied by 20 times in the World. One of the keys to keep/increase this market share is to find better absorber materials.

Antimony selenide has recently emerged as an attractive absorber material with outstanding properties: appropriate bandgap width, strong absorption of the solar spectrum, low cost and low toxicity raw materials, simple composition and unique stable phase in the binary system.

Different techniques have been used for preparing Sb<sub>2</sub>Se<sub>3</sub> based thin film solar cells. The as-deposited thin films are generally amorphous and a controlled crystallization is the key to improve the conversion efficiency of the PV devices. The objective is to obtain big and well-crystallized grains in order to minimize the recombination of the photogenerated charge carriers.

One of the issues associated with Sb<sub>2</sub>Se<sub>3</sub> is the anisotropic structure and its electronic properties, such as the mobility of charge carriers, depend strongly on the direction. For facilitating the separation, the transport and the collection of the photogenerated charge carriers in a Sb<sub>2</sub>Se<sub>3</sub> based PV device, it is essential to promote the preferential crystalline growth of the [hk1] plans in the direction perpendicular to the substrate. Different strategies will be summarized in this talk.

# NMR and atomistic simulation reveal structural relaxation and crystallization in supercooled liquids and glasses

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This talk updates the previous one delivered by one of us (EDZ) at the 15th PNCS in 2018; it focuses on the numerous and significant advances in understanding crystallization in supercooled liquids and glasses. The Classical Nucleation Theory (CNT) has been used for over 70 years to analyze and describe the early stage of the crystallization process; however, numerous experimental reports indicate that it fails to explain the experimental nucleation rates in silicate glass-formers at low temperatures, below the glass transition,  $T_g$ . Recent work in our laboratories has shown, however, that this problem can be resolved by considering the interplay of structural relaxation and nucleation on the low-temperature side. We have further identified some common structural features of homogeneously nucleating liquids by using solid-state NMR observables sensitive to the local atomic environments and the spatial distribution, chiefly of the network modifier component. Using a new experimental strategy combining solid-state NMR and molecular dynamics simulations we have reached a better understanding of the atomic rearrangements occurring during spontaneous relaxation of lithium disilicate glass to the metastable supercooled liquid state and the simultaneous crystal nucleation process at  $\sim 20$  K below the laboratory  $T_g$ . Finally, a detailed structural model will be presented for the crystallization of the NASICON prototype glass,  $\text{NaGe}_2(\text{PO}_4)_3$ , from combined solid-state NMR and neutron diffraction experiments. The results reveal the power and potential of NMR – in combination with other structural techniques – to give new atomic-level insights into glass crystallization.

# Modern computer simulations of simple models for supercooled liquids and glasses

Ludovic Berthier

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Computer simulations give unique insights into the microscopic behavior of amorphous materials. It became recently possible to generate equilibrium configurations of deeply supercooled liquids using a simple swap Monte Carlo algorithm for a broad variety of model glass-formers. This novel computational tool, which provides an equilibration speedup of more than 10 orders of magnitude, has allowed the exploration of thermodynamic properties and putative equilibrium phase transitions underlying the formation of glasses with unprecedented accuracy. I will summarise these recent findings and provide a broad picture about the thermodynamic phase diagram describing the physics of liquids undergoing a glass transition.

# Hyperbonding in glassy tellurides: the case of phase-change memory materials

Tae Hoon Lee<sup>1,2</sup> & Stephen Elliott<sup>3</sup>

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Phase-change-memory (PCM) materials, such as  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST), are being used in new storage-class computer-memory products. Instead of storing electrons to represent binary bits of information, {0,1}, as in conventional Si-based CMOS data-storage technologies (e.g. flash and DRAM), PCM functions by storing binary bits as metastable structural states of the material with a property contrast: electrically-resistive glassy (RESET) state {0}, and electrically-conducting crystalline (SET) state {1}. Reversible and ultra-rapid ( $\sim\text{ns}$ ) transformations between RESET and SET states are produced by appropriate applied voltage pulses, causing Joule heating in the PCM cell. However, the origin of the property contrast between glassy (*g*-) and crystalline (*c*-) states is unclear, and the atomistic mechanism underlying the ultrafast *g-c* transformation is obscure.

One model that has been proposed to account for the unusual behaviour of PCM materials, in particular the electronic-property contrast, is the ‘metavalent-bonding’ model, proposed by Wuttig and coworkers,<sup>(1)</sup> where a completely new form of chemical bonding has been hypothesized for such crystalline tellurides, part way between *metallic* and *covalent* bonding – hence the name – with the bonding in the glassy state being covalent. However, the chemical origin underlying this metavalent bonding remains obscure.

We have proposed an alternative model,<sup>(2,3)</sup> based on hyperbonding in hypervalent structural units, where the 8-*N* rule is not obeyed. Hyperbonds involve dative-bonding-like interactions between chalcogen *p*-lone pairs (LPs) and antibonding orbitals of neighbouring cation-chalcogen bonds, forming characteristic linear trimeric units. In support of this proposal, we have performed *ab initio* molecular-dynamics simulations of models of glassy elemental chalcogens (S, Se, Te), binary chalcogenides ( $\text{GeTe}$  and  $\text{Sb}_2\text{Te}_3$ , on the compositional tie-line of GST), and ternary chalcogenides ( $\text{Ge}_2\text{Sb}_2\text{S}_5$ ,  $\text{Ge}_2\text{Sb}_2\text{Se}_5$  and GST), and calculated their electronic structure and bonding characteristics. It is found that the bonding characteristics of chalcogenides are the *same* between *c*- and *g*-states for the *same bond length*. However, longer, weaker hypervalent bonds predominate in the rocksalt-structure, octahedrally-coordinated *c*-tellurides, whereas shorter, stronger covalent bonds also occur in *g*-chalcogenides, e.g. in trigonal units, such as  $\text{Ge/SbTe}_3$ , or tetrahedral units, such as  $\text{GeTe}_4$ , and in the equatorial bonds in defective-octahedral units, such as  $\text{Ge/SbTe}_5$ , with the axial trimeric bonds being longer hyperbonds. Hyperbonds are found to be more polarizable than covalent bonds, as revealed by the relative calculated Born effective charges. Thus, the property contrast between *c*- and *g*-tellurides is therefore naturally accounted for by the prevalence of hyperbonds in the former class of materials.

1. Raty, J.-Y., Schumacher, M., Golub, P., Deringer, V. L., Gatti, C. & Wuttig, M. *Adv. Mater.*, 2019, **31**, 1806280.
2. Lee, J. H. & Elliott, S. R. *Adv. Mater.*, 2020, **32**, 2000340; *Phys. Stat. Sol. – RRL*, 2021, **15**, 2000516.

# Phase separation and structural evolution of oxyfluoride glasses from molecular dynamics simulations

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Oxyfluoride glass is a type of mixed anion glass that find applications from photonics to nuclear waste disposal. These glasses are also known for their tendency of phase separation and crystallization, hence suitable for glass-ceramics formation. In this talk, I will present our recent study of the structures and structural evolution of alkali earth aluminosilicate oxyfluoride glasses using large scale molecular dynamics simulations with effective partial charge potentials. Structural characteristics such as cation coordination of both anions,  $Q_n$  statistics and network connectivity are analysed. Based on these structural features and effective visualization analysis tools, the initial stage of phase separation of the glass into fluoride rich phase and aluminosilicate rich phase is observed and the evolution of both phase with temperature investigated. Interestingly, it was found that aluminium ions serve as a linkage between the fluoride rich regions and aluminosilicate network rich regions. These results were correlated with experimental structural characterization and optical photoluminescence measurements. Simulation results are discussed on the experimentally observed phase separation and the initial stage of crystallization in these inorganic glasses.



# Study of ultra-stable thin films using swapping in molecular dynamics simulations

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Swap Monte Carlo techniques used in molecular dynamics simulations have been shown to be very effective in equilibrating bulk disordered solids to temperatures much below their glass transition temperature,  $T_g$ . Experimentally, this can only be done in thin films – by slow, low-temperature vapor deposition. The success of this approach is attributed to the surface-enhanced mobility of newly incident particles; even below  $T_g$  they have sufficient mobility to explore for congenial sites until they are buried by subsequent deposition.

This study used molecular dynamics simulations to study the effect of artificially added mobility on the equilibration of simulated vapor deposited films. The film was composed of polydisperse Lennard–Jones spheres deposited at  $T \sim 0.75T_g$  at a rate such that neither bulk nor surface mobility was important. Mobility was provided by Metropolis Monte Carlo swaps in defined regions that followed the surface as it grew. The intensity of swaps defined by the average number of swaps an atom would undergo as it passed through the swap zone, was varied from 10 to 2000. The zones were of various thicknesses and distances from the surface. A swap efficiency factor for each zone could be calculated by rate of stabilization (measured by increase in density or relaxation temperature upon heating), with the logarithm of swap intensity.

Characterization of the increased relaxation temperature of these swapped films was limited by the increasing penetration of surface mobility with increasing temperature; that was prevented during thermocycling by freezing the top few atomic layers to make a floating cap. Maps of mobility *vs* height *vs* temperature showed that at intermediate swap intensities, the film initially relaxed by spreading from a few localized mobile regions. High swap intensities (e.g. 500–2000) sometimes eliminated the obviously heterogeneous mobility nucleation sites up to the point that the entire film relaxed simultaneously, at  $T_r \sim 1.34T_g$ . That factor depended on the heating rate, extrapolating to  $T \sim T_g$  at a rate  $\sim 10^{-4}$  of the standard rate we used.

The efficiency with which swaps stabilized these films peaked with a region of about six atoms thick that started a few atomic layers below the surface. It was considerably lower for thin layers, those that started at the surface, and swaps performed on preformed films.

The implications of these findings will be discussed.

# Engineered structural relaxation of amorphous phase-change memory materials via the application of electric fields

Konstantinos Konstantinou,<sup>1,2</sup> Felix C. Mocanu,<sup>3</sup> Jaakko Akola<sup>2</sup> & Stephen R. Elliott<sup>1</sup>

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Structural relaxation of amorphous phase-change memory materials has been attributed to defect-electronic-state annihilation from the band gap, leading to a time-dependent drift in the electrical resistance, which hinders the development of multi-level memory devices with increased data-storage density. In this study, the target is to achieve an understanding, at the atomistic level, of the effect that an applied electric field has on localized mid-gap defect electronic states in the glassy state of phase-change memory materials. We utilize the Berry-phase formalism, within the modern theory of polarization, to apply external, finite, periodic electric fields to glassy models of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST), combined with density-functional-theory calculations of the electronic structure using non-local exchange-correlation functionals. The results highlight that the application of a sufficiently high external electric field removes mid-gap defect states from the band gap of the glass and transforms them into electronic states lying at the bottom of the conduction band, due to the electric-field-induced atomic relaxations of the amorphous structure.<sup>(1)</sup> A lowering of the coordination number of Ge atoms seem to be essential for delocalization of conduction-band-edge states. We illustrate how the weak, polarizable bonds in 5-coordinated Ge atoms can break under the application of electric fields, resulting in an engineered (i.e. without thermal annealing) annihilation of mid-gap defect states from the band gap of the glassy GST model.<sup>(1)</sup> In that way, we demonstrate a materials-engineering concept for the structural relaxation of glassy phase-change memory materials by controlling the localized states in the band gap of the chalcogenide glass. We also show that spontaneous electron and hole trapping in the intrinsic almost-linear triatomic environments from the axial bonds in “see-saw” 4-coordinated or 5-coordinated configurations within the amorphous GST network results in weakening and potential breaking of the axial bonds in these defective octahedral-like sites.<sup>(2)</sup>

1. Konstantinou, K., Mocanu, F. C., Akola, J. & Elliott, S. R. *Acta Mater.*, 2022, **223**, 117465.
2. Konstantinou, K., Elliott, S. R. & Akola, J. *unpublished*.

# Energy landscapes and structure in ion conducting solids

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The potential energy landscape (PEL) of mobile ions in solid-state materials and the atomic scale structure are intimately interrelated. This interrelation and the resultant properties, e.g. the mobility of the ions, is of paramount interest in contemporary material science with direct applications in energy storage and conversion. Understanding the interplay of structure, energy landscape and ionic transport of ionic solids is of crucial importance for a knowledge-based development of improved and new functionalities of these materials.

In this contribution we will present recent progress in the quantification of energy landscapes and the relevance for ionic transport in amorphous materials.

In contrast to crystals, amorphous solids do not exhibit a long-range but only a short range order. On a microscopic level, the amorphous structure and the lack of translational periodicity, leads to a non-periodic PEL such that a distribution of site energies is operative for the mobile ions.<sup>(1)</sup> This site energy distribution (SED) is a measure for the static disorder in the glass. Experimentally such a SED in a glass is difficult to access. Solid state NMR measurements of the distribution of relaxation times addresses all ions of a kind and thus reflects the SED.<sup>(2)</sup> But quantification has not yet been reached. The only quantitative experimental determination of a SED reported to date emerged from a charge attachment induced transport (CAIT) experiment in combination with calculations based on the Nernst–Planck and Poisson equations.<sup>(3–5)</sup> Significant progress has recently also been achieved in the theoretical description of such energy landscapes.<sup>(6,7)</sup> The goal is to reach a unifying description of CAIT and solid state NMR experiments on one hand and theory on the other.

The progress and the perspectives of research in this field will be discussed.

1. Kirchheim, R. J. *Non-Cryst. Solids*, 2000, **272**, 85–102.
2. Vogel, M. J. *Non-Cryst. Solids*, 2004, **70**, 1222.
3. Schäfer, M. & Weitzel, K.-M. *Mater. Today Physics*, 2018, **5**, 12–19.
4. Schäfer, M., Budina, D. & Weitzel, K.-M. *Phys. Chem. Chem. Phys.*, 2019, **21** (47), 26251–26261.
5. Wiemer, J. L., Schäfer, M. & Weitzel, K.-M. *J. Phys. Chem. C*, 2021, **125**, 4977–4985.
6. Bosi, M., Fischer, J. & Maass, P. J. *Phys. Chem. C*, 2021, **125**, 6260–6268.
7. Bosi, M., & Maass, P. Z. *Phys. Chemie*, in press, 2022. (<https://doi.org/10.1515/zpch-2021-3137>)

# Structure factor of a phase segregating binary mixture affected by natural and forceful molecular interconversion

Thomas J. Longo, Nikolay A. Shumovskyi, Salim M. Asadov, Sergey V. Buldryev  
& Mikhail A. Anisimov

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Using a modified Cahn–Hilliard–Cook theory for spinodal decomposition in a binary mixture that exhibits both diffusion and interconversion dynamics, we derive the time-dependent structure factor for concentration fluctuations. We compare the theory and obtain a qualitative agreement with simulations of the temporal evolution of the order parameter and structure factor in a nonequilibrium Ising/lattice-gas hybrid model in the presence of an external source of forceful interconversion. In particular, the characteristic size of the steady-state phase domain is predicted from the lower cut-off wavenumber of the amplification factor in the generalized spinodal-decomposition theory.

# Atomic-scale modeling of tellurium oxide glass: network topology and third-order non-linear properties

Raghvender Assil Bouzid, Philippe Thomas & Olivier Masson

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TeO<sub>2</sub> glasses exhibit third order non-linear optical properties 50 times higher than conventional silicate glasses,<sup>(1)</sup> making them promising candidates for frequency conversion mechanism, optical switches and other applications. The existence of 5s<sup>2</sup> lone pair on Te atom in the glassy network is at the origin of these outstanding properties<sup>(2)</sup> Despite the fact that several previous studies have investigated the structure of TeO<sub>2</sub> glass, the short and medium range orders in this material remain a matter of debate.

In this contribution, we resort to first principles molecular dynamics techniques to produce quantitative TeO<sub>2</sub> amorphous models featuring a good agreement with the experimental measurements (NMR, Raman spectroscopy). These models are then used to study the network topology of TeO<sub>2</sub> and its evolution as a function of temperature. A detailed study of the short-range order correlated to the electronic properties of this material will be presented. Furthermore, we also present calculated linear ( $\chi^1$ ) and non-linear ( $\chi^3$ ) optical properties of glassy TeO<sub>2</sub> and compare it to those achieved in silicate glass.

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# A perspective on the fragility of glass-forming liquids

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We discuss possible extraneous effects entering in the conventional measures of “fragility” at atmospheric pressure, effects that may obscure a characterization of the genuine super-Arrhenius slowdown of relaxation. We first consider the role of density, which increases with decreasing temperature at constant pressure, and then the potential influence of the high-temperature dynamical behavior and of the associated effective activation energy scale. These two effects involve on the one hand thermodynamic parameters such as the coefficient of thermal expansivity and on the other, the strength of the ‘bare’ activation energy associated to the specific bonding between neighboring molecules. They vary from system to system with, most likely, little connection with any putative collective or cooperative behavior associated with glass formation. We show how one can scale these effects out by refining the definition of fragility and modifying the celebrated Angell plot.

We would like to dedicate this note to our great and so inspiring friend, C. Austen Angell.

# The glass transition of water, insight from phase change materials

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Water may be regarded as the most important molecules on earth for its role in creating and sustaining life. Water on earth is found in the liquid and crystalline ice form, yet the majority of water in the universe exists in the amorphous state on the surface of interstellar grains. The first artificial form of amorphous water was produced in 1935 by vapor deposition, yet to this day, one of the most essential properties of amorphous water: its glass transition temperature, remains unclear. In fact, the topic of the glass transition of water has been mired in controversy for more than four decades. In this presentation, The calorimetric features that have been broadly used to assign a glass transition temperature  $T_g$  of 136 K to amorphous water are qualitatively reproduced with a phase change material. Annealing treatments and ultrafast calorimetry measurements indicate that this feature is only a shadow- $T_g$  and that the real  $T_g$  lies at higher temperature above the glass transition. A Kissinger analysis of the crystallization kinetics confirms that crystallization occurs below  $T_g$  from the glassy state at conventional heating rates. These results strongly suggest that the amorphous water endotherm at 136 K is indeed a shadow- $T_g$  and that the real  $T_g$  lies at higher temperature as predicted from structural relaxation considerations.



# Anomalous liquids on a new landscape: from water to phase-change materials

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A liquid that is cooled below its melting temperature, referred to as a supercooled liquid, can solidify into an amorphous rigid state (i.e. glass), if cooling is fast enough and crystallization is avoided. The phenomenology of supercooled liquids has been in general established. However, there are pronounced exceptions (e.g. water) which do not fall into the class of ‘normal’ liquids but exhibit a transition behavior in their liquid states. The latest advances connect the unusual aspect of liquids to the properties of Phase-Change Materials (PCMs) that are the basis for non-volatile memory and neuromorphic technologies. Here we demonstrate that the “water-like” liquid anomalies exist in many alloys based on group-IV, V, VI elements including technologically important PCMs<sup>(1,2)</sup> an in-depth understanding of the physical factors that determine their success is still lacking. Recently, we have argued for a liquid-phase metal-to-semiconductor transition (M-SC. Heat capacity, density, and thermal expansivity maxima were observed in the (supercooled) liquid states of those alloys<sup>(3)</sup> we analyze the data on Te<sub>85</sub>–Ge<sub>15</sub> using the Speedy-Angell power-law form, and find a good account with a singularity  $T_s$  only 25 K below the eutectic temperature. However, the heat capacity data in this case are not diverging, but instead exhibit a sharp maximum like that observed in fast cooling in the Molinero–Moore model of water. Applying the Adam–Gibbs viscosity equation to these calorimetric data, we find that there must be a fragile-to-strong liquid transition at the heat capacity peak temperature, and then predict the “strong” liquid course of the viscosity down to  $T_g$  at 406 K (403.6 K at 20 K/min in this study. Structural changes were monitored using *in-situ* X-ray scattering and femtosecond X-ray diffractions.<sup>(4)</sup> Dynamic properties were characterized by quasi-elastic neutrons scattering<sup>(5,6)</sup> such as viscosity  $\eta$  and the atomic self-diffusion coefficient  $D$ , play an essential role in the ultrafast phase switching behavior of novel nonvolatile phase-change memory applications. To connect  $\eta$  to  $D$ , the Stokes–Einstein relation (SER. Their anomalous behaviors can be rationalized in terms of liquid–liquid (metal–semiconductor, and fragile–strong) transitions. These transition behaviors have important implications for understanding the unusual phase switching behaviors in PCMs, in which amorphous phase can crystallize rapidly within tens of nanoseconds at an elevated temperature, while it retains excellent amorphous stability for ten years at room temperature.

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# Fragility and the rate of change of the energy landscape topography

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We conduct a comparative analysis of the mechanical response of a glass forming oxide melt, juxtaposing the adiabatic complex modulus measured at GHz frequencies using Brillouin light scattering and the steady-state shear viscosity measured at zero Hz. We analyze a sodium borate and sodium tellurite glass compositions representing a range of moderate to significant liquid fragilities. We show that the zero- and high-frequency data sets are perfectly compatible with one another by fitting both components of the high-frequency complex modulus using a modified Maxwell–Wiechert model, transforming the loss modulus to viscosity, and extrapolating to zero frequency. We find that this procedure yields an excellent fit to the steady-state viscosity under the condition that we allow for static and relaxational moduli, as well as the activation energy for viscous dissipation to be temperature dependent. This dependence is modulated by the logistic function, which accounts for the structural changes that take place in the material as it transitions from liquid to glass. Accordingly, the fragility of a glass forming liquid can be regarded as a measure to the rate of change in the energy landscape topography.

# How much do we know about the fragility of glass-forming liquids?

## In honour of Austen Angell

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The slow dynamics of glass-forming liquids is a complex but highly intriguing subject of the condensed matter science. It is also a critical factor that should be considered when designing new glass materials and in optimizing glass production process. It is generally accepted that Angell's liquid fragility concept is a key to understand the slow dynamics. The well-known  $\log(\text{viscosity})-T_g/T$  plot was obtained first in 1957 by Oldekop, and then in 1972 by Laughlin & Uhlmann. However, they did not interpret the physical meaning of this plot. In 1985, Angell proposed the liquid fragility concept to describe the dynamics of a significantly extended glass systems by the  $\log(\text{viscosity or relaxation time})$  versus  $T_g/T$  plot, i.e. the Angell plot.<sup>(1)</sup> He was the first who gave the term "liquid fragility", classified the glass-forming liquids into the "strong" and "fragile" categories, and quantified the liquid fragility. Through experiments and theoretical studies, he and his co-workers provided deep insight into physics of liquid fragility.<sup>(2,3)</sup> More importantly, his liquid fragility concept sparked great interest among physicists and glass scientists. Over the past three decades, substantial progress has been made in understanding the structural and thermodynamic origin of liquid fragility. In 1999, Angell *et al* published another seminal paper that reported on the fragile-to-strong (F-S) transition in water.<sup>(4)</sup> This made liquid fragility even more complex and fascinating.<sup>(5)</sup> It is indeed challenging to directly probe the structural, topological, and thermodynamic changes during this transition despite some recent interesting observations.<sup>(6-9)</sup> However, the microscopic theory describing the F-S transition has not been fully established. In this talk, I will describe the current understandings about both the liquid fragility and the F-S transition. I will point out the major challenges and perspectives in exploring the microscopic origin of the liquid fragility and in finding the connections between the F-S transition, liquid-liquid transition, and structural evolution.

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# Characterisation of the dynamics and structure of the boson peak in a supercooled and vitrified small-molecule liquid

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A phenomenon often associated with the glass is the boson peak, which is observed as an excess intensity of modes around  $\sim 1$  THz in spectroscopic studies or as an excess heat capacity. The boson peak is intermolecular in nature and as such is typically (partially) obscured by other terahertz frequency bands, such as low-frequency vibrations, librations, and (above  $T_g$ ) orientational and translational relaxation bands. We have shown that symmetry can be used to simplify depolarised Raman spectra of liquids in the terahertz range. However, symmetric molecules tend to crystallise rather than vitrify. Here we show that tetrabutyl orthosilicate (TBOS) is an example of a class of monomeric tetrahedrally symmetric molecular liquids that nonetheless vitrify. In fact, it has been impossible to make these compounds crystallise at all. TBOS was studied with broadband depolarised Raman spectroscopy, synchrotron x-ray scattering, calorimetry, and molecular dynamics simulations to gain insights into relaxation processes and their dynamic signatures, in relation to structural changes that occur within the liquid and glassy states. Detailed temperature-dependent lineshape analysis of the intermolecular modes shows that in TBOS, they are inhomogeneously broadened and split into two clearly identifiable bands, the lower frequency of which is the boson peak. Analysis of the first sharp diffraction peak in temperature-dependent WAXS experiments shows inhomogeneous broadening and a weak pre-peak in the glass—corresponding to clusters about three TBOS molecules across. MD simulations reproducing the WAXS data, show icosahedral ordering above  $T_g$  and a sudden appearance of BCC-like ordering below  $T_g$ . Taken together, these experiments and simulations show a unique coherent picture of the molecular structure responsible for the boson peak.

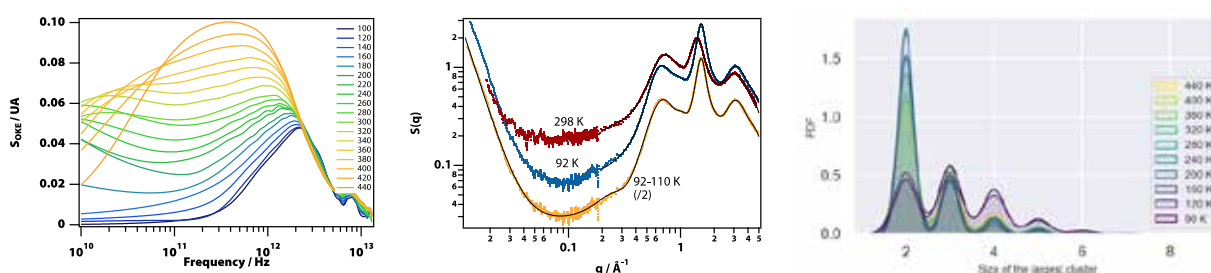


Figure. (left) Sub-terahertz Raman spectra of supercooled and vitrified tetrabutyl orthosilicate (TBOS,  $T_g=124$  K) from 100 to 440 K. (centre) Temperature dependent WAXS data showing a pre-peak in the glass at  $0.2 \text{ \AA}^{-1}$ . (right) 512-molecule MD simulations analysed in terms of Voronoi polyhedra show the formation of large clusters below  $T_g$ .

# A heart of glass – two-level systems in a fragile glass model

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The low-temperature quasi-universal behavior of the thermal and mechanical properties of amorphous solids has been attributed to the existence of localized tunneling two-level systems, found at the bottom of the potential energy landscape. The density of these excitations was found to decrease with increasing glass stability, however, simulations have overestimated their absolute number.<sup>1</sup> The Kob-Andersen model has been recently optimized for Swap Monte Carlo dynamics, which allows for an efficient equilibration at low-temperatures.<sup>2,3</sup> An extensive exploration of the energy landscape of this model gives an estimated density of tunneling defects near the glass transition in good agreement with experimental measurements. We present results on the statistics of two-level systems, their real-space signatures and their connections to quasi-localized vibrational modes.

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# Neodymium titanate: exploring structure, viscosity and density for the fragile liquid of an octahedral network glass

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Rare-earth titanates form very fragile liquids that can be made into glasses with high refractive indices ( $>2.1$ ), low dispersion, and wide transmission range in the visible and infrared spectrum. To better understand these materials' structure–property relationships, we investigate the thermophysical properties and atomic structure of neodymium titanate ( $83\text{TiO}_2\text{--}17\text{Nd}_2\text{O}_3$ ) in the molten, supercooled liquid, and glassy states. Using the Electrostatic Levitation Furnace onboard the International Space Station, density is measured via silhouette image analysis during rapid cooling from above the liquidus temperature through quenching to a glass at room temperature. A droplet oscillation technique enables measurement of viscosity and surface tension over a wide temperature range in the molten and supercooled states. Density of the supercooled and equilibrium liquid decreases linearly with temperature in the range of 1100–1800°C. Viscosity ranges 11 to 35 mPas over 1850 to 1475°C, which suggests a high liquid fragility compared to other oxide network glasses.

Complementary structure measurements are made with X-ray diffraction for the liquid, and X-ray and neutron diffraction for the glass. Double isotope substitutions for both Ti and Nd in the glass enable analysis of six total structure factors (5 neutron + 1 X-ray), each with unique weighting of the atomic partial pair correlations. An empirical potential structure refinement (EPSR) provides a structural model consistent with diffraction measurements. Mean coordination numbers from EPSR are 5.72(6) for Ti–O and 7.70(26) for Nd–O, in reasonable agreement with neutron first order difference functions for Ti and Nd. The titanate glass network comprises distorted polyhedra of 73% Ti–O<sub>6</sub> and 26% Ti–O<sub>5</sub>, connected via 71% corner-sharing and 23% edge-sharing. This network of predominantly octahedral-coordinate Ti with significant edge-sharing is highly unusual, especially compared to traditional glass formers like SiO<sub>2</sub>, which comprises corner-sharing Si–O<sub>4</sub> tetrahedra.

# Graphitization of amorphous carbon

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Using first principles molecular dynamics (plane wave DFT using a PBE potential), we have shown that realistic models of amorphous carbon with densities near  $2.4 \text{ g/cm}^3$  undergo a remarkable disorder–order transition when annealed near 3000 K. Pre-existing  $\text{sp}^2$  regions in the amorphous network serve as “seeds”, and these organize and locally planarize and after 10–20 ps, flat planes of amorphous graphene emerge separated by approximately the experimental plane–plane distance of 0.33 nm. The amorphous graphene planes are  $\text{sp}^2$ , but with ring disorder (pentagons, hexagons, heptagons *etc.*) as discussed elsewhere.<sup>(1)</sup> The galleries are filled with a fairly homogeneous electron gas arising from the  $\pi$  orbitals. It is of interest that even with ring disorder in the amorphous graphene, long range planar order accrues, in some realizations almost perfectly flat, despite pentagonal puckering observed in monolayer amorphous graphene.<sup>(2)</sup> While the cohesion between planes is weak, it is clearly *not* due to van der Waals (fluctuating dipole) interactions as sometimes asserted for graphite (since these effects are not included in our simulations). We also show examples of defects, and an “undulating” phase which we have detected for particular thermal treatments and densities. We have also observed graphitization for a random initial configuration, ultimately with more defects than for the case of the amorphous carbon initial state. For all the models, we discuss the electronic properties and the space-projected electronic conductivity.<sup>(3)</sup>

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# Effect of Ca/K replacement on the atomic structure of $P_2O_5$ – $K_2O$ – $CaO$ glasses – A molecular dynamics study

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A classical molecular dynamics method was used to model potassium and calcium metaphosphate glasses for the application of environment conscious glass-fertilizer. By controlling the glasses composition, the phosphate glasses are predicted to provide the slow-releasing nutrient fertilizers which are environmentally safe and widely applicable. Five models of composition  $50P_2O_5$ – $xCaO$ – $(50-x)K_2O$  ( $x=0, 10, 20, 30$ , and  $40$  mol%) system were developed. The models short range order parameters results are in good agreement with experimental results. The two P–O bond distances are well resolved on average at  $1.48 \text{ \AA}$  and  $1.55 \text{ \AA}$ . The O–O bond distance is peaked at  $2.46 \text{ \AA}$  with an average coordination number of 4. The Ca–O bond distance is well defined at  $2.40 \text{ \AA}$  with the coordination number of 6 on average. Ca acts as a network modifier, the model reported that the addition of CaO associated with disturbance of the bridges P–O–P and therefore depolymerize the phosphate network. The K–O coordination number was found to change insignificantly in dependence on composition with an average value of around 5. The bond angle distributions for the five models found the average O–P–O bond angle is tetrahedral, defined peak at  $110^\circ$ , while the P–O–P bond angles are peaked at around  $150^\circ$  which is in very good agreement with the reported values in the literature. As expected in metaphosphate composition, the models show the phosphate network to be dominated by  $Q^2$  units. The network connectivity is also examined through P–P coordination number with an average value of 2 and the bond distance is well resolved at  $3 \text{ \AA}$ .

*Key words:* phosphate glasses, molecular dynamics simulation, environmental issues, glass structure, short-range order.

# Connecting coordination change to configurational properties in glass-forming liquids

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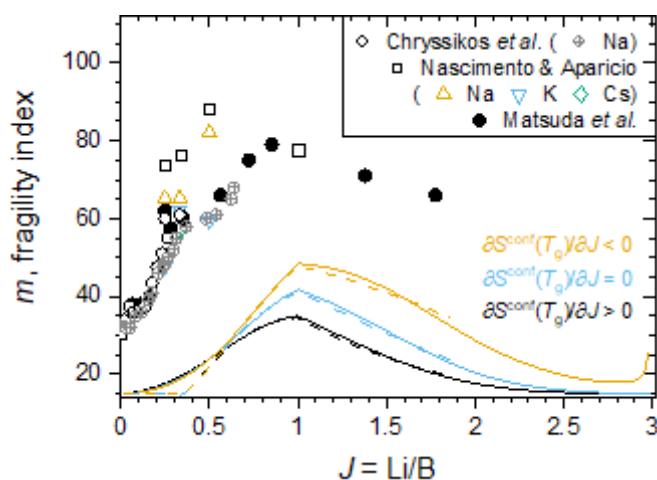
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Connecting structural changes to the associated dynamical arrest in supercooled liquids approaching the glass transition has remained elusive, particularly by direct experimental means. Herein we show that, in suitable systems such as borates, coordination numbers can be measured with remarkable accuracy, even on second timescales, using diffraction methods, via determination of the mean bond length in the pair distribution function. Applying this technique to the B–O bond length in liquid and glassy lithium pyro- and meta-borates over wide temperature ranges, a simple model based on chemical equilibrium between tetrahedral and trigonal planar charged borate isomers is developed and fitted to the experimental data, yielding insight into the temperature dependence of configurational heat capacities and entropies.<sup>(1)</sup>

Combined with earlier data on sodium borates, the influence of the borate isomerization reaction on the compositional trends of configurational heat capacity and, semi-quantitatively on liquid fragility, are revealed. In particular, a maximum in both properties is predicted at the metaborate composition, in agreement with the scarce available experimental data, and in contrast to more well-known borate anomaly extrema around the diborate composition.



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# Atomistic simulations of melting silicates

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Melting has been called the single most important phase change in fundamental materials science, and plays a central role in glass-forming processes. Notwithstanding, our understanding of the atomic scale mechanisms involved in the melting of silicates, whether crystalline or vitreous, is still rather limited. This is particularly true for cullet, that is, glass that is being recycled. Given the amount of energy consumed by them, it behooves us to find ways to optimizing these glass-forming processes. Such materials engineering requires an improved knowledge of silicate melting at the atomic scale.

To this end, we have undertaken a series of atomistic molecular dynamics simulations of melting of silicates, which we will describe in this talk.

Not surprisingly, the roles of surfaces, and surface structures, are found to be of central importance.

# New understanding of liquid thermodynamics, viscosity and its lower bounds

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Understanding most basic thermodynamic properties of the liquid state such as energy and heat capacity turned out to be a long-standing problem in physics.<sup>(1)</sup> Landau & Lifshitz textbook states that no general formulas can be derived for liquid thermodynamic functions because the interactions are both strong and system-specific. Phrased differently, liquids have no small parameter. Recent theoretical results open a new way to understand liquid thermodynamics on the basis of collective excitations (phonons) as is done in the solid state theory. Differently from solids, the phase space for these excitations reduces with temperature,<sup>(1,2)</sup> explaining the universal decrease of liquid constant-volume specific heat. I will discuss the implication of the above theory for fundamental understanding of liquids. I will also explain how this picture extends above the critical point where the Frenkel line separates two physically distinct states on the supercritical phase diagram.<sup>(3)</sup> I will subsequently describe how this leads to the theory of minimal quantum viscosity in terms of fundamental physical constants.<sup>(4)</sup> This answers the long-standing question discussed by Purcell & Weisskopf of why viscosity never drops below a certain value.<sup>(5)</sup> This also means that water and life are well attuned to the degree of quantumness of the physical world.<sup>(5)</sup> I will finally note that the kinematic viscosity of the quark-gluon plasma is surprisingly close to the kinematic viscosity of liquids at their minimum.<sup>(6)</sup>

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# Relaxation dynamics of glass forming metals: Study of aging, delayed elasticity and supercooled liquid behaviors in a ZrTiCuNiBe alloy

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The structural relaxation of supercooled liquids (SCL) and glasses involves spatial and temporal heterogeneity, a high degree of cooperativity and long timescales. The complex relaxation spectrum of disordered materials, the effects of aging and the wide range of experimental timescales make difficult to relate the different observations in a whole picture of the liquid-glass dynamics. We will present here our recent work on a  $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$  alloy. This glass forming alloy is characterized by an outstanding stability against crystallization and decomposition. In addition, the mechanical spectrum shows a single  $\alpha$  relaxation peak with no evidence of a secondary process. This makes this material a good model to get insight into the dynamics of metallic glasses discarding, as maximum as possible, the peculiarities of each particular composition. Firstly, we will present the anelastic, or delayed elasticity, behavior. This phenomenon is particularly large in glasses due to a broad distribution of reversible deformation modes. Recovery experiments after different loading times show that the time distribution of modes is invariant over a large range of temperatures with a  $\tau^n$  dependence, that can be directly related to the high-frequency wing of the  $\alpha$  relaxation. Secondly, we will show the evolution during aging by means of step strain tests after different isothermal annealing times. It is found that the atomic mobility decreases with an aging shift rate  $\mu \sim 0.5$  and the dynamical heterogeneity increases during the first stages of aging. Thirdly, we will compare the mechanical results with microscopic insights obtained by X-ray Photon Correlation Spectroscopy. At temperatures near and above  $T_g$ , the mechanical and microscopic results show a constant dynamical heterogeneity, fulfilling the time-temperature superposition principle. Below  $T_g$ , the microscopic and macroscopic dynamics disagree in both functional shape and timescale. The intermediate scattering function changes from a stretched shape in the SCL to a compressed and fast decay in the glass.<sup>(1)</sup> Taking into account the aging and anelasticity behaviors, this effect can be explained by how aging and stress relaxation is observed in the microscopic scale. Finally, we will summarize the complete view and compare with the results observed in other glass forming alloys.

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# The influence of ZrO<sub>2</sub> addition on thermal behavior and mechanical properties of Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> ceramics

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Glass microspheres in the system Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> were prepared by combination of the sol-gel Pechini method and flame synthesis. The eutectic compositions 76.8 mol% Al<sub>2</sub>O<sub>3</sub> and 23.2 mol%, Y<sub>2</sub>O<sub>3</sub> was selected as the basis. Then either 5 or 10 mol% of Al<sub>2</sub>O<sub>3</sub> was replaced by ZrO<sub>2</sub> (samples AYZr1 and AYZr2) or 5 and 10 mol% of Y<sub>2</sub>O<sub>3</sub> was replaced by ZrO<sub>2</sub> (samples AYZr3 and AYZr4). The prepared glass microspheres were characterized by X-ray diffraction (XRD), high-temperature X-ray diffraction (HT XRD), differential scanning calorimetry/thermo gravimetry (DSC/TG) and SEM analysis. DSC/TG analysis was performed in nitrogen atmosphere in the temperature interval 25–1200°C at a heating rate of 10°C/min. All DSC curves, except of AYZr4, contain three exothermic effects with maxima in the temperature interval 937–1142°C. Only one exothermic effect with the maximum at 939°C was present in the DSC curve of AYZr4. For detailed study of phase development, HT XRD analyses were performed at a heating rate of 5°C/min in an ambient atmosphere, in the temperature interval 750–1200°C. The evaluation of XRD patterns confirmed crystallization of mainly ZrO<sub>2</sub> phases (cubic and orthorhombic) in the whole temperature range. The onset of ZrO<sub>2</sub> crystallization was observed in the temperature interval 980–1000°C. Crystallization of YAG (yttrium-aluminium garnet, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>) was observed in all prepared samples with the onset in the temperature interval 1080–1100°C. Preliminary hot press experiments at T=1500°C, p=30 MPa and 15 min holding time were also performed. The microstructure of sintered bodies was examined by SEM. The  $H_V$  and the indentation fracture resistance were determined from Vickers indentations at a load of 10 N. The material AYZr4 with a fine-grained eutectic microstructure,  $H_V=17.1\pm0.5$  GPa and indentation fracture resistance of  $3.9\pm0.4$  MPa<sup>1/2</sup> was prepared.

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# Enhanced mobility of lithium and sodium ions in phosphate glasses obtained by $\text{WO}_3$ and $\text{MoO}_3$ addition

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Increased demand for stable and efficient electrolytes in batteries puts the focus of recent studies on the improvement of relatively low ionic conductivity in various oxide glasses containing alkali ions. A popular approach in achieving this goal is to add the second glass-forming oxide to the glass in order to induce structural changes which have a facilitating effect on the ionic transport (mixed glass-former effect). In this study, we show that a significant increase in ionic conductivity can be achieved by the replacement of glass-forming oxide  $\text{P}_2\text{O}_5$  with  $\text{WO}_3$  and  $\text{MoO}_3$  which are not conventional glass-formers but conditional ones. For that purpose, four series of glasses  $40\text{Na}_2\text{O}-x\text{MoO}_3-(60-x)\text{P}_2\text{O}_5$ ,  $40\text{Na}_2\text{O}-x\text{WO}_3-(60-x)\text{P}_2\text{O}_5$ ,  $40\text{Li}_2\text{O}-x\text{MoO}_3-(60-x)\text{P}_2\text{O}_5$  and  $40\text{Li}_2\text{O}-x\text{WO}_3-(60-x)\text{P}_2\text{O}_5$ ;  $x=0-50$  mol% were prepared by melt-quenching. The electrical characterization was performed by impedance spectroscopy in a wide frequency and temperature range while the structural changes were followed by the  $^{31}\text{P}$  MAS-NMR and Raman spectroscopy.

Comparing the phosphate glasses with different conducting ions, it was found that an increase in DC conductivity with the addition of transition metal oxides was more pronounced in lithium series as a result of a smaller ionic radius and therefore higher mobility of lithium ions in contrast to the sodium ones. The trend in conductivity of sodium phosphate glasses was found to be non-linear, which is typical for the mixed glass former effect, exhibiting the maximal value at 30 mol% of  $\text{MoO}_3$  and 40 mol% of  $\text{WO}_3$ . Similar compositional dependence was also found in the fraction of mixed molybdate/tungstate-phosphate units and the number of P–O–Mo/W linkages. These findings indicate that the fastest transport of sodium ions occurs at the maximally interconnected phosphate and molybdenum/tungsten units. On the other hand, lithium containing phosphate glasses did not show the typical effect of mixed glass formers on the electrical conductivity, even though the addition of  $\text{WO}_3$  and  $\text{MoO}_3$  produced similar network modification as in sodium containing glasses. In both series, the enhancement of ionic conductivity was found to be continuous for glasses containing up to 40 mol% of  $\text{WO}_3$  and  $\text{MoO}_3$  but retained for a higher fraction of these oxides. Here, similarly as in the sodium phosphate series, the formation of mixed molybdenum/tungsten phosphate units strongly facilitates the transport of ions. However, at the highest amounts of  $\text{WO}_3$  and  $\text{MoO}_3$ , smaller  $\text{Li}^+$  ions are less affected by the hindering nature of the glass network composed predominantly of molybdate and tungstate units, so the characteristic maximum in conductivity was not observed rather high values were retained.

# Thermal, chemical and phase property changes in Hanford analogue glasses with varying Fe<sub>2</sub>O<sub>3</sub> contents

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In 1943, Hanford was selected as the site that would produce weapons grade plutonium for the Manhattan project. To do this, various plutonium and uranium extraction processes were employed during the 46 years the site was actively producing radioactive materials. Presently, there are large quantities of complex hazardous wastes stored in steel tanks that are past their expected lifespan resulting in an urgent drive to process the waste in attempt to avoid significant environmental damage that would result from significant leakage from the tanks.<sup>(1)</sup> The desired method to process the waste is “direct feed” vitrification into borosilicate glasses<sup>(2)</sup> with no pre-treatment of the waste. This means the impact of the complexities of the waste on the final wasteform properties must be better understood before the clean-up efforts begin in earnest. One such complexity is the high concentrations of iron within some of the wastes, which originated from the various Pu and U extraction processes using chemicals such as ferrous sulphamate as reducing agents.<sup>(3)</sup>

This research looks to build on established research into high-Fe wastes by studying the effects on an existing non-radioactive surrogate waste glass, HLW-Ng-Fe2,<sup>(4)</sup> of varying the Fe<sub>2</sub>O<sub>3</sub> content on a pro-rata basis from 0 to 10 mol%. Two sub-series of glass have been studied, one that will be annealed/quenched to represent the glass on the outside of the steel canister that the waste glasses will be poured into; and the other sub-series will be subjected to a canister centerline cooling (CCC) heat treatment to represent the glass formed as a result of the slower cooling in the centre of the canister. The two sub-series have been subjected to 7-day method-B product consistency tests (PCT-B), as well as X-ray diffraction (XRD) with Rietveld analysis, and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDXS). These tests will show the initial dissolution rates of the glass and the difference in secondary phases that will stabilise in the glass between the two sub-series, while also providing some insight as to how the concentration of iron impacts these properties within both sub-series.

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# **Structure and dynamics in densified silica glass**

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Silica ( $\text{SiO}_2$ ) is a prototypical glass forming material on which numerous studies have been reported. Nevertheless, the mechanism of densification is still not well understood. We have synthesized glasses by hot compression at 7.7 GPa and up to 1200°C. Molecular dynamics–reverse Monte Carlo modelling based on neutron and X-ray diffraction data, followed by topological analyses, indicated that the glass exhibits inter-tetrahedral oxygen–oxygen correlations. Such correlations do not exist in the crystalline phase with a comparable density ( $\alpha$ -cristobalite), but are observed in a higher density crystalline phase (coesite). Moreover, topological analyses demonstrated that silicon–silicon correlations, manifested by the first sharp diffraction peak, and the increased packing fraction of oxygen atoms associated with the ordering of inter-tetrahedral oxygen–oxygen correlations, manifested by the second principal peak, are the origin of densification by a hot compression. Specific heat and X-ray diffraction measurements, supported by inelastic neutron scattering measurements, suggest that the original glass transforms to a glass with a longer correlation length at temperatures greater than 800°C at 7.7 GPa. The glass synthesized at 1200°C at 7.7 GPa exhibits a correlation length of approximately 60% longer than the glass with a comparable density synthesized at room temperature at 20 GPa (cold compression).<sup>(1)</sup>

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# Thermal relaxation of electron irradiated densified silica phases

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Silica glass is the backbone of many today's applications as in low-loss optical fibers, modern metal-oxide-semiconductor devices,<sup>(1)</sup> geology or optical telecommunications. Due to its large free volume, the densification of silica under high pressure is very efficient. Metamict phase is one dense phase obtained after neutron irradiation that was first discovered by Primak.<sup>(2)</sup> In this study, we are interested in comparing the thermal relaxation of the structure of densified silica studied by Raman spectroscopy. Dense silica samples were obtained under different pathways, firstly densified by High Pressure and High Temperature followed by 2.5 MeV electron irradiation at specific doses ( $10^7$  Gy & 11 GGy). The dose of 11 GGy allows reaching the silica metamict phase of  $2.26 \text{ g/cm}^3$ <sup>(3)</sup> whereas the  $10^7$  Gy irradiated sample displays a density of  $2.64 \text{ g/cm}^3$ . Densification indicators were monitored during 30 min step isochronal annealing using Raman spectroscopy. Namely  $D_1$  and  $D_2$  bands intensities assigned to respectively the breathing modes of the 4- and 3-membered rings decreased monotonously with  $T$  for the metamict phase while an anomalous sharp increase of their intensities arises between  $800^\circ\text{C}$  and  $1000^\circ\text{C}$  for the  $2.58 \text{ g/cm}^3$  silica. The density for all the samples ( $10^7$  Gy & 11 GGy) however monotonously decreased until reaching the density of pristine silica of  $2.2 \text{ g/cm}^3$  at  $1000^\circ\text{C}$ . Of interest the "recovery phase" of metamict silica after a  $1100^\circ\text{C}$  annealing does not correspond to pristine silica as confirmed by the main band position, its full width at half maximum as well as the  $D_1$  and  $D_2$  band intensities. These results indicate an amorphous-amorphous phase transitions between silica phases.

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# Structural approach and relaxation processes according to thermo-mechanical histories of densified silicate glasses

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Depending on the history of densified SiO<sub>2</sub> glass, structure exhibits differences, for a same density, in particular, at middle range order, inter-tetrahedral angles and distribution of rings.<sup>(1,2)</sup> Depending on pressure and temperature, above the elastic limit, the recovered densified glass will be more or less thermodynamically stable and stresses. It is therefore interesting to explore the opposite path, i.e. to recover to the initial density of the glass during an isothermal annealing. To this end, temperature relaxation experiments, far from the glass transition temperature, have been carried out on SiO<sub>2</sub> glasses that have been densified from hot or cold compression in order to explore a wide range of densification conditions and to better understand the impact of temperature and pressure separately. In-situ experiments by Raman spectroscopy, Small Angle X-Ray scattering and Wide Angle X-Ray scattering, at different annealing temperatures, have been performed to follow thermal relaxation of different densified SiO<sub>2</sub> glasses. For cold densification glasses, partially relaxation occurs at very low temperature showing firstly a fast structural reorganisation with an internal stress relieved. D<sub>2</sub> Raman line, corresponding to the three-membered ring population, density fluctuations and First Sharp Diffraction Peak width evolutions at a function of time during isothermal relaxation evidence a maximum.<sup>(3)</sup> These maxima, corresponding to different spatial range orders, occur at the same relaxation time for glasses recovered after a hot compression and then show the existence of a transitory state, which represents an increase of the structural inhomogeneity. First results on densified albite silicate and binary silicate with low sodium content glass exhibit same maximal behaviour during isothermal relaxation.

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# Tomographic spectroscopic of densification process of silicate glasses under micro-indentation

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A better understanding of the links between the structure of glasses and their macroscopic properties (mechanical, optical, etc.) is a highly topical technological issue. For example, improving the mechanical strength of glasses would have an essential impact in the fields of construction, smart-phones, etc. Silicate glasses are the glasses most commonly used in industry. In this context, the mechanical behavior and structural modifications of glasses under extreme pressure conditions have been studied for several years by ILM.<sup>(1)</sup> In order to deepen the understanding of the glass behavior under pressure and shear stress, we have performed a spectroscopic study of fused silica glasses and other glasses with compositions close to the chemical compositions used in industry. Our present study has probed the evolution of the structure, density and mechanical elastic constants under micro-indentation (Vickers indentation). This work has been mainly based on spectroscopic studies using micro-Brillouin and micro-Raman spectroscopies on indent. Our results seem to confirm a very different behavior under indentation for fused silica and float silica. By studying the spatial evolution of the acoustic modes for fused silica, it appears that the densification process is very localized, whereas for float glass, the densification of the glass is much more extensive and continuous. The three-dimensional spectroscopic mapping of micro-indents for different silicate glasses has been compared to previous results<sup>(2)</sup> and the simulated response<sup>(3)</sup> in order to progress in the understanding of the elementary mechanisms of glass plasticity and to test possible spectroscopic tools predicting plastic damage and crack initiation.

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# Pressure induced fast atomic motion in metallic glasses at extreme conditions

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Many fundamental aspects of glass formers and glasses are dynamical in nature, including the glass transition and physical aging. Over the past decade, experimental progress have been made to measure the dynamics of amorphous systems in a broader range of time and length scales. In particular, X-Ray Photon Correlation Spectroscopy (XPCS) made possible the monitoring of these internal dynamical processes down to the atomic scale. This led to the discovery of the dynamical crossover in metallic glass formers,<sup>(1)</sup> to a deeper understanding of physical aging,<sup>(2)</sup> or to a finer description of the relaxation processes through their length scale dependence.<sup>(3)</sup>

However, the effect of pressure on the dynamics remains elusive, mainly because of the higher experimental difficulty. The recent Extreme Brilliance Source (EBS) upgrade of the ESRF benefited largely to coherent based techniques such as XPCS, opening the possibility for high-pressure XPCS (HP-XPCS).

In this talk, I will present recent experimental results on the atomic motion in metallic glasses obtained with high energy HP-XPCS at ESRF-EBS. We find that while pressure induced a structural densification of the glass, the atomic motion is surprisingly accelerated by almost two orders of magnitude in time with respect to ambient condition. These pressure induced fast atomic rearrangements persist even after hours of isobaric measurements at 3 GPa and at room temperature, i.e. more than 200 K below the glass transition temperature. A time resolved study at 6 GPa shows how pressure induces a temporal aging of the dynamics which strongly resembles the temperature induced exponential evolution of the dynamics observed during isothermal annealing in rapidly quenched metallic glasses.<sup>(4)</sup>

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# **Structural transformation and phase change properties of Se substituted GeTe**

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GeTe<sub>1-x</sub>Se<sub>x</sub> (0 ≤ x ≤ 1.0) alloys have been prepared both in bulk and thin film forms to study the effect of selenium (Se) substitution for tellurium (Te) on the phase change properties. It is observed that with increasing Se substitution in GeTe, the structure transforms from rhombohedral structure to orthorhombic structure. Rietveld Refinement analysis support the phase transformation and show that the short and long bond lengths in crystalline GeTe decrease with increasing Se substitution but the rate of reduction of shorter bond length is more than the longer bond length. The GeTe<sub>1-x</sub>Se<sub>x</sub> thin films undergo amorphous to crystalline phase change when annealed at high temperatures. The transition temperature shows an increasing trend with the Se substitution. The contrast in electrical resistivity between the amorphous and crystalline states is 10<sup>4</sup> for GeTe, and with the Se substitution, the contrast increases considerably to 10<sup>6</sup> for GeTe<sub>0.5</sub>Se<sub>0.5</sub>. Devices fabricated with thin films show that the threshold current decreases with the Se substitution indicating a reduction in the power required for WRITE operation. The present study shows that the crystalline structure, resistance, bandgap, transition temperature and threshold voltage of GeTe can be effectively controlled and tuned by the substitution of Te by Se, which is conducive for phase change memory applications.

# Co-sputtered Ga–Sb–Te thin films: phase change material characterization

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The investigation and application of chalcogenides in the field of phase change materials (PCM) for data storage have been focused mainly on Ge–Sb–Te and Ag–In–Sb–Te systems.<sup>(1)</sup> The present work studies Ga–Sb–Te system as a potential medium for PCM. The radio-frequency magnetron co-sputtered thin films from two pseudo-binary tie-lines, i.e. GaSb–GaTe (keeping content of Ga at 50 of at% and changing the ratio between Sb and Te) and GaSb–Te (increasing the content of Te) are studied and characterized.

The process of phase-change was analyzed from both electrical and optical point of view. Temperatures of crystallization ( $T_c$ ) in Ga–Sb–Te thin films were determined via four-point probe measurements of temperature dependent electrical resistivity and grazing incidence temperature dependent X-ray diffraction data. The film thicknesses as well as their optical properties were described utilizing spectroscopic ellipsometry. The chemical composition of the deposited layers was obtained by energy-dispersive X-ray spectroscopy. The surface roughness was evaluated by means of atomic force microscopy.

The obtained characteristics of both as-deposited and annealed co-sputtered Ga–Sb–Te thin films are compared. It was found that  $T_c$  decreases with Te content. The results show large values of electrical contrast – resistance between amorphous and crystalline state decreases by up to 6 orders of magnitude. Phase transition from the amorphous to crystalline state further leads to changes of optical functions demonstrated by optical contrast values  $|\Delta n| + |\Delta k|$  of about 1.5 for wavelength of 400 nm.

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# Phase relations in heat treated sodium borosilicate glasses – investigations by thermal analysis and scanning electron microscopy

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Phase separation or crystallization are processes leading to heterogeneous glasses. In that context sodium borosilicate glasses are starting materials for the development of VYCOR<sup>®</sup> glass<sup>(1)</sup> and of porous glasses.<sup>(2)</sup> Background for these applications is the spinodal phase separation into to at least two glass phases with an interpenetrating microstructure. Haller reported the existence of an equilibrium between three liquids<sup>(3)</sup> in three-component glass systems. Polyakova<sup>(4)</sup> confirmed the existence of three glass transitions but questioned the phase relation proposed by Haller. Easily soluble materials like a sodium borate rich phase are removed by leaching. Sintering then leads to VYCOR glasses. Without sintering to a fully dense glass, pores with sizes between 2 and 100 nm are generated as state of the art. To widen the application range of sodium borosilicate glasses prolonged heat treatment was applied.

Different sodium borosilicate glasses with (in mol%) 7 to 8 Na<sub>2</sub>O, 20 to 30 B<sub>2</sub>O<sub>3</sub>, 55 to 72 SiO<sub>2</sub> were investigated. Isothermal heat treatment at temperatures between 630°C and 730°C for up to 64 days was applied. Some of the resulting materials were leached first in diluted acid and then in NaOH to develop porosity. As cast and heat treated glasses as well as porous materials were analyzed by dilatometry, differential thermal analysis, and high-resolution scanning electron microscopy combined with chemical analysis. Further characterization methods included mercury intrusion porosimetry and nitrogen sorption, if applicable. Thermal events and the developing microstructures will be discussed with respect to phase relations.

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# **Characterisation of crystalline material in simulated UK vitrified high-level waste using Raman spectroscopy**

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Since 1990 highly active liquor (HAL) generated during the recycling of used nuclear fuel at Sellafield in the UK has been converted into a glass wasteform using a high temperature vitrification process. This uses an alkali borosilicate composition melted at ~1050°C in an induction-heated melter. The high level waste (HLW) glass produced is highly durable and suitable for long term disposal in a Geological Disposal Facility (GDF).

The UK is currently exploring thermal treatment for a wider range of higher activity waste streams where there may be significant advantages over the current baseline of cement encapsulation in terms of volume reduction, passivity, or product performance. This will potentially involve a range of different melter technologies and glass compositions and require an expansion of the current capability to assess vitrified product. Hence, the NNL is developing a thermal product sampling, characterization and analysis center of excellence to meet this expected demand, part of which is an assessment of several active laboratory techniques available in its Central Laboratory at Sellafield.

One of these is fast Raman spectroscopy mapping, which has the potential to assess the homogeneity of vitreous samples along with the identity of any inclusions or crystalline material present. This paper describes Raman mapping of non-radioactive simulated HLW glass as proof-of-principle experiments to demonstrate the efficacy of the technique. A series of standard crystalline inclusions were observed in these tests, which were compared to those previously identified by Scanning Electron Microscopy (SEM). The results indicate that Raman mapping can complement SEM for determining the presence and identity of any crystalline material forming in the melt, or unreacted batch material.

# Characterization, structure refinement and durability of sodium iron phosphate glass ceramic materials for immobilization of spent fuel

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The UK holds a significant inventory of 'degraded orphan nuclear fuel materials', which has arisen through the development of civil nuclear technologies during the 20<sup>th</sup> century. Prolonged over-ground storage of these materials presents a high cost for shielding maintenance, with a notable risk due to the high actinide content and radiological hazard. Following a review of fuel pre-processing methods and thermal treatment options which could be compatible with UK nuclear decommissioning strategy, work was undertaken to prototype a matrix of sodium iron phosphate glass ceramic materials, loaded with fluorite structured cerium oxide as a fuel simulant.

Results are presented, showing potential for substantial waste loading, with high temperature melt solubility for oxide fuel simulant at around 20 mol%. A computer assisted, image-based phase quantification of arrays of BSE micrographs<sup>(1)</sup> was used to quantify cerium partitioning into vitreous and ceramic phases. Coordination environment and local structure were refined for iron and cerium absorbers, using <sup>57</sup>Fe Mössbauer spectroscopy coupled with Fe-K edge and Ce-L<sub>3</sub> edge EXAFS respectively.

Durability testing of the sodium iron phosphate glass loaded with 0 mol%, 8 mol% and 15 mol% cerium oxide fuel simulant was undertaken using 28-day PCT-B powder tests. Based on post-dissolution study of the glass alteration layers and solution analysis of sampled aliquots by ICP-OES,<sup>(2)</sup> and the prior structural refinement, we present a theory for the degradation mechanism for these materials under aqueous conditions.

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# Solubility of uranium oxide in aluminosilicate glass melts

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The immobilization of highly radioactive waste using vitrification process has been in application since many decades.<sup>(1)</sup> This process is now under investigation for conditioning Intermediate Level and Long Life Waste (ILW-LL) using aluminosilicate glasses as host matrices. The vitrification must be able to maintain, within a certain range of compositions and redox potential, the actinides solubility. It is known that uranium chemistry is complex in glass-forming systems due to the presence of many oxidation states (VI, V, IV).<sup>(2)</sup>

This paper presents the uranium solubility study in aluminosilicate glass melts as a function of melt composition and oxido-reduction potential (oxygen fugacity) (Figure 1). Ternary  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$  (CAS) and  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$  (MAS) systems are considered. In those glasses, Al content is increased while keeping the Si/Ca and Si/Mg ratio constant. Further XANES analyses on selected samples have allowed the precise quantification of uranium oxidation states. The specific experimental methodology is detailed and solubility results combined with uranium valencies data are discussed on a thermodynamic point of view.

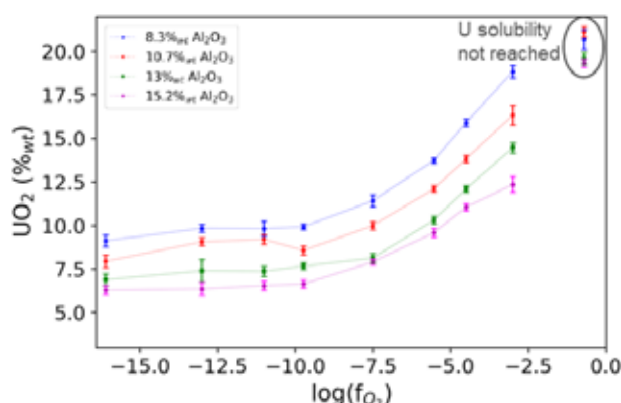


Figure 1. Solubilized uranium content (wt%  $\text{UO}_2$ ) as a function of oxygen fugacity for CAS system (1400°C)

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## Volatilisation from borosilicate radioactive waste glasses

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Vitrification of radioactive waste is currently undertaken for higher level waste and is being considered as a containment technique for intermediate level waste.<sup>(1,2)</sup> The UK has significant stores of this radioactive waste from legacy and ongoing operations. This project's objectives are to develop an understanding of intermediate waste thermal treatment to measure, reduce, control or constrain emissions. This is being researched using glassware bubblers and pyrolysis systems which capture gaseous emissions from the thermal treatment of simulant intermediate-level radioactive wastes to form glasses doped with radionuclide contaminants.

Low melting temperature glasses have been developed for emission experimentation by pyrolysis. Sodium lithium borosilicate glasses have been melted at 950°C with 0–50 wt% SiO<sub>2</sub> content for frit production. These frits were then blended with clinoptilolite and high magnesium sludge waste simulants, based on two common intermediate level radioactive wastes in the UK. Loaded waste glasses were then doped with inactive surrogates of common contaminants (Cs, Cl) and melted in a simulated thermal treatment system to determine the loss of those elements up to 950°C.

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## Radiation induced diffusion in UK-nuclear waste glasses

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Borosilicate glasses are the most common choices for nuclear waste glass due to their low processing temperature and ability to create a durable product capable of incorporating a vast range of radionuclides. The nuclear waste glass compositions used in the UK are Calcium Zinc (CaZn) and Mixed Windscale (MW) glasses. Nuclear waste glasses are designed to retain radionuclides for thousands of years, yet over time, the radiation produced by the high-level waste will interact with the structure of the glass causing defects in the glass network. These defects may lead to enhanced diffusion of glass species and those comprised of radioactive waste. The present work aims to understand the diffusion of Li and other species due to damage caused by recoils during alpha-decay of minor actinides. The recoil atoms are low energy heavy ions causing displacement of atoms within the glass matrix. Here, we are exploring the effect of Li as well the effect of simulated waste species (base glasses loaded with 25 wt% of only selected waste species) in these glasses on radiation induced diffusion. Eight types of glasses were irradiated with 8 MeV Au<sup>3+</sup> ions upto a fluence of 1e16 ions/cm<sup>2</sup>. These Au ions used simulate the effect of damage caused by recoils of alpha-decay processes where an actinide, e.g. <sup>239</sup>Pu gets converted to <sup>235</sup>U by releasing an  $\alpha$ -particle. The irradiated glasses were characterized using several complementary Ion Beam Analysis (IBA) techniques to enabled quantification of concentration and diffusion of various species in these glass samples. Rutherford Backscattering Spectrometry (RBS), Nuclear Reaction Analysis (NRA) and PIXE (Particle Induced X-ray Emission) were performed to obtain a depth profile of Li concentration and diffusion of heavy elements in these glasses. Data obtained from IBA will be correlated and presented with swelling observed using a profilometer and local coordination changes using Raman Spec and IR microscopy.

# Alternative foam reductants for the vitrification of high-iron Hanford High Level Waste (HLW) feeds

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Foaming during the vitrification of nuclear waste in Joule-Heated Ceramic Melters (JHCMS) is caused by trapping of feed gases such as CO<sub>2</sub>, NO<sub>x</sub> and O<sub>2</sub>, beneath a highly viscous reaction layer called the “cold cap”. Foaming restricts heat transfer during melting and, in extreme cases, can cause blockages of melter components. Sucrose is effective in reducing foam generation during vitrification of wastes rich in nitrates by reacting with them at temperatures below the foam onset. However, given the high-temperature redox reactions likely causing high-foaming in High-Level Wastes, it is questioned whether sucrose is the optimal reducing agent. A range of other carbon-based reductants were explored in melting a high-iron High-Level Waste feed, including coke, graphite, formic acid and HEDTA. Of these coke and graphite showed the greatest reduction in foam volume during melting, which is expected due to their high carbon content.

The effects of mixed-multivalent species in complex feed compositions was investigated, using X-ray absorption spectroscopy and <sup>57</sup>Fe Mössbauer spectroscopy and the main contributions to O<sub>2</sub> evolution in the high-iron waste feed were uncovered. Despite Fe being the most abundant species in the feed, contributions from the reduction of Mn from Mn<sup>4+</sup> to Mn<sup>2+</sup>/Mn<sup>3+</sup> outweigh the net contribution to O<sub>2</sub> evolved during redox reactions. These mechanisms of gas evolution and foam revolution in these complex waste streams is fundamental to understanding the effects of reductants on the glass melting process and melting of glasses with mixed-multivalent species.<sup>(1,2)</sup> The work provides a basis to further explore reductants in feeds high in multivalent species. The investigation of redox reactions in a complex feed with multiple mixed multivalent species is not just relevant to the waste vitrification process at the Hanford site but also other vitrification programmes and industrial glass making processes globally.

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# Structural versus chemical disorder in modified random networks

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It was nearly four decades ago that the concept of the *Modified Random Network* (MRN) was introduced in glass science by Neville Greaves as a nanoscale structural description of network glasses. The MRN model has since remained one of the most influential structural models of amorphous materials with profound implications in our current understanding of the static and dynamic properties of network glasses and their parent liquids. In this talk we will present experimental results obtained using two-dimensional NMR and electrical impedance spectroscopic techniques that will allow for a detailed parametrization of the nature of the MRN in two types of amorphous networks, namely: (i) silica and simple binary alkali silicates; and (ii) amorphous silicon oxycarbide polymer-derived ceramics. These experimental results provide novel understanding of the links between the structural and chemical disorder in glassy MRNs.

# Investigation of the properties and structure of fragile metal oxide liquids

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Molten metal oxides are frequently precursors to functional glass materials. Understanding of their processing–property–structure relationships is often limited by the difficulty in obtaining accurate thermophysical property data for the supercooled liquid state. This research used the Japan Aerospace Exploration Agency (JAXA) Electrostatic Levitation Furnace (ELF) on the International Space Station to study molten metal oxides over a wide range of temperatures both above and below the equilibrium melting point. The density, viscosity and surface tension of several titanate, aluminate, and silicate composition liquids were measured. The effects of the ionic radius of rare earth oxide additions were investigated by using scandium, neodymium, ytterbium and lanthanum as components of binary compositions. In some cases, the atomic structure of the liquids has been measured over similar temperature ranges to those used for property measurements. This talk will briefly describe the experimental methods, present results of the measurements, and discuss the data in the context of property and structure evolution in fragile oxide liquids when they are supercooled towards the glass transition.

This work is supported by NASA under grants 80NSSC18K0059 and 80NSSC19K1288 and US Department of Energy under grant DE-SC0018601.



# **Combined X-ray diffraction and X-ray absorption spectroscopy: a valuable tool to determine atomic architecture of reacting solids**

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Development of the combined measurements, using X-ray diffraction and X-ray absorption spectroscopy, has been a valuable addition to a suite of structural methods available in a synchrotron radiation source, in the determination of long and short-range order structures in a variety of solids. A range of functional materials, including solid catalysts, electronic materials, ceramics etc. have benefitted using this method. Significant advantage of this combined measurement is that the same solid is investigated under identical reaction conditions. Furthermore, this combined method can provide atomic architecture of a solid, that is undergoing changes at different length scales in the same material, under reaction conditions, that can be gained in a single experiment. Here, examples of converting an amorphous gel to a crystalline microporous solids containing small amounts of cobalt and phase transformation of zinc peroxide to zinc oxide through the formation of amorphous intermediate will be shown as examples to demonstrate the power of this combined measurements.

# Sodium silicate glasses: the structural roles of sodium and oxygen

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It is shown that modelling the first oxygen-oxygen peak in the neutron correlation function of a glass enables structural information about other correlations to be obtained, and the method is illustrated by application to a sodium silicate glass. The first O–O coordination number can be calculated from network theory, and sodium silicate crystal structures show that the mean O–O distance can be calculated from the Si–O distance, despite the distortion of the SiO<sub>4</sub> tetrahedra. Modelling the O–O peak for a sodium silicate glass allows the Na–O bond length distribution to be determined. For a binary glass with 42.5 mol% Na<sub>2</sub>O, it is found that the Na–O coordination number is 4.8(2) with an average bond length of 2.45 Å, and the Na–O bond lengths are more widely distributed than in sodium silicate crystal structures. Sodium ions are bonded mostly to non-bridging oxygens (NBOs), and the Na–NBO coordination number may be four as in crystals. Sodium ions are also bonded to a smaller number of bridging oxygens (BOs). Contrary to previous reports, it is not concluded that Na–NBO bonds are shorter than Na–BO bonds, but instead that the Na–BO distribution is relatively narrow, whilst the Na–NBO distribution extends to both shorter and longer distance. The broad distribution of Na–O bond lengths arises from a relatively broad distribution of Na–NBO bond valences, subject to the overall requirement of charge balance.

# The influence of nitrogen on the structure and properties of lithium and sodium metaphosphate glass electrolytes

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Lithium and sodium metaphosphate glasses are known to incorporate nitrogen under flowing nitrogen, forming LiPON and NaPON glasses with the oxygen partly replaced by nitrogen. This not only improves the physical and chemical properties but also improves the ionic conductivity which means that both LiPON and NaPON glasses are suitable candidates for solid state electrolytes. Of particular interest are the sodium-bearing variants since the availability of sodium make these much more favourable than lithium and as such the NaPON glasses offer a potential alternative to less sustainable lithium-based batteries. The performance of these electrolytes is related to both amorphous structure and to nitrogen content yet there are only limited available studies of the role of nitrogen in these metaphosphate glasses. In this study both X-ray and neutron total scattering methods have been used to evaluate the glass structure and the diffraction information has been combined with molecular dynamics simulation to develop structural models for these technically important materials.

Glasses have been produced by ammonolysis at Iowa State University and Raman spectroscopy has been used to identify new bands associated with nitrogen. These are associated with the formation of various types of  $\text{PO}_{4-y}\text{N}_y$  tetrahedra that link to form networks defining the glass structure. High energy X-ray diffraction measurements have been performed at the APS on six compositions in the Li-P-O-N and Na-P-O-N series. For the lithium system, the weak scatter from lithium reveals the P-O, P-P and P-N contributions to the total structure and shows significant changes in the structure as nitrogen replaces oxygen. Neutron diffraction data collected on the GEM instrument at the ISIS neutron source for three lithium and three sodium compositions also show changes in the phosphate glass structure as nitrogen replaces oxygen. In both systems there are changes in structure on the addition of nitrogen seen as changes in the first peak in the diffraction pattern, notably in the 0–10  $\text{\AA}^{-1}$  range consistent with changes in the connectivity of the phosphate polyhedral units (intermediate range order). These changes include the development of sharp peaks at  $\sim 1$  and  $\sim 2.7$   $\text{\AA}^{-1}$  in both lithium and sodium systems, shift to lower Q of peaks at higher Q and changes in the phase of oscillations at higher values of Q, all suggesting changes in structure over a range of different length scales as nitrogen is added. Initial structural modeling suggests at least two types of nitrogen incorporated into the metaphosphate structure, trigonal nitrogen atoms that link three  $\text{PO}_4$  tetrahedra and nitrogen atoms that link two  $\text{PO}_4$  units. There are also different degrees of distortion of the phosphate polyhedra linked to differences in viscosity and melt dynamics.

# A critical evaluation of barium silicate glass network polymerization

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The state of polymerization in silicate glasses and melts provides a fundamental control on their properties and phenomena, such as crystallization and phase separation. Here polymerization across the standard glass-forming range in the barium oxide–silica system,  $x\text{BaO} \cdot (1-x)\text{SiO}_2$  ( $0.28 \leq x \leq 0.45$ ), has been studied with both experiment (electron-probe microanalyzer, Raman, static and magic angle spinning  $^{29}\text{Si}$  nuclear magnetic resonance (NMR) spectroscopy) and theory, i.e. (Vashishta–Rahman-type and Du–Cormack-type potentials). In this study, no a priori assumptions were made about the number of  $Q^n$  species, specific mean polymerization nor presence or absence of oxygen species. This allows us to test the relationships between these structural aspects.

The relationships between oxygen speciation,  $Q^n$  connectivity and composition are established using multiple structural probes to develop a valid interpretation for three parameters: O/Si, NBO/T and  $Q^n$  distribution. Consistent equilibria,  $k_{Q^n}$  provide further evidence that our interpretation is correct. Having confidently determined a  $Q^n$  distribution the apparent Raman scattering cross sections are determined for each of the  $Q^n$  species. These results show that the  $Q^1$  cross section is  $1.01 \pm 0.15$ , that the  $Q^2$  cross section is  $\sim 1.1$  but changes strongly with composition/ $Q^2$  concentration, and that the  $Q^3$  cross section is  $1.14 \pm 0.04$ . Furthermore, these results show that the  $Q^4$  cross section approaches 0, at low concentrations, highlighting an apparent fundamental difference in polarizability between its symmetric stretching mode versus those of the other  $Q^n$  species.

# Computer modelling of pressure-induced structural disorder in $\text{ZrW}_2\text{O}_8$ to explore paradigms for solid state amorphization

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Zirconium tungstate,  $\text{ZrW}_2\text{O}_8$ , has received attention due to its negative thermal expansion (NTE) over a temperature range of 1000 K.<sup>(1)</sup> The crystalline phases of  $\text{ZrW}_2\text{O}_8$  are all comprised of  $\text{ZrO}_6$  octahedra which are corner linked to  $\text{WO}_n$  units with  $n=4$  or 5, but the latter have different linkages in each phase. Attention has also been focused on  $\text{ZrW}_2\text{O}_8$  because it undergoes pressure induced amorphization above 1.5 GPa.<sup>(2)</sup> Limited previous computer modelling studies have used classical molecular dynamics to study thermal motion in crystalline  $\text{ZrW}_2\text{O}_8$  in relation to NTE,<sup>(3)</sup> and the reverse Monte Carlo method to study structural disorder in the amorphous phase.<sup>(4)</sup> This presentation will show new results from using classical interatomic potentials to study pressure induced amorphization in  $\text{ZrW}_2\text{O}_8$ . The features of structural disorder observed can be assessed in the context of solid-state amorphization, in contrast with the structural disorder typical of glasses (i.e. melt-quenching).

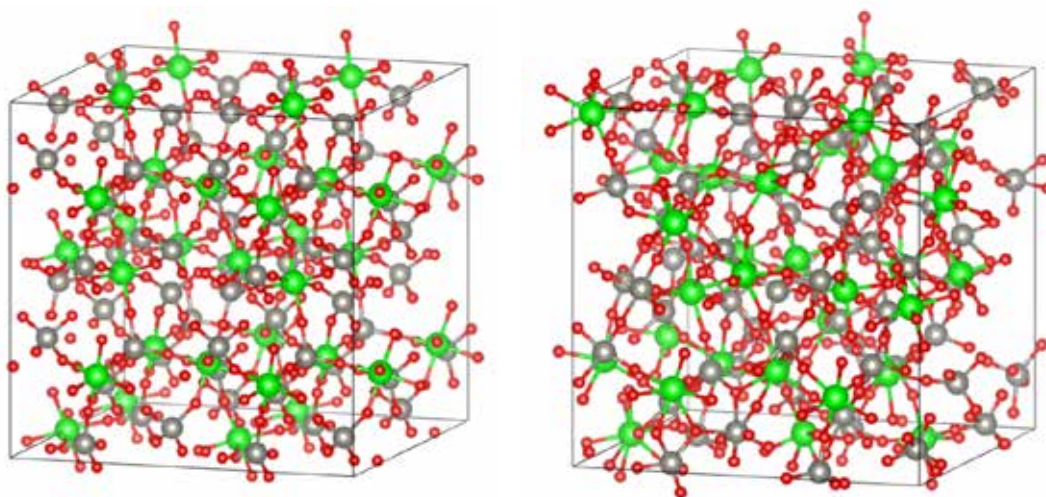


Figure 1. (left)  $\alpha\text{-ZrW}_2\text{O}_8$  and (right) pressure induced structural disorder in  $\alpha\text{-ZrW}_2\text{O}_8$

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# Electric transport and crystallization in $V_2O_5$ – $TeO_2$ glass and glass-ceramics

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It was found in the late 1970s that glasses after temperature treatment above  $T_g$  point show a major increase in the electrical conductivity.<sup>(1,2)</sup> Such material can find multiple applications as cathodes, anodes, and memory switching because of its high density, stability, and no need of adding extra elements to increase its conductivity. The crystallization process and conductive mechanism in binary glass-ceramics are still not fully understood which makes these materials very interesting to study. We choose  $V_2O_5$ – $TeO_2$  glass as the studying object due to the low temperature of preparation and high conductivity increase due to crystallization.

In this work the results of the investigation of the crystallization process, structure, and electrical properties of different vanadium content glass will be presented. Crystallization parameters were determined through DSC study and dynamic d.c. measurements. Such a method of crystallization was successfully used in  $V_2O_5$ – $P_2O_5$  system.<sup>(3)</sup> The structure of glass and glass-ceramics were studied by XRD, FTIR, and SEM methods. Electric properties were examined by EIS. Charge transport models such as Schnakenberg's, Friedan–Triberis, VRH by Mott & Greaves, and Shimakawa multi-phonon tunneling model were examined along with temperature dependence of activation energy.

The low complexity of the binary system makes it possible to correlate structural changes, such as phase separation and crystallization, with charge transport properties. A low melting point is an additional advantage that lowers production costs.

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# Characterisation of metastable phase formation in binary AuGe via correlated flash differential scanning calorimetry and electron microscopy

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Via correlated fast differential scanning calorimetry (FDSC) and scanning electron microscopy (SEM), we investigate metastable phase formation in eutectic AuGe. This alloy system reveals a simple eutectic phase diagram with a eutectic point at Au<sub>72</sub>Ge<sub>28</sub> and 361 °C. It is the second Au-containing alloy for which glass formation has been observed after solidification at sufficiently high cooling rates.

With the help of ex-situ FDSC, which enables cooling and heating rates of several 1000 K/s, we show that metastable crystalline  $\beta$  and  $\gamma$  phases form in AuGe due to crystallisation of the amorphous phase upon heating, or due to rapid cooling from the melt with a rate slower than the critical cooling rate for glass formation. Via ex-situ FDSC and correlated FDSC/SEM, experiments we are able to determine the transformation kinetics and thermodynamics of these metastable phases. Producing thin TEM lamellae from the FDSC-processed samples, we also analysed the nano-sized metastable phases by electron diffraction and electron-dispersive X-ray diffraction (EDX) within a transmission electron microscope.

## **NMR studies of glass structure: current issues**

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Nuclear magnetic resonance (NMR) as a tool for investigating glass structure has a long and rich history. While the disorder in glass precludes the use of the most subtle experiments used in liquid state NMR, nevertheless a variety of sophisticated measurements can be made, which help elucidate the local and intermediate glass structure. As such, NMR provides in many cases information that is complementary to other measurements, such as neutron and x-ray diffraction, and vibrational spectroscopy.

In this talk I will outline several of the outstanding problems in NMR study of glass, centered around the interpretation of the results: how are the observable quantities best related to local structure, and how is the disorder best modeled? These topics will be addressed through discussion of several recent works in my lab, on parameter distributions and first principles computations.



# Multinuclear NMR investigation of the composition-dependent structural role of $\text{Pb}^{2+}$ in lead borogallate and boroaluminate glasses

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Knowledge about network connectivity in lead aluminoborate glasses remains poor despite diverse applications ranging from optical materials to nuclear waste immobilization. Several investigations on lead-bearing glass systems have shown that  $\text{Pb}^{2+}$  can function as a network former or modifier or both, depending on its concentration, however the mechanism governing these roles is unclear. In this work,  $^{207}\text{Pb}$ ,  $^{11}\text{B}$ ,  $^{27}\text{Al}$  and  $^{71}\text{Ga}$  nuclear magnetic resonance (NMR) spectroscopy are used to examine the short-range structure of parallel series of lead boroaluminate and borogallate glasses. The chemical similarity of Al and Ga provides a sensitive measure of the role of cation-field strength in driving structural arrangements. High-field  $^{71}\text{Ga}$  magic-angle spinning NMR indicates that Ga is present in three different coordination environments, similar to the polyhedral distribution of Al, confirming that the isostructural nature of Al and Ga in borates is consistent with previous observations in silicate and phosphate glass systems. Spectroscopic analysis of these glasses implies a hierarchy in the charge compensation of network-forming units following the order:  $[\text{AlO}_4]^- > [\text{BO}_4]^- > [\text{GaO}_4]^-$ .  $^{207}\text{Pb}$  CPMG NMR spectra consist of signals spanning large spectral breadths resulting from overlapping peaks associated with different Pb coordination numbers and large chemical shift anisotropies. The relative fractions of  $\text{Pb}^{2+}$  in low- and high-coordinate environments estimated by peak-fitting suggest the presence of low-coordinate “network-forming”  $\text{Pb}^{2+}$  even at low PbO contents. This behaviour can be rationalized by considering the respective cation-field strengths of the constituents.

# Study of the short- and medium-range structural order in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses doped with $\text{P}_2\text{O}_5$

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The aims of this work are to establish the structural effects caused by the increasing additions of  $\text{P}_2\text{O}_5$  in a  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  glass system, to enable a better understanding of the phase separation mechanism and crystallisation behaviour, and subsequently how these can affect the properties of the glass. X-ray diffraction (XRD) and Rietveld analysis confirmed that the glasses were X-ray amorphous between 0.0–3.0 mol%  $\text{P}_2\text{O}_5$ , and that 4.0 mol%  $\text{P}_2\text{O}_5$  was the onset of crystallinity with the formation of  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_4\text{P}_2\text{O}_7$ . The amorphous material content reduced from 100.00–74.56 wt%, whilst  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_4\text{P}_2\text{O}_7$  both increased from 0.00–13.16 wt% and 0.00–23.31 wt%, respectively. Back scattered SEM images suggested that phase separation had occurred via liquid–liquid phase separation, where there was evidence of a droplet like morphology closely resembling the nucleation and growth mechanism between NBSP4.0–6.0. However, the exact mechanism cannot be confirmed as based purely on its morphology. <sup>11</sup>B MAS NMR results showed that the relative concentration between <sup>3</sup>B and <sup>4</sup>B stayed constant. The distinct lack of sharp spectral features in the partially crystallised samples suggested that boron was not involved in the crystallised material. There was also a negligible change in the shift of <sup>3</sup>B sites with 6.0 mol%  $\text{P}_2\text{O}_5$ . All the above statements suggest that phosphorus is mostly found in the vicinity of the charged <sup>4</sup>B sites. The <sup>31</sup>P MAS NMR results suggested that the number of non-bridging oxygens on the phosphorus from the starting material  $\text{P}_2\text{O}_5$  to the observed pyrophosphate, P1, and their compensating cations, likely sodium, came from the silicate and/or borate glass network. The <sup>23</sup>Na MAS NMR results confirmed the findings of the <sup>31</sup>P MAS NMR data, where the sodium environment was affected by the introduction of  $\text{P}_2\text{O}_5$ , suggesting that sodium was in the vicinity of the phosphorus atoms, especially when crystals were formed at 4.0 mol%  $\text{P}_2\text{O}_5$  and above, but that sodium was still abundant in the glassy environments. The <sup>29</sup>Si MAS NMR results confirmed that there was an increase in the network polymerisation with increased phosphate contents, which was consistent with the formation and precipitation of sodium phosphate crystals.

# Extent of structural disorder in $\text{SrO-Ga}_2\text{O}_3\text{-2SiO}_2$ glass and $\text{SrGa}_2\text{Si}_2\text{O}_8$ transparent ceramic from advanced solid-state NMR spectroscopy

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Transparent inorganic materials, like glasses, single-crystals, or polycrystalline ceramics, are used for many key technological applications such as optical and lighting applications. However, the synthesis of such polycrystalline transparent materials usually requires complex powder sintering conditions. We have recently shown that highly-transparent polycrystalline samples can be obtained from full and congruent crystallization of bulk parent glasses, allowing to elaborate new large-scale transparent ceramics with different compositions.<sup>(1,2)</sup>

In this work, we will describe the synthesis and characterization of novel transparent polycrystalline  $\text{SrGa}_2\text{Si}_2\text{O}_8$  ceramic obtained by full and congruent crystallization from the parent glass. High temperature  $\text{SrGa}_2\text{Si}_2\text{O}_8$  polymorph, already well known in literature,<sup>(3)</sup> is obtained by annealing the glass at higher temperature, giving rise to an opaque ceramic. Using congruent crystallization from the parent glass enables to reach an unclassified metastable  $\text{SrGa}_2\text{Si}_2\text{O}_8$  polymorph at lower temperature. The metastable phase is shown to adopt the same polymerized network topology as that of the stable crystalline phase but without Ga/Si ordering in the tetrahedral sites. The presence of chemical disorder in this new polymorph leads to a dense and transparent polycrystalline ceramic. By using  $^{29}\text{Si}$  and high field  $^{71}\text{Ga}$  solid state NMR spectroscopy, it was possible to characterize and quantify this chemical disorder in both metastable ceramic and parent glass. It is shown that, while positional and topological ordering occurs in the metastable phase, the Ga/Si chemical disorder remains very close to that in the glass. Adding dopants in this materials, such as Rare-Earth element ( $\text{Dy}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Eu}^{3+}$ ), triggers interesting optical properties.<sup>(4)</sup> We demonstrate that the degree and nature of disorder in  $\text{SrGa}_2\text{Si}_2\text{O}_8$  materials affect dramatically the luminescence properties as shown for strontium alumino-silicate  $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$  compositions.<sup>(2)</sup>

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# Development of glass optical fibers 1978–2021 providing us the digitalized communication world

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First optical fibers became commercially available in cables during 1976–79 in Japan, USA, UK, European countries, etc. First installations of optical cable networks in Finland and Sweden occurred during 1979. The fibers were developed, because signal attenuation and dispersion could be made much, much lower in glass fibers than in the coaxial and other metal cables.<sup>(1)</sup> The first systems had 1.5 Mbit/s capacity over 1 km distance. Now we have fiber systems around the earth (42000 km) over 100 Tbit/s per link.<sup>(2)</sup>

The first fibers had parabolic refractive index profile, and the bandwidth of 1 km fiber could be over 1 GHz, but it mainly varied between 50–500 MHz. The attenuation at the first (830–900 nm) and second window (around 1300 nm) was below 10 dB/km.<sup>(3)</sup> Typically, fiber dimensions and the shape of the profile varied along the fiber length and both bend attenuation and dispersion varied. The first preforms were only 2 cm thick and 10–30 cm long.<sup>(3)</sup> Now the preforms are 25 cm thick and 5–10 m long.

The outer cladding was made of natural SiO<sub>2</sub>, dug out from the ground and melted into glass. In about 10 years it was realized that the mechanical properties would be much better, and fibers would become more accurate in properties, if also the cladding glass was made by the CVD method. The coating materials have also been developed further and both the multimode MM-50/125- and SM-fibers have become very good and reliable. Current cables can have a thickness of a couple cm and contain up to 7000 fibers having attenuation at 1550 nm below 0.2 dB/km.<sup>(4)</sup>

To obtain the good mechanical reliability and quality, fibers and cables need to be manufactured and installed, so that they fulfill the international standards. –Such networks provide us the digitalized, live-picture communication, TV, etc. The signal, that travels inside fibers, does not heat up any particles or gasses of the air, and thus the fibers also help us to control the climate change. Special milestones during the period 1980 through 2020 regarding fiber reliability and transmission properties will be presented. Glass purity and structure, coating development and transmission (like PMD) will be discussed thoroughly.

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# Erbium fluorescence by energy transfer from defects states in As–Se thin films

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Chalcogenide glasses are the best alternative for taking advantage of the mid-infrared emission of rare-earth ions. Their excellent transmission in the infrared region, high oscillator strengths, high refractive index, and lowest phonons energies between the glassy materials have proven to be of great benefit for decreasing the probability of non-radiative relaxation through multiphonon relaxation and increasing the emission efficiency.<sup>(1,2)</sup> The use of rare-earth doped chalcogenide as active media on integrated optical circuits is however hindered due to the low concentrations that chalcogenide glasses can sustain without presenting agglomeration or phase separation. In this work, we use the co-evaporation of metallic erbium and glassy As–Se to create highly homogeneous thin films with excellent optical quality. This highly out-of-equilibrium method enables us to rapidly quench the glass and to introduce large concentrations of erbium without inducing phase segregation or glass devitrification. Our results show that the properties of the As–Se glass host and the absence of co-dopants or structural mediators lead to excellent luminescence properties and the highest cross-section emission reported in Er-doped glasses until now. Furthermore, erbium emission is observed for excitation in a continuous range of wavelengths corresponding to the glass absorption region. Such mechanism is described in terms of energy transfer from defects states in the middle of the matrix bandgap and the erbium energy levels. The abundance of inter-bandgap states and the efficiency of the energy transfer mechanism are related to the arsenic concentration and the thin film structure.

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# Photo-thermal precipitation of PbS quantum dots in glass using $\text{Co}^{2+}$ light absorption

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PbS quantum dots (QDs) provide potentials for tunable optoelectronic devices such as optical amplifiers because of their size-sensitive optical properties together with a large Bohr exciton radius (18nm). In glasses, PbS QDs can generally be precipitated by heat treatment, ion implantation and laser irradiation. It is not trivial to control the size of QDs accurately using the heat treatment. Laser irradiation can provide an alternative way for the improved control in sizes and site selective precipitation. Continuous wave (CW) green laser irradiation with  $\lambda=532$  nm led to the precipitation of QDs near to the ion-exchanged Ag clusters.

In this study, we attempted the absorption of the same laser light by the transition metal ions and converted into heat energy by non-radiative relaxation process. First, we prepared silicate glasses doped with four different transition metals to compare their absorptivity for a 532 nm laser. Among these,  $\text{Co}^{2+}$ -doped glasses showed the strongest absorption for the green ( $\lambda=532$  nm) laser. Photoluminescences within 1000~1500 nm in wavelength were recorded from the glass exposed for ~ 15 min. The peak emission wavelengths shifted from 1020 nm to 1245 nm by increasing the laser power from 6 W/cm<sup>2</sup> to 7.4 W/cm<sup>2</sup> (Figure 1). From transmission electron microscopy along with electron diffraction patterns, the crystals precipitated in glasses were identified as PbS nanocrystals. Electron energy loss spectroscopy mapping shows that cobalt ions are incorporated into PbS QDs. The magnetic phases formed in the laser irradiated region of the glass due to  $\text{Co}^{2+}$  incorporation into QDs region were further confirmed from the magnetic force microscope. Optical thermometry using fluorescence intensity ratios from  $\text{Nd}^{3+}$  emissions excited by a 532 nm CW laser were used to investigate the temperature during the laser irradiation.

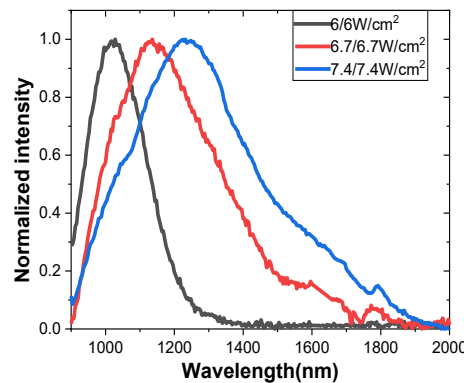


Figure 1. Photoluminescence of glasses irradiated with the laser beam of three different intensities.

## Carbon dots in mesoporous silica matrices: promoting green emission

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Fluorescence features of citric acid and urea-based carbon dots (CDs) are modified with the enhancement of the green contribution when the samples are synthesized within mesoporous silica matrices. Silica plays the role of nanoreactor and host for the fluorescent carbon nanoparticles, in view of a solid-state emitting hybrid device. The hybrid systems were characterized by a full-fledged photo-physical investigation to ascertain the effect of the silica-nanoparticles interaction. The latter, indeed, as compared to CDs dispersed in water, display a larger emission in the green range whose contribution can be increased by UV and blue laser irradiation, partly at the expense of blue contribution. This phenomenon is framed within the molecular model as the origin of the emission in CDs, hypothesizing the presence of at least two different emitting molecular centers, one for the blue and one for the green emission. The irradiation experiments suggest that some photo-activated reaction mechanisms among the two emitting centers is ignited by laser light. The analysis of hybrids synthesized within silica with different nanosize and morphology by means of XPS measurements and time-resolved photoluminescence measurements calls for an active role of the matrix in directing the synthesis toward the formation of CDs with different relative content of the two emitting centers and in promoting a larger content of graphitic N with respect to reference CDs. DFT quantum chemistry modeling by means of selected molecular models for the two centers, like CZA, IPCA and HPPT typically formed in citric acid and urea synthesis of CDs, shows that, on average, the optical efficiency of the blue centers is reduced by the interaction with the silica cage whilst the optical efficiency of green ones is increased, thus promoting the green emission in CDs-silica hybrids, as experimentally observed.

# Automated development of machine learning inter-atomic potentials driven by diffraction experiments

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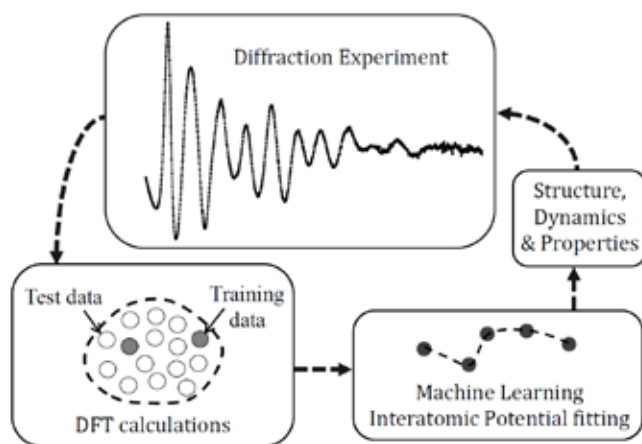
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High-energy x-ray diffraction and neutron Pair Distribution Function (PDF) measurements enable a unique insight into the structure of disordered materials. This presentation describes a new machine learning (ML) scheme, in which experimental PDF data drives an active learning algorithm that tests *ab initio* molecular dynamics (AIMD) simulations using a Gaussian Approximation Potential (GAP) approach [1]. The method uses an automated closed loop via an active-learner, which is initialized by x-ray and neutron diffraction measurements, and sequentially improves an unsupervised machine-learning model until the experimentally predetermined phase space is covered. The resulting classical GAP MD simulations reproduce all the experimental phases with near *ab initio* precision, and yields quench rates of 1K/ps not accessible via AIMD. The method significantly reduces model development time and human effort.



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# Interpolation method for calculation of disorder in PDF and XAS

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Combination of PDF and XAS methods is an excellent choice to gain insights into the structure of complex atomic systems and, indeed, has already been used to obtain information about particle size and stoichiometry of, for example, Magic Size Clusters (MSCs).<sup>(1-3)</sup> However, structural parameters such as coordination numbers and interatomic distances are typically extracted by fitting routines that include disorder as one of the variable parameters. Disorder is typically modelled phenomenologically by using Debye–Waller (DW) correction that accounts for the average disorder. The current state-of-the-art in real-space modelling extends this method further by simply applying varying DW factors as a function of correlation length. This, while increasing the number of variables, it doesn't provide adequately description the effects of correlated motion of atoms and the shape of distributions grounded in the physics of these phenomena. Ab-initio calculations can address this, but are rather time consuming and, crucially, require the knowledge of the atomic structure. Consequently, it can be difficult to reliably extract sufficiently accurate structural information (i.e. interatomic distances and coordination numbers) in complex disordered systems; since multiple correlations can occur at similar length scales and may have different distributions, resulting in errors in structural analysis.

Recently a fast semi-analytical Interpolation Method has been proposed and tested<sup>(4)</sup> by us for calculation of interatomic correlations, based on linking the nearest neighbours (NN) delocalisation probability (at a given temperature) with the interatomic potential (IP). The distance-dependent atomic correlations can then be extended beyond NN by being factorised into the local (NN) delocalisation probability (calculated from the IP) and the path length connecting the atoms. This approach allows for the shape of the correlation peaks in xPDF (and in XAS) to be calculated precisely at a given temperature. Thus, when the IPs are known one can model disorder and, hence, the structure more accurately. Moreover, when these potentials are unknown, one can parametrise them from the experimentally measured data for a known structure and then use this parametrisation to calculate correlations in an unknown structure.

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# **Diffusion in metallic and in oxide glasses – an overview**

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We remind the reader to some common features of metallic and oxide glasses. We then introduce the radiotracer method for diffusion studies, which can be applied for both types of glasses. We provide an overview on diffusion in metallic glasses in which we consider both types of metallic glasses – conventional and bulk metallic glasses. In the last part we discuss diffusion and ionic conduction in oxide glasses. For ionic glasses conductivity measurements are an important complement to tracer diffusion studies. We remind the reader to the method of impedance spectroscopy. We discuss results for soda-lime silicate glasses, single alkali borate glasses and mixed alkali borate glasses and present evidence for collective jump processes in glasses.

# The Invar effect of Fe-based bulk metallic glasses at the atomic scale

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Ferromagnetic Fe-based bulk metallic glasses (BMGs) universally show the Invar effect, i.e. an anomalously low coefficient of thermal expansion (CTE) below their Curie temperature. This effect is rarely seen in crystalline alloys (Fe<sub>65</sub>Ni<sub>35</sub> being a notable exception), but appears to be present in all Fe-based BMGs over a wide range of chemical compositions and irrespective of minor alloying elements.<sup>(1)</sup> The Invar effect is only present in the glassy state and disappears after crystallization.

Most observations of the Invar effect in BMGs focus on the macroscopic scale and thus cannot explain its relationship to the amorphous structure. However, in a recent in-situ X-ray diffraction (XRD) experiment, we provide evidence for the Invar effect to occur at the atomic scale and explain its origin.<sup>(2)</sup> We find that the magnetic interactions of Fe–Fe pairs counteract thermal expansion and can even cause a net contraction of Fe–Fe bonds below the Curie temperature, where the effect vanishes and the CTE increases by a factor of 3 to 10. The Invar effect is also seen in the thermal expansion of higher-order atomic shells. Our results thus show that the Invar effect in Fe-based BMGs occurs over multiple length scales: it originates at the atomic scale from the magnetic interactions of Fe–Fe pairs, translates into all atomic shells, and eventually manifests itself macroscopically without the need of any long-range order.

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# Viscoelastic behavior of high-entropy metallic glasses

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In order to fully understand the mechanical behavior and physical properties of high-entropy metallic glasses it is necessary to investigate the structural relaxation dynamics at different temporal and spatial scales and their evolution with time. In this contribution, we will present an overview of our recent works, in which we used dynamic mechanical analysis, stress relaxation, and dynamic cyclic loading experiments. A linear relaxation model was developed to describe the whole process of stress relaxation in a wide range of temperatures. Hierarchical dynamics, due to structural heterogeneity, was found to accommodate the viscoelastic deformation of high-entropy metallic glasses.<sup>(1)</sup> Furthermore, the anelastic deformation behavior of  $\text{Pd}_{20}\text{Pt}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}$  was probed by stress relaxation and recovery. This allowed us to understand the effect of atomic free-volume zones and the anelastic deformation, providing an important insight into how atomic structural features affect the deformation behavior of this high-entropy metallic glass.<sup>(2)</sup> The confined flow defects of free-volume zones and the inelastic deformation behavior were found to produce a significant mechanical hysteresis loop in dynamic cyclic loadings, which were described with a viscoelastic model.<sup>(3)</sup> Finally, the evolution of stress relaxation of high-entropy metallic glasses with distinct  $\beta\beta$ -relaxation behavior was studied. The stress relaxation timescale and the apparent activation energy of the mechanical relaxation were found to change with the intensity of the  $\beta\beta$ -relaxation mode. In parallel, it was found that the high-entropy metallic glasses show a higher apparent activation energy of mechanical relaxation as compared to other metallic glasses.<sup>(4)</sup>

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# Color–structure relationships in transition element bearing borate glasses

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By contrast to most glasses, the structure of alkali borate glasses is based on rigid superstructural units incorporating various possible combinations between  $^{13}\text{B}$  and  $^{14}\text{B}$  and non-bridging oxygens. Binary alkali borate glasses containing transition elements exhibit one of the most spectacular color changes as a function of the alkali nature and content of the glass. We review structural data on the local environment around Co, Ni, Cu, Zn and U in alkali borate glasses obtained using UV–VIS–NIR (crystal field) spectroscopy, synchrotron X-ray absorption spectroscopy (XAS) and Electron Paramagnetic Resonance (EPR). Using extended series of alkali (K, Na, Li) borate glasses, the coordination numbers and oxidation states of the cations are determined. In low-alkali borate and borosilicate glasses, XANES and EXAFS indicate that transition elements (Ni, Co, Zn) are octahedrally coordinated, a co-ordination state that is unusual in most oxide glasses. This peculiar structure is based on edge-sharing octahedra forming nanometric clusters in a defective cfc arrangement. They result from the presence of rigid superstructural units in low-alkali borate glasses. Similar domains, though smaller in size, have been found in low alkali-borosilicate glasses. Despite Zn is not a transition element, it shows the same behavior as divalent Co and Ni, due to a similar size. Cobalt- and nickel bearing alkali borate glasses show a well-known exceptional diversity of coloration from pink- to blue and from green to yellow, brown, and purple with increasing alkali content. This spectacular modification of colors arises from a coordination change from 6- to 5- and 4-fold, not only with increasing alkalinity but also at decreasing cation strength of the alkali (Galoisy & Calas, 2021; Hunault *et al*, 2016). Borosilicate glasses show an original orange color, resulting from the coexistence of  $\text{Ni}^{2+}$  in borate-like and silicate-like surroundings, illustrating the role of  $\text{Ni}^{2+}$  as a structural probe (Galoisy *et al*, 2005).

The structural behavior of  $\text{Cu}^{2+}$  in  $\text{R}_2\text{O}$  glasses is different from the other transition elements: there is no coordination change with glass alkalinity, nor clustering in low-alkali glasses. The  $\text{Cu}^{2+}$  sites are more distorted but less distributed in alkali-poor compositions than at higher alkali content. This causes a color change from light cyan to sky blue with increasing alkali content. These differences are a consequence of the Jahn–Teller distortion affecting octahedral  $\text{Cu}^{2+}$ . Similarly to 3d elements, the coordination number of uranyl groups in borate glasses decreases with increasing glass alkalinity, as shown by the smaller number of equatorial ligands. This explains the color change from green to yellow already mentioned by Weyl (1951) in the same compositions.

Transition elements are therefore sensitive to their environment, probing the local structure in the glass. In borate systems, the systematic comparison of the glass data with the data obtained on crystalline 3d- and 5f-bearing alkali borates allows the use of Pauling rules to provide credible molecular scale scenarios for linking transition elements to the borate polymeric network.

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# Controlling glass properties through surface mediated equilibration

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Physical vapor deposition (PVD) has been shown to produce glasses that are denser and thermally more stable than glasses produced by cooling the supercooled liquid. PVD provides a direct path into the deep states of the energy landscape, by taking advantage of the enhanced mobility at the glass surface and layers directly below.

Surface mediated equilibrium (SME) during PVD can involve multiple steps of molecular orientation at the interface, equilibrium relaxation near the surface layer, and accelerated aging when the surface layer falls out of equilibrium as the surface molecules are buried further into the film. Given its kinetic nature, the details of SME strongly depend on the molecular shape, the deposition temperature, and the deposition rate. In this presentation, we will discuss how this process can be used to our advantage to produce glasses with unique amorphous structures.

In molecular glasses, we control the molecular shape through dihedral rotations or by adding specific inter-molecular interactions to show that glasses with varying degrees of stability, packing anisotropy, and microphase separation can be produced. In addition, the film thickness can play a major role in the properties of the surface mobile layer, and thus the SME process, allowing us to observe a previously unidentified liquid-liquid phase transitions at temperatures well below the glass transition temperature.<sup>(1)</sup> In amorphous selenium, light can be used to modify the molecular weight and dynamics of the mobile surface layer, producing glassy structures that cannot be produced through the liquid-quenched path.<sup>(2)</sup> As such, light can be used as another variable to control properties of PVD glasses and access unique amorphous phases with unique density and kinetic stability signatures.

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# Impact of glass composition on electro-magnetic radiation effects observed in phosphate optical and photonic glass materials

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Radiation interactions with optical and photonic glass materials continue to be an area of significance due to the use of such materials in applications where they are deliberately, or through use, exposed to high energy electro-magnetic radiation (e.g. satellite components, fibre Bragg gratings, etc.).

This work explored the impact of x-ray radiation on a range of phosphate glass compositions containing varying levels of the transition metals Cr and Mn and lanthanides Er, Yb and Ce. The goal of this activity was to obtain an understanding of how these elements effect the extent and nature of the radiation induced changes resulting from x-ray exposure, with a view to potentially applying such effects to applications in photonics.

The resultant radiation effected glasses were studied under UV/Vis, FT-IR and EPR spectroscopy, in order to characterize the defects generated in each glass and their effects on the optical properties and network connectivity of the materials.

Results demonstrated that the presence of Ce, Mn and Cr resulted in the suppression of defect formation in proportion to the extent of doping. This effect was attributed to the impact of  $\text{Ce}^{3+}/\text{Ce}^{4+}$ ,  $\text{Mn}^{2+}/\text{Mn}^{3+}$  and  $\text{Cr}^{3+}/\text{Cr}^{6+}$  redox pairs quenching radiation generated  $e^-$  and  $h^+$ , through a mechanism similar to that previously seen in glasses containing  $\text{Fe}^{(1)}$

Changes in bulk density and network connectivity were observed in all glasses despite the quenching of defect sites in those containing sufficient Ce, Mn or Cr. As such it was shown that the redox pair quenching mechanism resulted in impacts to the glass forming network through changes in the coordination of the dopant elements. As such despite defects being suppressed a degree of network modification is incurred by electromagnetic radiation.

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# Effect of batch content and preparation conditions on the colour of glass: iron–manganese coloured soda–lime–silica glasses

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The literature on coloured glass is vast, yet there are few systematic surveys of the effect of batch content together with preparation conditions over the wide range presented here. We report experiments relevant to small scale production for art glass. The iron–manganese redox couple has been chosen on account of its sensitivity to batch content and preparation conditions. Our experiments cover the range 1350 to 1500°C,  $pO_2$  from reducing  $10^{-6}$  atm to oxidising  $10^{-2}$  atm, and concentrations of the oxides of iron and manganese from zero to 1 mol%. Several preparation methods include the presence or absence of refining agents sodium sulphate and sodium nitrate, and examination of the effect of stirring or not stirring melts. The glasses were prepared in quantities of up to 350 g in multi-litre crucibles in gas fired or electric furnaces.

The resulting glasses were analysed by optical absorption spectroscopy over the range 200 to 3000 nm. Some luminescence spectra were also obtained.

The results show a strong quantitative dependence on preparation conditions. The concentrations of the significant chromophores:  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Mn^{3+}$  were determined. Colours ranging from deep lilac to pale pink were obtained by control of furnace atmosphere alone. The effect of replacing sodium by potassium in the batch changed the colour from lilac to deep purple. Furthermore, by use of oxidising conditions and a potash rich batch, golden colours could be obtained from melts at low furnace temperatures.

This presentation will contain examples of the qualitative and quantitative link between colour, batch content, and preparation conditions for a large range of glasses coloured by the oxides of iron and manganese.



# Network-forming oxides with non-centrosymmetric structural groups – diffraction results of molybdate and antimonite glasses

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Regardless of acting covalent bonds, the basic building pieces that make up the structures of oxide glasses (or crystals) are often considered as spherical cations and anions. The relations of the ionic radii suggest the possible coordination polyhedra<sup>(1)</sup>. The network-forming units  $AO_n$  are mostly tetrahedra whereas also  $AO_3$ ,  $AO_5$  and  $AO_6$  units are known, the latter only in minor portions. The shapes of the  $AO_5$  have some variations. According to Zachariasen,<sup>(2)</sup> an oxygen should not form more than two A–O bonds. Radial distributions from diffraction are analyzed (coordination numbers, distances) to determine the groups.

Some conditional network-formers possess such structural groups that do not follow simple rules of packing or bonding symmetries. In order to avoid misinterpretations, it is necessary to use the building blocks of related crystal structures, knowing well that this only gives an incomplete picture. Here, the structural units of some special glasses are analyzed which cannot be extracted simply from their radial distributions. Silver molybdate glasses<sup>(3)</sup> are partially formed of  $MoO_6$  units that are anything but regular octahedra. Based on crystal structures, it has been suggested that some  $d^0$  transition metal cations prefer off-center sites in  $AO_6$  octahedra for electronic reasons.<sup>(4)</sup> The phenomenon is associated with the second-order Jahn–Teller effect.<sup>(5)</sup> The distorted oxygen environments of some other cations are due to the steric effects of their lone-pairs.<sup>(6)</sup> The antimony phosphate glasses measured by neutron and X-ray diffraction are formed of  $SbO_3$  and  $SbO_4$  pyramids with O–Sb–O angles of  $\sim 90^\circ$ .<sup>(7)</sup> Their shapes are similar to those of the related crystal structures. The first diffraction peaks of the 80 mol%  $Sb_2O_3$  glass remind the first Bragg reflections of the orthorhombic  $Sb_2O_3$  which suggests the existence of stacked layers of oxygen triangles.

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# Novel insights into the roles of $\text{WO}_3$ and $\text{MoO}_3$ in the electrical conductivity of phosphate glasses

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Phosphate glasses containing transition metal oxides such as  $\text{MoO}_3$  and  $\text{WO}_3$  are well-known for their semiconducting nature with polaronic conduction mechanism. In these glasses, molybdenum and tungsten ions are present in different oxidation states and the conduction takes place by small polaron hopping between them. Also, these glasses can accommodate a relatively high amount of alkali oxides which give rise to ionic conductivity. Such a large compositional and preparation variability enables tuning of the mechanism of the electrical conduction (polaronic and/or ionic) and makes these materials attractive for application in modern electrochemical devices.

In this contribution, we discuss various factors that influence electrical transport in these glasses, from simple binary  $\text{WO}_3/\text{MoO}_3\text{-P}_2\text{O}_5$  systems to complex ones containing variable amounts of alkali/silver oxides. Interestingly,  $\text{WO}_3$  and  $\text{MoO}_3$  can have very different roles in the electrical conduction in these materials. While polaronic conduction in  $\text{MoO}_3\text{-P}_2\text{O}_5$  glasses depends strongly on the amount of  $\text{MoO}_3$  and fraction of molybdenum ions in different oxidation states, in phosphate glasses containing  $\text{WO}_3$  it is governed mainly by the features of the glass structure, in particular clustering of tungsten units which facilitates the transport of polarons. In combination with alkali/silver oxides,  $\text{MoO}_3$  contributes weakly via polaronic transport but it strongly increases the mobility of alkali/silver ions by forming the mixed phosphate-molybdate network. On the other hand, the role of  $\text{WO}_3$  depends on the glass composition; it can contribute either directly, by introducing significant polaronic conductivity, or indirectly, by facilitating the transport of alkali/silver ions. The former behaviour is related to the formation of clusters of tungsten units in the glass network whereas the latter one originates from the facilitating effect of mixed phosphate-tungstate units on the dynamics of alkali/silver ions.

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# Structural role of lanthanum and yttrium onto heavy metal oxide (HMO) gallio–germanate glass network for infrared optical fiber applications

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The ability to produce robust fiber-based integrated optical systems operating over a wide spectral domain from the ultra-violet up to mid-infrared is one of today's key challenges in photonics. For this purpose, there is a critical need in the design of novel materials capable of filling in the gaps of the widely used silica fibers in terms of infrared transparency, nonlinear optical properties and rare-earth (RE) solubility. Over recent decades, several glass systems (fluorides, heavy metal oxides, and chalcogenides) appeared to be promising alternatives to SiO<sub>2</sub> glasses, but have not yet been able to compete with its high thermal robustness and remarkable mechanical assets. Recently, we reported<sup>(1)</sup> on the production of light guiding fibers from rich rare-earth gallium oxide-based glass composition in the multi-component system GaO<sub>3/2</sub>–GeO<sub>2</sub>–BaO–REO<sub>3/2</sub> (RE=La and/or Y), outperforming the thermal and the surface micro-hardness assets compared to those reported in fluoride and chalcogenide glasses.<sup>(2)</sup> Herein, taking advantage of structural information from vibrational spectroscopies (Raman/Infrared) and <sup>71</sup>Ga and <sup>89</sup>Y solid-state Nuclear Magnetic Resonance (SSNMR), we describe the key role of lanthanum and yttrium rare-earth elements onto the glass structure and the impact on the capability to draw those new glass compositions into optical fibers using the classical pre-form-to-fiber process. This study remains particularly relevant for the development of highly robust power scaled fiber devices operating from the visible up to the challenging 2–6 μm optical domain while being capable of combining superior thermal, mechanical and optical properties.

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# Structure and properties of potassium niobato-phosphate glasses

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Glasses of the ternary system  $K_2O-Nb_2O_5-P_2O_5$  were studied in three compositional series  $(60-x)K_2O-xNb_2O_5-40P_2O_5$  (series A) with 10–40 mol%  $Nb_2O_5$ ,  $40K_2O-yNb_2O_5-(60-y)P_2O_5$  (series B) with 10–30 mol%  $Nb_2O_5$  and  $zK_2O-20Nb_2O_5-(80-z)P_2O_5$  (series C) with 20–50 mol%  $K_2O$ . The basic physical parameters of glasses were also determined. Almost all glasses were colourless, only two glasses with a higher  $Nb_2O_5$  content were blue colored due to the presence of a small amount of  $Nb^{4+}$  ions. The glass transition temperature in the series A and B increases with increasing  $Nb_2O_5$  content, whereas in the series C it increases only slightly. The highest value of 757 °C was found for the glass  $20K_2O-40Nb_2O_5-40P_2O_5$  from the A series. Chemical durability of most glasses is high, their dissolution rate is lower than  $1.5 \times 10^{-6}$  g/cm<sup>2</sup>min. The refraction index only increases significantly in the glasses of the series A and B with increasing  $Nb_2O_5$  content; glass  $20K_2O-40Nb_2O_5-40P_2O_5$  from the series A had the highest value of 1.809 at 587.6 nm.

The glass structure was evaluated from the analysis of their <sup>31</sup>P MAS NMR and Raman spectra. On the Raman of A glass series A  $(60-x)K_2O-xNb_2O_5-40P_2O_5$  at low  $Nb_2O_5$  content there is a strong vibrational band of 895 cm<sup>-1</sup>, which can be assigned to the vibration of terminating Nb–O<sup>-</sup> bonds in the NbO<sub>6</sub> octahedra. This band shifts steadily with increasing  $Nb_2O_5$  content to higher wavelengths at 935 cm<sup>-1</sup>. The efficiency of Raman scattering by NbO<sub>6</sub> units is higher than that of PO<sub>4</sub> units, which results in the suppression of phosphate vibrational bands in the Raman spectra of glasses with a higher  $Nb_2O_5$  content. In the glasses with 30–40 mol%  $Nb_2O_5$ , Raman spectra showed on the presence of chains Nb–O–Nb, interconnecting NbO<sub>6</sub> octahedra, and even on the formation of 3D niobate clusters.

Samples containing less than 30 mol%  $P_2O_5$  revealed a tendency to form glass-crystalline materials containing potassium niobate crystals. Their crystalline structure has not been identified, but according to their Raman spectra, they contain NbO<sub>6</sub> octahedra similar to those in KNbO<sub>3</sub>.

# Insights on the relationship between structural and electrical properties in sodium vanadium niobium phosphate glasses

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Ever since the alkali phosphate-based glasses have emerged as promising candidates for application as electrolytes and/or electrode materials in solid-state batteries, research has largely focused on the elucidation of the relationship between composition, structure, and electrical properties in order to enhance the conductivity in these glasses.<sup>(1)</sup> Numerous studies have shown that the ionic transport in oxide glasses can be strongly affected by the addition of a second glass-former, resulting in a non-linear variation of ionic conductivity with a maximum (or minimum) at a certain glass composition, known as the *mixed glass former effect* (MGFE).<sup>(2)</sup> While MGFE has been extensively studied in glasses with conventional glass-formers ( $B_2O_3$ ,  $SiO_2$ ,  $P_2O_5$ ,  $GeO_2$ ), the glass systems where a conventional glass-former is substituted by the conditional one, such as transition metal oxide (TMO) are scarce.<sup>(3,4)</sup>

In the presented study, two series of glasses from the system  $Na_2O-V_2O_5-P_2O_5-Nb_2O_5$  are prepared and investigated to verify the MGFE in the presence of two conditional glass formers,  $V_2O_5$  and  $Nb_2O_5$ . In both series, the content of  $V_2O_5$  is kept constant, while  $P_2O_5$  is gradually replaced by  $Nb_2O_5$ . The glasses are synthesized by the melt-quenching technique and their amorphous character is confirmed by PXRD. The thermal behaviour of the glasses is analyzed by DTA, while their structural properties are evaluated by SEM-EDS analysis and IR-ATR spectroscopy. The electrical properties of the prepared glasses are investigated by solid-state impedance spectroscopy (SS-IS) in a wide range of frequencies (0.01 Hz–1 MHz) and temperatures (−90°C–240°C). The relationship between the structural changes that occur upon glass-formers exchange, and certain physico-chemical properties of these glasses is discussed in detail.

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# **The use of controlled dissolution glasses for the consolidation and strengthening of loose rock soil and sediments**

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This presentation describes work carried out to develop controlled dissolution glasses with the purpose of reacting with loose rock formations in order to cause consolidation and prevent collapse. GTS have been undertaking research in this area for the past 12 years and have developed a number of glass compositions which when injected into porous chalk formations result in mineralization reactions. Working with colleagues at NORCE Research in Stavanger it has been proven that a phosphate glass-based solution can deliver a strength increase of up to five times in whilst retaining over 80 percent of the original permeability of the rock. Related compositions have been developed that result in strength increase in loose sand, sandstone and clays and can be tailored to create impermeable seals. This technology has numerous applications from the construction industry, energy sector and environmental remediation. Extensive laboratory research has been carried out on one glass composition for the stabilization of chalk materials. These experiments led to the development and implementation of a commercial scale production process enabling a full-scale field trial to be performed to verify the products viability in the oil and gas sector. This trial demonstrated the potential for a glass based solution to overcome some of the traditional problems associated with resin and polymer treatments, namely difficulties in injecting into low porosity areas and the reduction in permeability.

# **An approach to using biomass ashes as glass batch materials: towards net zero glass production**

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In 2015 the UK Government and British Glass published their Glass Decarbonisation Roadmaps to 2050 to help coordinate and support achievement of decarbonisation goals within the glass sector. Both Roadmaps highlight glass batch reformulation as one enabler for the glass industry to reduce its energy consumption and CO<sub>2</sub> emissions.

We give a general introduction about current decarbonisation policy and discuss how the glass industry may evolve during this transition period. We also summarise the history of alternative raw materials including biomass ash in glassmaking from our recent research.

Biomass ash was selected and studied as alternative industrial glass raw material in this research. The ash was characterized by XRF and LECO and identified as a rich source of alkali (19 to 26wt% K<sub>2</sub>O) with low impurities such as Cl, P, Fe and C. Simple, ancient processes such as sieving and washing were applied to purify the composition of ash. After sieving, sample fractions rich in C and Cl were concentrated in fine particles of the ash, with high concentrations of K<sub>2</sub>O in larger size fractions. Washing processes also can remove Cl from the ash. The microstructure and elemental distribution of the ash, before and after washing, were researched and compared with a simulated ancient glass raw material bracken ash, by SEM and EDX. Finally, different amounts of original and post-treated biomass ashes were introduced as batch raw materials into laboratory-scale green container glass compositions, and its impact on the composition and properties, colour and redox of the glass was characterised.

# **The use of secondary raw materials derived from industrial wastes in glass manufacture enabling increasing recycled content beyond cullet**

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As the world moves towards a low carbon and circular economy, it is now necessary to look beyond traditional glass recycling to be able to deliver the non-virgin raw material required to maximize recycled content and achieve further energy savings.

Glass Technology Services have been working with colleagues at Sheffield Hallam University and the glass industry to investigate how ashes and other waste products can be beneficiated for use as a substitute raw material in glass batch recipes.

Detailed studies on the composition and variability of a range of materials have been undertaken, allowing ash and waste products to be matched to the raw material requirements of container glass manufacture. From this information, new batch recipes have been created to incorporate these materials whilst still retaining the desired properties of the finished glass, and these have been demonstrated in laboratory and pilot scale melts.

Modelling has demonstrated that these new glasses have the potential to reduce energy requirements for industrial glass manufacture by up to 6% and CO<sub>2</sub> emissions by up to 7%.

Modelling of processing costs and a pilot scale beneficiation trial has demonstrated that the economic cost of using the recycled ash material can be similar to traditional raw materials and when energy and carbon trading costs are accounted for a cost saving is achieved. As increased focus is placed on carbon reduction and energy cost rise the adoption of these materials becomes increasingly attractive.



# Nanotectonic effect, viscosity anomaly, transient immiscibility and semiconductor-metal transition in Ga–Te liquids and glasses

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Emerging brain-inspired computing, including artificial optical synapses, photonic tensor cores, neuromorphic networks, etc., needs phase-change materials (PCMs) of the next generation with lower energy consumption and a wider temperature range for reliable long-term operation. Gallium tellurides with higher melting and crystallization temperatures appear to be promising candidates and enable achieving the necessary requirements. In addition, Ga–Te binaries appear to be quite unusual PCMs revealing a tetrahedral gallium local structure and hybridization in contrast to a vast majority of typical PCMs. Nevertheless, optical pump–probe laser experiments revealed high-contrast, fast and reversible multilevel SET-RESET transitions raising a question related to the phase change mechanism.<sup>(1)</sup> A recently observed nanotectonic compression in bulk glassy Ga–Te alloys<sup>(2)</sup> seems to be responsible for the PCM performance. Pulsed neutron and high-energy X-ray diffraction supported by first-principles simulations allow a deep insight into the glass and liquid structure and dynamics following the viscosity anomaly just above melting accompanied by transient mesoscopic immiscibility and semiconductor – metal transition.

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## Short range order in glassy $\text{KSb}_5\text{S}_8$

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Glassy and crystalline  $\text{ASb}_5\text{S}_8$  ( $\text{A}=\text{K}, \text{Rb}$ ) alloys have attracted recently attention due to their non-linear optical properties, reversible glass-crystal transition and the huge contrast between the optical properties of the glassy and crystalline phases.<sup>(1)</sup> While the crystal structure has already been determined short- and medium range order of the glassy phase is still not known properly.

The atomic level structure of glassy  $\text{KSb}_5\text{S}_8$  was investigated by neutron- and X-ray diffraction as well as Sb K-edge extended X-ray absorption fine structure measurements. Large scale structural models were generated by fitting experimental datasets simultaneously in the framework of reverse Monte Carlo simulation technique (RMC). Bond lengths, coordination numbers and their uncertainties were determined. Partial pair correlation functions of the glass were compared to their crystalline counterparts. Real-space models generated by RMC were also used to determine the connectivity of  $\text{SbS}_x$  polyhedra.

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## Short range order in binary Ge–S glasses

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Ge–S glasses have been studied for half a century now. During the years several experimental and theoretical works have dealt with the atomic scale structure of these glasses. Despite the huge effort made in this field, numerous open questions have remained: such as the amount of corner and edge-sharing  $\text{GeS}_{4/2}$  tetrahedra in S-rich or in Ge-rich glasses; or the necessity of Ge–Ge bonds in Ge-rich glasses.

In our work we investigated the structure of  $\text{Ge}_x\text{S}_{100-x}$  glasses over a broad composition range ( $20 \leq x \leq 42$ ). For all compositions two or three diffraction and EXAFS data sets were used to generate large scale structural models within the framework of RMC simulation method. The resulting atomic configurations were used to calculate short range order parameters.

It was found that both constituents satisfy the Mott-rule in all investigated glasses: Ge and S atoms have 4 and 2 neighbors, respectively. The structure of these glasses can be described with the chemically ordered network model: Ge–S bonds are preferred, S–S bonds are present only in S-rich glasses. Dedicated simulations showed that Ge–Ge bonds are necessary in Ge-rich glasses. Connections between Ge atoms (such as edge-sharing  $\text{GeS}_{4/2}$  tetrahedra) in stoichiometric and S-rich glasses were also analysed.

# Structure of magnesium aluminosilicate glass

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Magnesium is an essential element in amorphous aluminosilicates that have widespread applications ranging from display glass to the models for magmatic materials. The structural role of Mg in oxide glasses is, however, largely unknown because of (i) its ability to change its coordination number from 4 to 6 and (ii) the absence of definitive structural information from experiment. For example, information from <sup>25</sup>Mg magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments is scarce because of the low natural abundance (10%), low gyromagnetic ratio, and significant quadrupole moment (nuclear spin  $I = 5/2$ ) of the <sup>25</sup>Mg isotope. Here, we address this issue by employing neutron and x-ray diffraction and <sup>27</sup>Al MAS NMR spectroscopy to explore the structure of magnesium aluminosilicates over a wide composition range. Site-specific information on the coordination environment of magnesium is obtained by employing the method of neutron diffraction with isotope substitution. The results are interpreted with the aid of a newly developed analytical model for aluminosilicate glasses [Gammond, L. V. D. *et al. J. Chem. Phys.*, 2022, **156**, 064503], which gives the composition dependence of (i) the network-modifying versus charge-compensating roles for the Mg<sup>2+</sup> ions, and (ii) the network-forming versus network-modifying/charge-compensating roles for the fourfold versus higher-coordinated Al atoms, respectively.

# Amorphous chalcogenide thin films: tailoring of multisource sputtering conditions towards required chemical composition

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Current research effort addressed to development of new materials is partially focused to determination of composition influence onto studied functional properties of the material. In case of thin films a multisource deposition is beneficial technique for preparation of compositional sample series. However exact determination of process parameters towards required thin film compositions is not described yet. For that purpose, simplified calculation model utilizes basic physicochemical constants of source materials together with reduced number of trial depositions covering basic instrument characteristics (tool-constants) was developed.

The above mentioned calculations are performed and experimentally verified for a two-source depositions of a chalcogenide thin films of amorphous nature, particularly from Ga–Sb–Te system (tie lines GaSb–GaTe and GaSb–Te). The thin films are deposited by radiofrequency (RF) magnetron sputtering from targets with the uttermost compositions of the given tie lines. Within the aim of the presented work prepared thin films are characterized namely by means of Energy Dispersive X-Ray Analysis coupled with Scanning Electron Microscope (SEM-EDX) to determine the chemical composition and by Variable Angle Spectroscopic Ellipsometry (VASE) to establish film thickness.

Good agreement between results of calculations and experimentally determined compositions of the co-deposited thin films is achieved for both the above-mentioned tie-lines. Composition differences of co-sputtered thin films are up to ~3.5 at% in case of GaSb–GaTe and ~1.5 at% in case of GaSb–Te pseudobinaries, respectively. Thus the compositional differences are comparable to compositional differences of single source deposited thin films (up to ~2 at% for GaSb and ~3 at% for GaTe) within the SEM-EDX technique accuracy.

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## Phosphate glasses – chemical point of view

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Phosphate glass exhibits in comparison with silicate glasses attractive properties such as low glass transition and melting temperatures, high thermal expansion coefficients, biocompatibility, and high refractive indices. These specifications are suitable for many applications in photonics, glass-to-metal seals, low-temperature enamels and biomedical engineering. Phosphate glasses, especially glasses containing transition metals, are versatile as their properties can be tailored by altering their composition.

The structure and properties of oxide glasses are generally explained on the basis of formal composition, i.e. on the basis of the perception of glass as a mixture of oxides from which the glass should be prepared. However, in fact glasses are mixtures of stable chemical compounds formed in high-temperature synthesis, the crystallization of which was prevented. Thus, it is an obvious mistake to interpret the properties of such a complex system only on the basis of the ratio of oxides used. Recently, the composition–structure–property relationships for glasses and melts of various multicomponent glassforming systems have been interpreted using thermodynamic modeling. The approach is based on a rigorous thermodynamic model of associated solutions and glasses are considered as a product of chemical interactions between oxide components of given system rather than as a result of batch melting.<sup>(1)</sup> A large number of thermodynamic quantities must be available for the calculation, and the disadvantage is that the required thermodynamic data are often not found in any current thermodynamic database.<sup>(2)</sup> Model is also unable to describe the redox reactions in the preparation of the glass, so it fails, e.g. for glasses with transition metals.

In contrast, the proposed chemical model of phosphate glasses is based on the chemistry of phosphorus and the chemistry of the elements forming the cations. The principle of the chemical model is the balance of elements and the principle of electroneutrality. The model requires results from currently common experimental methods, such as XRF, <sup>31</sup>P MAS NMR and ESR or magnetic susceptibility (if redox reactions are expected).

In this work the use of the chemical model was verified on glasses with a transition metal, which is in the structure in multiple oxidation states. Three composite series of calcium phosphate glasses with molybdenum, which is partially reduced from Mo (VI) to Mo (V) during the synthesis, were prepared. The model was used to calculate their chemical composition and explain selected physicochemical properties.

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# The structure of glasses – as seen through their behaviour in a magnetic field and now under a simple microscope

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While the atomic-range (almost that of a crystal) and long-range (that of a frozen liquid) structure of glasses are basically agreed upon, the intermediate-range has witnessed controversy since the early 1930s. In this talk I shall argue that low-temperature experiments (particularly in a magnetic field) have recently contributed enormously to elucidate such intermediate structure as being characterized by frozen-in heterogeneities that issue from the super-cooled liquid state. When creating glass through avoided-crystallization, the liquid becomes unstable and is characterized by solid-like fluctuations already in the proximity of  $T_x$  (the crystallization temperature). A highly correlated liquid ensues upon rapid cooling and the seeding with spontaneous or generated (dirt or the highest- $T_x$  components' microcrystals) solid-like particles creates growing quasi-ordered zones (Regions of Enhanced Regularity, RER) that jam-pack at the onset of glass formation. The RER become static and trap in their "voids" particles that remain liquid-like all the way down to the lowest temperatures ( $T \ll T_g$ ,  $T_g$  the nominal "glass transition" temperature). These liquid-like regions are responsible for a plethora of new phenomena known as cryogenic anomalies: I will show that the magnetic (and other) effects see some new collective yet localized modes as responsible for new puzzling physical phenomena.

I shall review the most-probable explanation for the magnetic and other anomalies, including a rationale for the so-called Two-Level Systems (TLS). The discovery of a new unexpected true magnetic effect will be reported and explained in its unusual details in the light of a new microscopic theory that relies on the existence of collective tunneling modes in the said "voids" between the RER. These modes (Anomalous Tunneling Systems, ATS) have staggering new physics properties.

At the same time, the creation in the laboratory of a glassy multi-silicate specimen provides the confirmation at milli-metric scales of the proposed cellular intermediate structure at the nano-metric scale characterizing all glasses. Visible to the naked eye, and well-characterized in an optical and better in a scanning electron-microscope, the cells remain non-crystalline though seeded by dirt and nano-crystals and providing the solidity of the whole specimen. Images taken with a simple smart-phone camera and an optical microscope reveal a cellular, self-similar and fractal structure where the solid-like regions are jam-packed and yet present no crystallinity.

The two investigations (SQUID-magnetometry and purpose-seeding of the hot liquid) corroborate each other and give full support to the cellular model of glasses.

# Structure–property relationships of ferrous and ferric iron containing glasses

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Iron remains an element of considerable interest in glass science and technology. In most cases, it may be present as an unwanted impurity or it may be added intentionally to develop peculiar glass and melt properties. Glass color, thermal control in buildings, heat transfer in furnaces, Fe-poor solar ultrawhite glasses represent just a few areas in which Fe-speciation in glasses and melts governs important applications. As the structural properties of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are different, due to their distinct, charge, size and electronic properties, there is a need to understand iron speciation, mostly the redox state and the local structure around each oxidation state.

A positive point is that iron may be investigated by several spectroscopic and diffraction methods. A coherent image can result from a crossing of the data obtained by these different approaches in the light of some scenarios provided by numerical modeling. This presentation will review some literature data provided by optical absorption spectroscopy, EPR, XANES and HERFD-XANES, EXAFS, neutron diffraction, etc. Fe-speciation in the model system  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Na}_2\text{O}$  will be privileged and compared to that in soda-lime and more complex glasses. Such a comparison illustrates the chemical dependence of the properties of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in oxide glasses. By considering the additional constraints provided by the dependence of Fe-speciation on glass composition and synthesis conditions, the available structural data show the importance of “exotic” sites such as 5-coordinated  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  or the influence of the medium-range organization of the glass in heterogeneous domains. As a final remark, this talk will use the “oxide transfer concept” introduced by Austen Angell and the “modified random network” concept introduced by Neville Greaves. This will be the occasion to remember the major contributions of these two exceptional scientists.



# Charge transfer transitions in glasses

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Even low levels of dopants or impurities can give rise to very intense and broad charge absorption bands in glasses. These are caused by transfer transitions from ligands (e.g. oxygen or fluorine ions) to the metal ion (L→M) and absorb often strongly in the short wavelength and ultraviolet region. Inter valence charge transfer (IVCT) transitions directly from one metal ion to a neighboring metal ion (M→M) of the same element or metal to metal charge transfer (MM-CT) between ions of different elements can also induce strong visible absorption and deep coloring.

Based on the compilation of experimental data from the last decades, obtained from high purity, highly transparent glasses ranging from (fluoride) phosphate to (alumo/boro)silicate glasses, we attempt a systematic review of charge transfer transitions, involving cations of different electronic configurations. Absorption and photo-luminescence phenomena in the ultraviolet and visible spectral region were recorded by optical spectroscopy.

Charge transfer transitions were considered for empty valence orbitals, that is, for the high valent 3d, 4d and 5d ions, and for Zn<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>+</sup> with full d<sup>10</sup> orbitals, and 3d, 4d and 5d ions with partially filled valence orbitals that could be stabilized in the named glasses. Doping concentrations for these allowed transitions typically ranged from 5 to 5000 wt-ppm of metal ions, with some samples also displaying higher dopant levels.

We observed a decrease in CT transition energies for higher charge of the same dopant species and an increase in CT transition energies for heavier ions of the same valence electron configuration (5d > 4d > 3d), especially for ions with empty or full (half full) valence orbitals. Zigzag patterns were observed for increasing mass of M<sup>Z+</sup> ions of the same charge Z=2 and 3, the most obtainable charges for a wide range of transition metal ions in glasses. These patterns reflect a dependence of the CT transition with the electron configuration and electron repulsion energies. The glass matrix has a distinct influence on the observed transition energies, due to the nephelauxetic effect, coordination, L–M distances, or even the stabilization of additional oxidation states. The glass type might also favor an inhomogeneous ion distribution such as clustering of transition metal ions in low alkali borosilicate glasses like Duran or, the observed transitions energies are affected by low energy acceptor levels as seen for phosphate groups in fluoride-phosphate glasses where dopants are homogeneously distributed.

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# Functionalisation of hydrated phosphate glasses with tungsten oxide nanoparticles for optical applications

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Phosphate glasses are known for their good chemical stability, good thermal and optical properties making them compatible with processing at moderate temperatures (<500°C). Here, we report the synthesis of novel optically transparent hydrated amorphous phosphates containing up to 40 mol% of water and exhibiting glass transition temperature of 85°C and softening temperature around 150°C. The structure of these transparent materials was investigated by Raman, FTIR and NMR spectroscopies. The network of the hydrated phosphates would consist of short phosphate chains and isolated phosphate groups connected through hydrogen bonds. Zinc oxide addition up to 25 mol% in the phosphate glass composition offers better stability against moisture while preserving low glass thermal characteristics. The optical and physicochemical properties of those materials will be discussed.

Through the low-temperature processing of the hydrated phosphate glasses, photochromic nanoparticles of oxygen-deficient tungsten oxide (WO<sub>3-x</sub>)<sup>(1,2)</sup> were successfully incorporated in a hydrated phosphate glass matrix. X-ray diffraction, electron paramagnetic resonance and transmission electron microscopy were performed to characterize the nanoparticles before and after incorporation in the phosphate compounds. Optical properties of the functionalised glasses, such as luminescence and photochromism, will be discussed. This study opens new perspectives for the use of novel low processing temperature hydrated phosphate matrix for the incorporation of functional nanoparticles.

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# X-ray beam as a source and probe of defects nucleation

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The microscopic description of the glass transition process is at the forefront of research in the condensed matter physics. X-ray Photon Correlation Spectroscopy (XPCS) is a powerful technique to probe relaxation processes at the atomic length-scale. In oxide glasses this technique becomes a pump-probe experiment where the light-matter interaction triggers the atomic motion in a process described as beam induced dynamics<sup>(1,2)</sup>. Radiolysis is the proposed mechanism to explain the emergence of this artificial effect: the photoelectron emitted after x-ray absorption increases the local energy and induces nearby atoms to move inside the illuminated volume. In the first stage of the process, no clear modification in the structure is evident (see inset in Figure 1) because the irradiation makes the system to explore equiprobable states<sup>(1)</sup>. By irradiating further, we will show that the damage leads to an irreversible structural modification whose features present analogies with that caused by neutron irradiation, both in crystalline and in amorphous samples. The radiolytic damage manifests itself in creation of defects, such as the Non Bridging Oxygen Hole Center (NBOHC) and the O<sup>2-</sup> peroxy linkage. The x-ray beam triggers a gradual crystalline to amorphous transition enucleated from the defects generated by the beam itself and those act as centres of stress. The same metamictization process has been reported also in  $\alpha$ -quartz samples under the intense illumination of a scanning or transmission electron microscope<sup>(3)</sup>. Differently from the aforementioned techniques, thanks to XPCS we can follow the dynamics of the metamictization process. Our data show how any intense and focused x-ray illumination entails the enucleation of defects in solids with covalent bonding. The research in this field is essential for the next generation synchrotrons. Moreover, the large use of silicon dioxide in several branches of physics and the advent of the new devices based on phase change materials make the understanding of this phenomenon of prior importance.

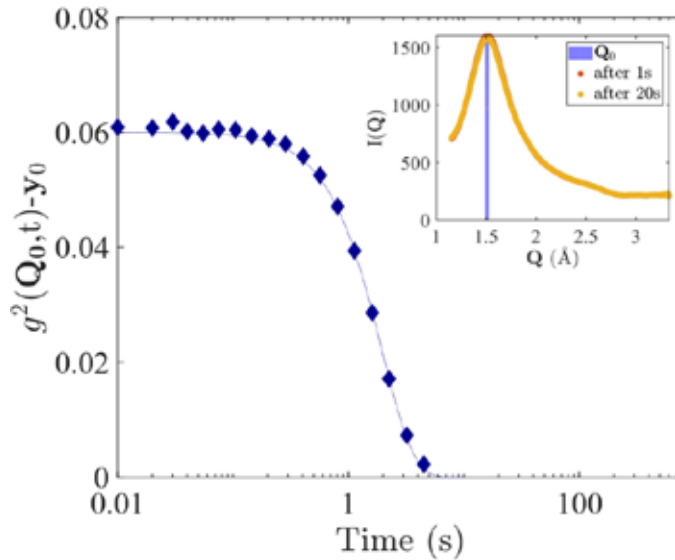


Figure 1. X-ray photon correlation measurement and relative fit<sup>(1,2)</sup> on silica sample. Inset: Scattered intensity as a function of the exchanged wavevector ( $Q$ ) for the same silica sample. Vertical line is placed at the wavevector of the XPCS measurement.

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# 3D localization beyond diffraction limit of near-IR emission excited by resonant energy transfers from silver clusters in phosphate glasses

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Photonics is a key enabling technology thanks to its wide application in many industrial fields. Femtosecond (fs) Direct Laser Writing (DLW) already plays a major role because it is flexible, fast, cost-effective, highly transferable to industrial processes and because it enables highly-integrated optical functionalities and photonic integrated circuits (PIC). Nowadays, there is a growing demand for developing all-optical approaches to create 3D multi-scale architectures with sub-wavelength dimensions for different sectors of the economy. Recently, we developed new expertise in fabricating multi-scale photonic architectures using all-optical fs laser writing in specialty-designed photosensitive silver-containing glasses. One of the challenges relies on the capability of structuring the local luminescent properties. Femtosecond DLW in silver-containing glasses allows for the local creation of an elementary brick with inner features below the diffraction limit.<sup>(1)</sup> Such a modification is composed of highly luminescent silver clusters that result from the migration and chemical reactivity of silver elements, these clusters emitting in the whole visible range. Luminescence, local chemical analysis, and structural properties by vibrational spectroscopy have been carried out in order to clarify the structure/property relationship and the impact of the glass matrix. It clearly appears that the all-optical structuration is highly dependent on the glass host, the silver species environment in the pristine glass, and the DLW parameters.<sup>(2)</sup> We recently demonstrated that co-doping with ions such as rare earth (Eu<sup>3+</sup>, Yb<sup>3+</sup>) allows for tuning the luminescence emission spectrum thanks to the production of highly-localized 3D fluorescence structures of rare-earth ions showing high optical contrast.<sup>(3)</sup> The ability to use laser-inscribed silver cluster structures as templates exhibiting high absorption starting from the UV until 530 nm, leads to local high luminescence with different colors, from the visible to IR range. The efficient non-radiative transfer mechanism operating between the silver clusters and the emitting ions will be discussed, including experimental evidences from confocal hyper-spectral lifetime-resolved imaging.

Indeed, the unique combination of fs DLW in adapted photosensitive glass allows for the fabrication of 3D architectures with sub-diffraction high luminescence contrast. The obtained results offer a unique opportunity for developing robust 3D integrated photonic components in which the emission spectrum can be adapted. These findings will offer new opportunities for the development of high-precision fluorescent optical integrated components in the red/near-infrared range for health and life sciences for instance.

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# Photoluminescence studies of transition metal doped soda–lime–silica glasses

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Soda15-lime15-silica70 (mol%) glasses, doped singly or doubly with Ti, V, Cr, Mn, Fe, Co, Ni and Cu at 0 - 1 mol %, were at first studied with absorption spectroscopy measurements.<sup>(1)</sup> It was found to be a major work to develop the fitting parameters for all their ions and the coordination structures of their sites.<sup>(2)</sup> There are many types of absorbing elements (OH- groups, Fe-S-, some Cu- and/or Fe-contaminants etc.) in glasses made of normal commercial powder ingredients. Reflection losses had to be removed<sup>(3)</sup> before the dopant absorption spectrum could be fitted. Furthermore, in several cases, the absorption peaks of several different ions, sites or dopants are located at the same wavelengths. Therefore, it is difficult to find the right fitting parameters. To find a tool to get more information about the ions and structural sites, we made photoluminescence (PL) studies at Uppsala University on most of the glass samples prepared in the research project of Volotinen<sup>(1)</sup>. The equipment used was not a normal broad-band light source containing photoluminescence equipment, but originally a unit containing a few narrow-band, high power lasers, which are normally used to measure Rayleigh scattering- or Raman-scattering. It was found that all transition metals studied in our glasses gave measurable PL spectra. Comparison of the PL spectra of the singly doped and doubly doped glasses helped us to resolve the problems in determination of which ions and how much of their sites are in the glasses. The PL spectra were easier to interpret than the absorption spectra. The PL spectra originate from only the lower oxidation states of the transition metal ions, and from only one type of site, in this kind of glass.<sup>(4)</sup>

In this presentation the PL spectra measured at 355 nm shall be shown for the singly doped glasses, with a few examples also shown for the doubly doped ones. An example of how the PL data helped the analysis of the absorption spectrum, shall be also presented.

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## Structure–property relationships in Ge–Sb–Se chalcogenide glasses

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Chalcogenide glasses are highly promising for a range of photonic applications because of their excellent optical properties, including large linear and non-linear refractive indices and exceptional transmission range into the mid-infrared. Chalcogenide glasses also offer large scope for optimising physical properties such as  $T_g$  (glass transition temperature), viscosity and glass forming region, thanks to their ability to incorporate both hetero- and homo-polar bonds. This paper will present recent work to investigate the relationships between composition, network structure and physical properties for a series of germanium – antimony – selenium glasses. Neutron diffraction, X-ray diffraction,  $^{77}\text{Se}$  NMR (nuclear magnetic resonance spectroscopy) and Raman results will be presented for the series of glasses to investigate the change in bonding which occurs as the glass composition changes from stoichiometric ( $\text{GeSe}_2\text{--Sb}_2\text{Se}_3$ ) to pure selenium and links between structural changes and physical properties will be shown.

# Mercury iodide containing chalcogenide glasses: structural, macroscopic and electric properties

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Mercury-containing chalcogenide systems are well-established materials for optical, photonic and chemical sensors applications.<sup>(1,2)</sup> However, despite their technological and scientific interest very little is known about their structure and properties. For this purpose we have synthesized and characterized bulk glasses in the HgI<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-GeS<sub>2</sub> system.

The glass-forming range for (HgI<sub>2</sub>)<sub>x</sub>(GeS<sub>2</sub>)<sub>1-x</sub> and (HgI<sub>2</sub>)<sub>x</sub>[(Ga<sub>2</sub>S<sub>3</sub>)<sub>0.2</sub>(GeS<sub>2</sub>)<sub>0.8</sub>]<sub>1-x</sub> compositions extends up to  $x=0.4$ . The evolution of the macroscopic properties including density ( $d$ ), glass transition temperature ( $T_g$ ) and total electrical conductivity ( $\sigma$ ) was studied as a function of metal halide addition. The density of samples increases monotonically with increasing HgI<sub>2</sub> content. DSC measurements show that the  $T_g$  decreases with increasing  $x$  and this is coherent with the progressive distraction of the chalcogenide glassy matrix. The mercury iodide addition to the Ga-Ge-S host glass leads to a monotonic conductivity increase, however the HgI<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-GeS<sub>2</sub> glasses are electronic insulators with  $10^{-16} \text{ S/cm} \leq \sigma_{298}(x) \leq 10^{-13} \text{ S/cm}$ .

The structural investigations in the quasi-binary (HgI<sub>2</sub>)<sub>x</sub>(GeS<sub>2</sub>)<sub>1-x</sub> glasses were carried out using Raman spectroscopy and pulsed neutron diffraction supported by structural and vibrational modelling. The Raman spectra reveal the appearance of the new low-frequency features at  $\approx 150$  and  $\approx 190 \text{ cm}^{-1}$  with the addition of HgI<sub>2</sub> to the GeS<sub>2</sub> matrix and their increase monotonically with  $x$ . The DFT modelling results are consistent with the structural hypothesis of bent noncentrosymmetric HgI<sub>2</sub> molecules in the glassy host. The changes in the macroscopic properties of glasses with metal halide addition are studied in relation to the structural changes.

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## Thermal and optical properties of Ge–Te–Se glasses for infrared transmitting glasses

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Chalcogenide glasses have become an important enabling materials for various applications, one of them is Infrared imaging device. The IR transparent materials are key element required to build these devices. Tellurium based chalcogenide glasses are well explored to transmit IR over a wide range but Te based glasses are difficult to form. We worked on Ge–Te–Se systems to study thermal, optical and structural properties for their applications. For various application, the glass should have high glass forming ability, thermal stability and high transparency in IR region.  $\text{Ge}_x\text{Te}_y\text{Se}_{(1-x-y)}$  glasses with x between 10 and 40 have been prepared by melt quench technique. The prepared bulk glasses found to have high glass forming ability and high thermal stability. Glass transition temperature shows an increasing trend which represents polymerization of network even with increasing Ge and absence of nanoscale phase separation. Fragility index has been calculated using different method which varies between 20 and 35 indicating that prepared glasses are strong structurally. To study structural relaxation MDSC has been performed which show the variation of  $\Delta C_p$  and  $\Delta H_{nr}$  with atomic % of Ge. The calculated Optical band gap shows high values for Se rich glass (x=20) and lowest to Te rich (x=25). The high glass forming ability, thermal stability and high optical band gap of these glasses make them useful for many applications particularly for making IR lenses and optical fibres.



# Structural insight into sodium thiogermanate $\text{Na}_2\text{S-GeS}_2$ glasses and relation to properties

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A new generation of sodium solid state batteries operating at room temperature needs new sodium solid electrolytes with enhanced  $\text{Na}^+$  ion conductivity and good reversibility and stability towards electrode active materials. Among the materials exhibiting high ionic conductivity values, and thus promising for application as inorganic solid electrolytes in all solid state sodium ion batteries, we found sodium glassy/glassy ceramic chalcogenide systems. However, unlike their silver homologues, the ion transport and structural information related to sodium systems is sparse. With this in mind, sodium thiogermanate  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses,  $0.0 \leq x \leq 0.6$ , were synthesized, characterized and a comparison with  $(\text{Ag}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses was established when possible.

The macroscopic properties of glasses including density, mean atomic volume and glass transition were studied with increasing sodium content  $x$ . The glasses, belonging to  $\text{Na}^+$  ionic conductors, show an increase in room temperature conductivity by  $\sim 9$  orders of magnitude from  $6.6 \times 10^{-15}$  S/cm to  $1.4 \times 10^{-6}$  S/cm in the sodium content  $y$ ,  $0 \leq y \leq 40.0$  at% Na. The conductivity activation energy shows an overall decrease by 5 factors from  $\sim 0.91$  eV ( $x=0.0$ ) to  $\sim 0.41$  eV ( $x=0.6$ ). Comparing to the silver thiogermanate, the room temperature conductivity was 2.5-3.5 orders of magnitude lower for same metal content M (M=Na or Ag).

To verify whether the structural patterns in a glass follow those of the crystalline counterparts, the structural analysis, using Raman spectra of the  $\text{Na}_2\text{S-GeS}_2$  glasses along with three crystals known in this system, i.e. orthorhombic  $\text{Na}_4\text{Ge}_4\text{S}_{10}$  ( $x=0.33$ ), monoclinic  $\text{Na}_2\text{GeS}_3$  ( $x=0.5$ ) and monoclinic  $\text{Na}_6\text{Ge}_2\text{S}_7$  ( $x=0.6$ ), were carried out.

In addition, two  $\text{Na}_2\text{S-GeS}_2$  glass compositions have been studied using pulsed neutron diffraction on the ISIS spallation neutron source, i.e.  $(\text{Na}_2\text{S})_{0.3}(\text{GeS}_2)_{0.7}$  and  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ . First Principle Molecular Dynamic (FPMD) modelling of  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  and  $(\text{Ag}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  were also performed. The connectivity analysis of the AIMD simulation boxes for both compositions has revealed that 19% of sulfur species (isolated sulfur, Siso) are connected to sodium against 28% connected to silver in  $(\text{Ag}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ .

**Keywords:** Chalcogenide glasses, Conductivity, Raman, Neutron diffusion, FPMD modelling

## Structural model for amorphous aluminosilicates

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Amorphous aluminosilicates are ubiquitous, finding widespread commercial applications and appearing in the geosciences as a major constituent of magmatic fluids. A key to predicting their properties is a detailed understanding of the atomic scale structure and how this structure changes with the composition and nature of the constituent oxides. Here, an analytical model is developed for the structure of  $(M_2O)_x(Al_2O_3)_y(SiO_2)_{1-x-y}$  and  $(MO)_x(Al_2O_3)_y(SiO_2)_{1-x-y}$  glasses ( $0 \leq x \leq 1$  and  $0 \leq y \leq 1$ ) by considering a simple set of chemical reactions.<sup>(1)</sup> The model contains a single adjustable parameter  $p$ , which controls the relative importance of the competing reaction schemes. The latter is found from <sup>27</sup>Al solid-state nuclear magnetic resonance (NMR) experiments in the regime where  $R = x/y \geq 1$ . The value of  $p$  decreases linearly as the cation field strength of  $M^+$  or  $M^{2+}$  increases and Al–O–Al bonds become more prevalent in a progressive breakdown of Loewenstein's aluminium avoidance rule. The model gives a good account of the composition-dependent fraction of non-bridging oxygen (NBO) atoms for  $R \geq 1$  as assessed from the results obtained from solid-state NMR experiments. The model delivers the composition dependence of the network-modifying versus charge-compensating roles for the  $M^+$  or  $M^{2+}$  ions. It also delivers the network-forming versus network-modifying/charge-compensating roles for the fourfold versus higher-coordinated Al atoms, respectively. The results are used to inform the interpretation of the pair-distribution functions measured using neutron and x-ray diffraction.

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# Misconceptions and flawed assumptions, with regard to silicate glasses: the high frequency bands of vitreous SiO<sub>2</sub>

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Pervasive throughout the glass literature are several misconceptions and/or poor assumptions made with respect to the structure of silicate glasses. These have, and continue, to cloud our understanding of the structure of these glasses, and Q<sup>n</sup> species distributions. This is particularly true of Raman spectroscopic studies, as well as, numerical approaches and curve fitting (deconvolution) of spectroscopic data. Some of the issues are: #1: Lack of chemical analyses and plotting of data versus nominal rather than actual chemical compositions; #2 fitting of data using NBO/T (T=tetrahedral cation) values based on nominal compositions and assumptions involving Q<sup>n</sup> species distributions; #3: Raman Lineshapes and Linewidths and “extra” peaks in the high frequency Raman envelope; #4: Assumptions regarding the origin of the high frequency Raman bands: Distinct SiO<sub>4</sub> tetrahedral vibrations versus symmetric and antisymmetric type motions of the bridging oxygens (BO); #5: Lack of consideration of cation involvement in the vibrations (M–BO) and finally, #6: Raman cross sections. The high frequency envelope of the Raman spectrum of vitreous SiO<sub>2</sub> (v-SiO<sub>2</sub>) is an example of some of these issues. Currently, v-SiO<sub>2</sub> is considered to have two high frequency bands at ~1060 and 1200 cm<sup>-1</sup> with the two bands assigned to the T<sub>2</sub> and A<sub>1</sub> modes of an isolated tetrahedron. However both bands are composed of doublets with peaks at 1054 cm<sup>-1</sup>, 1090 cm<sup>-1</sup>, and 1181 cm<sup>-1</sup> and 1235 cm<sup>-1</sup>, respectively. Both bands can be fit by 100% Gaussian curves. A tetrahedron of T<sub>d</sub> symmetry can have several vibrational modes: one A<sub>1</sub> mode, one doubly degenerate E mode and two triply degenerate T modes. The presence of the *two peaks*, one at 1181 cm<sup>-1</sup> and the other at 1235 cm<sup>-1</sup>, makes unlikely that either one is an A<sub>1</sub> symmetric stretch. They likely are E<sub>1</sub> and E<sub>2</sub> modes. Furthermore, all tetrahedra are connected and a *pure* A<sub>1</sub> motion probably is not possible, or at least not prevalent, unless there is extensive cooperative movement by the glass network. We suggest that the high frequency 1200 cm<sup>-1</sup> band is more logically assigned to the E modes while the lower frequency bands are assigned to the T<sub>2</sub> modes (ν<sub>3</sub> and ν<sub>4</sub>). We shall discuss these assignments in more detail and will provide examples of the impact of the above points on glass structure and Raman data in the literature.

## Two-point bend studies of the inert failure characteristics of pristine glasses

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The two-point bend (2pb) test was originally developed to quickly evaluate the failure characteristics of silica optical fibers under a variety of conditions.<sup>(1)</sup> Fibers are bent between two faceplates into a U-shape until failure, and a failure strain can then be calculated from the fiber diameter and the distance between the faceplates. This technique has been used to characterize the effects of environmental fatigue on silicate glasses<sup>(2)</sup> and 2pb results have been used to estimate the strengths of pristine glasses tested in ambient and inert conditions.<sup>(3)</sup> In this paper, the results of 2pb studies of pristine silicate and borate glass fibers, drawn to about 100 microns in diameter and then immediately tested under liquid nitrogen using different faceplate velocities ( $V_{fp}$ ) are described. In general, glasses with more topologically cross-linked structures have lower inert failure strains than do glasses with less-crosslinked structures. In addition, glasses with less rigid structures have greater failure strains when tested at slower  $V_{fp}$ , and compositions classified as “less brittle”<sup>(4)</sup> exhibit greater degrees of this inert delayed failure effect (IDFE). Recent MD simulations of the mechanical properties of alkali silicate glasses<sup>(5)</sup> offer insight to the IDFE and to the initiation of failure of pristine glasses.

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# Dynamical relaxations in a model metallic glass investigated by atomistic simulations

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Dynamical mechanical analysis (DMA) is a useful tool to probe the relaxation dynamics in amorphous solids and to measure the complex moduli characterizing the elastic and viscoelastic properties of these materials. For metallic glasses, in particular, the energy dissipated during cyclic deformation is a key parameter for various applications, such as resonating electro-mechanical systems. In this work, the dynamic mechanical behavior of a model  $\text{Cu}_{64}\text{Zr}_{36}$  metallic glass is systematically analyzed by non-equilibrium molecular dynamics (MD) simulations. The storage and loss moduli are obtained by applying sinusoidal strains under different loading conditions. It is well known that in the static case, only two independent moduli exist and that all other moduli can be derived from any two of them. The so-called dynamic correspondence principle states that the same relations hold in the dynamic case.

We show here by direct MD simulations that this principle is indeed satisfied<sup>(1)</sup>. We find that the storage and loss moduli evolve with temperature, and the main relaxation appears around the glass transition temperature  $T_g$ . Numerical results show that the dynamic mechanical behavior is highly frequency dependent: the main relaxation peak is shifted to low temperatures as the loading frequency decreases, which is consistent with experimental observations of typical metallic glasses<sup>(2)</sup>. We also determined the debated dynamic Poisson's ratio. In order to establish the atomic mechanisms of energy dissipation, we analyzed the atomic displacements as a function of temperature. At low temperature, the atomic displacements after each loading cycle are almost zero. Around the glass transition temperature  $T_g$ , the displacements of most atoms increase after each cycle, contributing to the energy dissipation. On the contrary, the icosahedra clusters are stable and remain close to their original positions, thus accounting for the stored elastic energy.

This work provides a numerical verification of the dynamic correspondence principle, and our findings convey insightful information for better understanding the microstructural processes occurring during the glass transition.

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# Atomistic simulation study of lithium aluminosilicate glass scintillators

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Radiation sensors are an important enabling technology in a number of fields, such as medicine, research, energy, military and homeland security. Glass base scintillators have been in use for more than 50 years and offer some benefits including their ability to respond to different types of radiation, and to be formed into various shapes. There is, however the possibility to discover and improve glass scintillators. With this in mind, this work provides insight from atomic scale simulations on the cerium doped lithium aluminosilicate ( $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO--Li}_2\text{O--Ce}_2\text{O}_3$ ) glass scintillators. Three glass compositions were studied using Molecular Dynamics (MD) and Density Functional Theory (DFT) to investigate the effect of the ratio

$$R = \frac{[\text{Al}_2\text{O}_3]}{[\text{MgO}]+[\text{Li}_2\text{O}]}$$

(with  $R=[0.3, 0.8 \text{ and } 2]$ ) on structural, electronic and optical properties. The effect of  $R$  on the complex structure of the system of interest was mainly associated to the increase of  $Q_4$  population that replaced  $Q_3$  within the network, while electronic mid gap defects were found to be present when  $R<1$ . The optical properties including absorption coefficients and energy loss spectra are calculated and analysed based on the electronic structures.

# Evolution of local structures in alkali-borate glasses

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We analyze the dependence of relative proportion of various characteristic clusters in binary alkali-borate glasses on modifier concentration  $x$ .

A pure  $B_2O_3$  glass contains a huge amount of boroxol rings and some amount of boron atoms in between, linking the boroxol rings via oxygen bonds. The addition of the  $Na_2O$  modifier creates four-coordinated borons, but the resulting network glass remains totally connected.

We study local transformations that lead to creation of new configurations like *tetraborates*, *pentaborates*, *diborates*, etc. and set forth a non-linear differential system similar to the Lotka–Volterra model.

The resulting density curves of various local configurations as functions of  $x$  are obtained. Then the average rigidity is evaluated, enabling us to compute the glass transition temperature  $T_g(x)$  for a given  $x$ .

# **Tuning bioactive glass properties via their phosphate/silicate ratio: imaging using TEM and nano-CT**

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Bioactive glasses typically are phospho-silicate glasses, and they are used as temporary implants to regenerate bone. They degrade in the body, release ions and enhance bone formation. Bioactive glasses also convert to a biomimetic apatite when in contact with physiological solutions. The type of phases precipitating during immersion depends on glass composition and reactivity, and phosphate in particular is a key component here. In the present study, we varied the phosphate/silicate ratio in bioactive glasses in the system  $\text{SiO}_2\text{--CaO--P}_2\text{O}_5\text{--CaF}_2$  by increasing the phosphate content while adding stoichiometric amounts of calcium oxide. P-31 solid-state NMR showed this to maintain phosphate in an orthophosphate environment in the glass. Transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDX) showed the presence of phosphate clustering and nearly crystalline calcium fluoride environments in the glasses. A combination of analytical methods, including solid-state NMR, showed how with increasing phosphate/silicate ratio in the glass, apatite precipitation increased, with fluorapatite superseding calcium fluoride as the main phase formed during immersion. We also visualise surface mineralisation during immersion of the glasses in Tris-HCl buffer solution using TEM with EDX and X-ray nano-computed tomography (nano-CT), illustrating how compositional changes in the glass affect the microstructure at a sub-micrometre to nanometre level during mineralisation.



# Reactive molecular dynamics simulation of ternary phosphate-based bioactive glasses

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Phosphate-based glasses (PBGs) in the  $\text{CaO-Na}_2\text{O-P}_2\text{O}_5$  system have diverse applications as biomaterials due to their unique dissolution properties in an aqueous environment.<sup>(1)</sup> It is crucial to understand the factors which control their dissolution rate. Considerable efforts have been devoted in our group over the past few years to study ternary phosphate glasses.<sup>(2)</sup> To characterize the dissolution of these glasses fully at the atomic scale, reactive MD simulations using ReaxFF forcefield will be needed. The ReaxFF forcefield can describe the formation and breaking of chemical bonds by bond orders calculated from the interatomic distances in every time-step during molecular simulation.<sup>(3)</sup>

Firstly, we have investigated available ReaxFF parameters to see how well they can describe the structural properties of binary sodium phosphate glasses. To validate the parameters, the structural characterizations of bulk glasses have been compared with those from simulations using a formal-charge polarizable forcefield.<sup>(4)</sup> All simulations have been done using LAMMPS. The P-O and Na-O coordination number obtained from simulation with the best edited ReaxFF parameters is in good agreement with the results from the core-shell model, including appropriate bonding of phosphorus to bridging and non-bridging oxygen atoms. As a complete set of ReaxFF parameters for PBGs have not been so far developed, we develop and reparametrize the ReaxFF parameters for the ternary PBGs which includes the interaction between phosphorus and calcium atoms. ReaxFF parameters are obtained via optimization against an accurate and large training set of quantum mechanical data, mostly interatomic forces. To do this, we use the GARFFfield framework, a force field optimizer method based on genetic algorithms, hill climbing routines and conjugate-gradient minimization<sup>(5)</sup>.

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# Ultra-low network connectivity fluoride containing bioactive glasses: glass structure, design, crystallization and bioactive properties

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Bioactive glasses (BAGs) are commonly used in medicine and dentistry due to their ion releasing properties and capability to facilitate the formation of an apatite layer. For dental composites, this apatite layer can potentially form in the marginal gap caused by polymerization shrinkage, provide a marginal seal and prevent recurrent tooth decay. These BAGs commonly have a network connectivity (NC) value between 2.0 to 2.6. In the present study, high phosphate and fluoride containing bioactive glasses with varying NCs from 1.45 to 2.70 were designed and the effect of NC on crystallization behaviour and bioactive properties were characterised.

Seven BAG compositions with varying NCs were synthesised using the melt-quench technique, milled and sieved to obtain a particle size of <38  $\mu\text{m}$ . ATR-FTIR, XRD and DSC were performed on the glass powders to characterise the non-bridging oxygens, crystallinity and glass transition temperatures ( $T_g$ ), respectively. To investigate the bioactive properties, 75 mg of each glass powder was immersed into 50 mL of artificial saliva at pH7 (AS7) for multiple timepoints. At each timepoint, the glass was filtered from solution, dried overnight and characterised using ATR-FTIR, XRD, and <sup>31</sup>P-NMR to detect apatite formation and <sup>19</sup>F-NMR was used to distinguish between hydroxyapatite and fluorapatite (FAp). Ion selective electrode (ISE) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to measure the ion concentration in solution.

As the NC decreased, the amount of non-bridging oxygen (NBO) increased. When the NC reduced below 2, a silicate crystal phase formed, which dissolved upon immersion into AS7 and was replaced by apatite. The  $T_g$ , crystal phase present and processing window were also affected by NC. The glass with NC=2.70 slightly crystallised to FAp upon quenching, whereas the glasses with NC<2 crystallised to a silicate phase. ATR-FTIR showed that upon immersion, the glasses with a lower NC lost the NBO signal more rapidly than the glass with the higher NC, suggesting faster degradation of the glass particles. XRD and <sup>31</sup>P-NMR showed that the original glass was amorphous before immersion, then crystallised upon immersion to form apatite. ISE and ICP-OES showed fluctuations for the ion concentrations, suggesting release followed by consumption of the ions to form apatite, and <sup>19</sup>F-NMR confirmed that the type of apatite formed was FAp.

Understanding the crystallisation behavior is crucial when designing BAGs, as crystallization upon quenching could reduce the amount of ions readily available for ion release and apatite formation. The bioactive properties of BAGs could potentially conquer acid attack and recurrent decay, making these BAG fillers attractive in restorative dentistry.

# Nano scale amorphous phase separation and its role in subsequent crystal nucleation

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Crystal nucleation via prior Amorphous Phase Separation (APS) is widely believed to occur in many glass-ceramics. In most cases it is often inferred from nucleation of the primary crystal phase occurring just above the glass transition temperature,  $T_g$  in the absence of any obvious crystal nucleant phase.

$\text{SiO}_2\text{--Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--CaO--CaF}_2$  glasses have been shown to undergo APS prior to crystallising to fluorapatite (FAP), however in the compositions studied to date the APS process takes place during quenching. Recently we have found a glass that is single phase initially, but undergoes APS on holding at temperatures above the glass transition temperature ( $T_g$ ). This glass exhibits one  $T_g$  by DSC, as prepared, but two  $T_g$ s upon heat treatment at  $T_g+X$  where  $X$  is from 10 to 70. The two  $T_g$ s provide evidence for APS. The presence of one glass phase prior to heat treatment, but two glass phases after heat treatment is supported by Small Angle Neutron Scattering (SANS) studies where a peak in  $I(q)$  is found for the glasses held at  $T_g+X$  corresponding to a phase size of 10 to 60 nm. At  $T_g+70$  and above, the glass crystallises to FAP and the lower temperature  $T_g$  disappears.

APS has a pronounced influence on subsequent crystal nucleation and the optimum nucleation temperature correlates with the observation of two  $T_g$ s and APS observed by SANS, which is the first time this has been observed.

Surprisingly solid state nuclear magnetic resonance spectroscopy (ssNMR) shows no evidence that the APS process results in a glass phase closer in composition to that of the primary crystal phase, FAP. This might indicate that the APS process facilitates crystal nucleation by providing internal surfaces for heterogeneous crystal nucleation, rather than by lowering the activation energy for nucleation by providing a composition closer to the crystal phase.

# Into the light of a dark black night: glasses for mid-infrared applications

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The MIR (mid-infrared) spectral region spans 3-50 microns' wavelength (ISO BS 20473:2007). Many molecular absorptions lie within the 3-15  $\mu\text{m}$  wavelength, coinciding with the low optical loss window of chalcogenide glass fibre-optics, giving a 'window of opportunity' for a new generation of fibre molecular-sensors. New bright, fibre MIR-supercontinuum (-SC) laser sources have been demonstrated in chalcogenide glass for wideband MIR molecular sensing. Recently we announced lasing for the first time beyond 4 microns' wavelength in a  $\text{Ce}^{3+}$  doped chalcogenide glass fibre, with potential for long wavelength fibre lasing for pumping fibre MIR-SC and new machining of soft materials including new wavelengths for fibre laser surgery. Our goal is for new portable, MIR sensing systems for *in vivo* detection and treatment in healthcare, and compact portable systems for detection of toxins, pollutants and product purity in defence/security, environmental-monitoring and manufacturing, respectively.

Key words: fibre-optics, fibre lasers, mid-infrared, sensors

# A comparative evaluation of “House of Cards” and “Cabbage Head” fluormica glass-cramics

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**Introduction:** Fluormica glass-ceramics are well known for its excellent machinability, which is attributed to its unique “House of Cards” microstructure. Another interesting microstructure “Cabbage Head” has been developed claiming better mechanical and machinable properties. MACOR® (MAC) and VITRONIT® (VIT) are two commercially available examples of both microstructures. This work compares MAC and VIT fluormica glass-ceramics and the effect of their microstructures on different properties.

**Materials and Methods:** Both glass-ceramics were characterized using X-ray diffraction (XRD), Scanning electron microscope (SEM), <sup>19</sup>F and <sup>27</sup>Al MAS-NMR. M and V were then tested using Knoop hardness (KH), Biaxial flexural strength (BFS) and their machinability have been evaluated.

**Results:** XRD of both showed crystallisation of potassium fluorophlogopite with almost no difference in number or intensity of diffraction lines, SEM of MAC showed plate-like crystals forming “House of cards” microstructure while that of VIT showed curved crystals aggregates with amorphous centre forming “Cabbage head” microstructure. Knoop hardness of VIT was significantly higher than that of MAC, same as forces needed to machine them.

**Conclusions:** Commercial fluormica glass-ceramics with House of Cards microstructure has a better machinability and biaxial flexural strength than the with Cabbage head microstructure. However, the latter has higher hardness.

# Two-dimensional wide angle x-ray diffraction on a radioactive borosilicate glass in a beryllium container

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In the context of a better characterization of alpha self-irradiation effects of incorporated nuclear waste in glass matrices for long term disposal, we present the results of an X-ray diffraction experiment on a curium doped six-oxide borosilicate glass (ISG-C or “Cm-doped International Simple Glass”). This glass was melted in 2007 in ATALANTE facility and has already accumulated an  $\alpha$ -decay dose greater than  $7 \times 10^{18} \alpha \cdot g^{-1}$ , a value corresponding to a damaged but stabilized structural state.

For the first time, we managed to apply 2-D Wide Angle X-ray diffraction technique to ISG-C glass in a beryllium container. The experiment was operated on ACT beamline at KARA synchrotron (Germany), by combining a 50 keV high energy X-ray beam and an image plate. A special container filled with ISG-C glass was built using three concentric beryllium tubes nested as Russian dolls, with each tube closed at one end with a threaded cap, in order to reach safety synchrotron regulations.<sup>(1)</sup> Even if such configuration brings some drawbacks as for example large Cm fluorescence or Be crystalline contributions which partially blur the diffraction patterns, it was possible to successfully extract the structure factors of both pristine and Cm-doped glass samples. Striking new substructures appear under the so-called first sharp diffraction peak (FSDP), which cannot be explained only by already known effects related to variations in glass composition or thermal effects. It is more likely that these new sub-structures be related to changes in the size distribution of large objects like rings or chains under the influence of mixed interactions between the glass network,  $\alpha$ -particles and recoil nuclei. All these issues will be discussed in relation with other ISG-C Raman scattering characterizations.

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# Surface engineering of silica and silicate glasses using femtosecond laser induced plasma

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The use of lasers for material processing is a rapidly growing area for research and industry. Most of these applications, however, exploit the effects of irradiation of focused laser beams on or within materials to cut, shape and inscribe. In all these processes plasma is produced which either serves just for materials removal or produces internal modifications within the material, such as density or defect generation. Recently, femtosecond-pulsed lasers have been used for surface patterning of materials at nanoscale for increasing hydrophobicity of surfaces and controlling light reflection. None of these processes uses the materials constituting the ablated plasma to create structural and compositional changes within glass or, for that matter, other materials. Deposition or coating using pulsed lasers is well known which can be used to deposit materials from plasma on substrates as layers but that won't make any compositional changes within a substrate. In terms of pulse duration, different types of lasers such as nanosecond, picosecond and femtosecond lasers can be used for such deposition processes. The plasma produced by femtosecond lasers in such a deposition process, especially that from a dielectric material such as glass, differs from other types of lasers. The femtosecond laser induced plasma of glasses predominantly contains nanoparticles than ions as opposed to say nanosecond laser induced plasma.

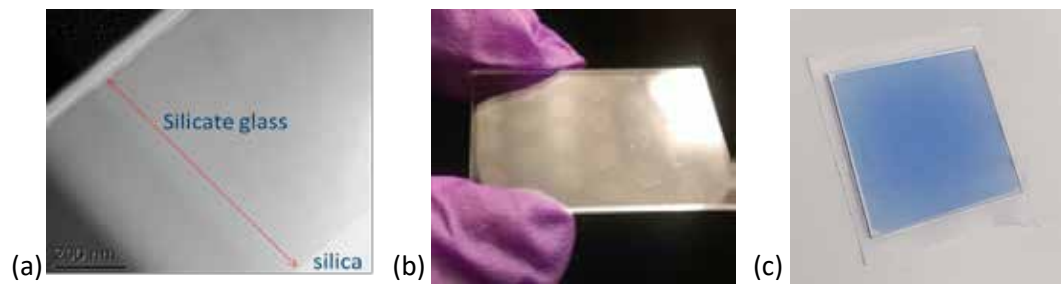


Figure 1. Here we report the innovation of using such femtosecond laser-induced plasma for creating structural and compositional changes, and therefore, mechanical, optical and spectroscopic properties at the surface of silica and silicate glass.<sup>(1-3)</sup> (a) shows the cross section from a silica glass modified to silicate by simultaneously doping with a number of ions including rare earth ions; (b) shows selective doping of using a shadow mask; and (c) blue colour produced in a silicate glass using the laser induced plasma. The physical, spectroscopic and mechanical properties that can be induced in glass after it being made offer a number of opportunities for glass industry say in packaging and security, integrated optics and photonics, glass strengthening and colouring for display screens, architectural glass and jewelry.

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# Hydrophobic silica aerogels containing magnetic nanoparticles

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Oil spills severely affect the environment year on year, making the development of effective sorbents to tackle this issue a topic attracting much attention. To this end, aerogels become a method of increasing interest due to their low toxicity, tailorable properties and light porous structure.

Hydrophobic silica aerogels have been synthesised via a sol-gel process which uses a mixture of tetraethyl orthosilicate (TEOS) and triethoxymethylsilane (TEMS) to provide oleophilic and hydrophobic character. Moreover, the method has been modified to incorporate pre-synthesised magnetite nanoparticles in the sol, in order to obtain magnetic samples which can be recovered after use, using an external magnet.

The sol-gel process has been optimised to achieve a homogenous dispersion of the nanoparticles in the obtained gels, which are submitted to supercritical drying to produce Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> aerogels. Samples with different amounts of magnetite nanoparticles and/or with the supplementary addition of carbon black have been synthesised. They are attracted by an external magnet, indicating that the magnetic nanoparticles do not deteriorate during the supercritical drying step. Moreover, the hydrophobic character of these nanocomposites is maintained over time, and they float on water for months without any degradation. They are also stable under thermal treatments in air up to 350°C. Adsorption tests show that the samples produced are able to adsorb large quantities of oil (up to eight times their weight).



# Towards low-cost radiation-resistant silicate and borosilicate glasses

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The development of inexpensive radiation-resistant glass is important for potential applications in displays, optics, and nuclear or space environments. This study considers the  $\gamma$ -ray and X-ray resistance of glasses relevant to low-cost commercial glasses, as well as other glasses relevant to radioactive waste immobilization, including glasses modified with different concentrations of active dopants. Various doses (0, 0.2, 2.0, and 5.0 MGy) of  $\gamma$ -rays from the decay of  $^{60}\text{Co}$  nuclei, and X-rays generated by an X-ray fluorescence (XRF) spectrometer, have been applied to series of modified float-type glasses and simulated borosilicate radioactive waste glasses to study their resistance to radiation-induced damage; and the nature of any damage that is created. Irradiation leads to the formation of various defect centres (including  $\text{HC}_2$ ,  $\text{HC}_1$ ,  $\text{TE}$ ,  $\text{E}'$ , and  $\text{E}^-$  types). These radiation-induced defects cause photo-darkening of glass, which reduces its visible-wavelength optical transparency. The addition of certain dopants, and careful control of glass composition, can lead to reductions in the formation of radiation-induced defect-centres, combined with forbidden bandgap narrowing which can lead to non-linear changes in visible-wavelength absorption. Some of the mechanisms of defect-formation, relationships between glass composition, dopant additions, and defect centres, will be elucidated in this presentation. This work confirms that it is possible to substantially modify or enhance radiation response of silicate and borosilicate glasses, including opportunities for low-cost solutions for radiation resistant applications and implications for the long-term radiation performance of radioactive waste glasses.

# Synthesis, structure and luminescence properties of $\text{Eu}^{3+}$ doped $50\text{ZnO}-40\text{B}_2\text{O}_3-5\text{WO}_3-5\text{Nb}_2\text{O}_5$ glass

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In this work we focused on the synthesis of  $\text{Eu}^{3+}$  doped zinc-borate glasses with nominal composition  $50\text{ZnO}-40\text{B}_2\text{O}_3-5\text{WO}_3-5\text{Nb}_2\text{O}_5-x\text{Eu}_2\text{O}_3$  (where  $x=0, 0.1, 0.5, 1, 2, 5$  and  $10$  mol%). The synthesized glasses are characterized with good transmittance and homogeneity. The thermal parameters such as glass transition temperature, glass crystallization temperature and thermal stability of the glasses were determined by differential thermal analysis. Physical parameters of the synthesized glasses such as density, molar volume, oxygen molar volume, oxygen and packing density were determined. Structural model for the glass network was suggested on the base of IR spectral investigations. It was established that  $\text{WO}_6$  and  $\text{WO}_4$ ,  $\text{NbO}_6$ ,  $\text{BO}_3$  and  $\text{BO}_4$  structural units build up the glass network. Photoluminescence emissions due to the 4f transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $j=0-4$ ) of  $\text{Eu}^{3+}$  ions were observed. Influence of the glass structure and  $\text{Eu}^{3+}$  content on the emission intensity of the prepared glasses was established.

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# The effect of lithium concentration on the radiation damage in UK nuclear waste glasses

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The glass compositions used in the UK to immobilise the highly radioactive waste arising from the reprocessing of used nuclear fuel are termed 'Calcium Zinc' (CaZn) and 'Mixture Windscale' (MW). In this work, CaZn and MW base glasses are studied with their full and half lithium content to evaluate the impact lithium concentration has on radiation damage in the glass network. Previous studies by others have been carried out to determine the role of lithium in the glass network and the impact lithium has on the aqueous durability of the glass.<sup>(1,2)</sup> With this knowledge, our work discusses the impact of lithium concentration on the degree of radiation damage caused by gamma rays. This information is fundamental for the long-term evolution of high-level nuclear waste immobilisation in the UK. Gamma irradiations were carried out for all four glass compositions at the Dalton Cumbrian Facility to simulate the effect of gamma radiation on the pristine glass network. Glasses were irradiated with 0.5 MGy and 5 MGy doses at a dose rate of 85 Gy/min. We postulate that since lithium is a network modifier, gamma irradiation-induced changes are more likely to occur in glasses with higher lithium concentration. The relationship between lithium concentration and change in depolymerisation of the glass can be probed by Nuclear Magnetic Resonance (NMR), Raman spectroscopy and thermal analysis. Multidimensional multinuclear Magic Angle Spinning (MAS) NMR and Raman spectroscopies investigations of the glass network were carried out to identify structural changes between pristine and irradiated glasses. Additionally, changes in the local atomic scale structures were correlated with thermal behaviours as obtained from glass transition temperature ( $T_g$ ) measurements.

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# **New pair distribution function analysis of International Simple Glass (ISG) from neutron and x-ray diffraction**

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Multicomponent borosilicate base glass is used to vitrify high level radioactive waste. To ensure the glass is able to contain all radioactive elements until radiation has decayed to safe levels, an understanding of glass structure is necessary to model long term glass performance in a geological disposal facility. A range of base and simulant glasses are used to study glass behaviour, preventing direct comparison between many different studies. To enable standardised glass leaching studies an aluminoborosilicate glass formulation known as ISG (mol%: 60.2 SiO<sub>2</sub>, 16.0 B<sub>2</sub>O<sub>3</sub>, 12.6 Na<sub>2</sub>O, 3.8 Al<sub>2</sub>O<sub>3</sub>, 5.7 CaO, 1.7 ZrO<sub>2</sub>) has been created. The structure of ISG has previously been studied through atomistic modeling with the aid of Pair Distribution Function (PDF) data, but a direct fit of X-ray and Neutron PDF data for ISG has never previously been reported. Here for the first time structural data has been extracted by directly fitting high Qmax PDF data collected using an <sup>11</sup>B isotopically enriched ISG sample using simultaneous fitting of X-ray and Neutron PDF aided by solid state <sup>27</sup>Al and <sup>11</sup>B NMR.

# Synthesis and characterisation of novel metal-organic framework–inorganic glass blends

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Metal-organic frameworks (MOFs) are a recently discovered class of crystalline hybrid materials comprising metal ion centres and organic linkers which self-assemble into a three-dimensional, periodic porous material.<sup>(1)</sup> In addition to their unique properties, several MOFs can be melt-quenched to form hybrid glasses, representative of the first new glass category elucidated since the 1970s.<sup>(2)</sup> A significant proportion of hybrid glasses are derived from zeolitic imidazolate frameworks (ZIFs), a type of crystalline MOF consisting of tetrahedral metal ions and imidazolate and imidazolate-derived linkers. A ZIF that has exhibited excellent glass forming ability is ZIF-62,  $[\text{Zn}(\text{Im})_{1.75}(\text{bIm})_{0.25}]$ , comprising  $\text{Zn}^{2+}$  ions and imidazolate and benzimidazolate linkers. However, ZIF-62 liquid has a high viscosity at its melting temperature, making it harder to mould it into shapes.<sup>(3)</sup>

To address these potential commercial barriers, attempts to synthesise a compositional series with ZIF-62 glass ( $a_g\text{ZIF-62}$ ) and a phosphate glass,  $30\text{Na}_2\text{O}-70\text{P}_2\text{O}_5$  (Figure 1) are presented. The synthesised materials were characterised by powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC), fourier-transformed infrared spectroscopy (FTIR), simultaneous DSC/TGA (SDT) and scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDX). Importantly, insights into bonding were provided by Pair distribution function (PDF) studies,  $^{31}\text{P}$  solid state NMR and Raman spectroscopy.

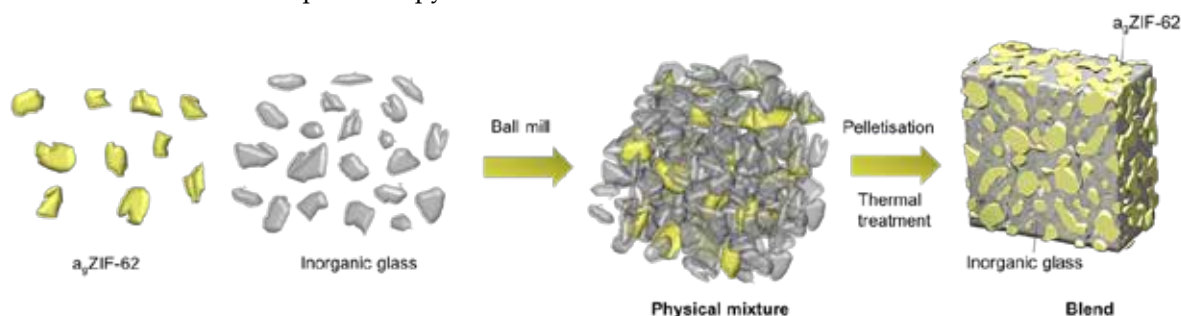


Figure 1. Synthesis of MOF glass–inorganic glass blends via ball-milling, pelletisation and thermal treatment.

It is hoped that these new hybrid materials will combine the processability and stability of inorganic glasses with the ubiquitous properties of MOFs for targeted applications.

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# Quasi-elastic neutron scattering investigation of intermediate range order dynamics in supercooled liquids and glass-formers

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Intermediate Range Order (IRO), the existence of structural organization at length scales larger than the intermolecular distance, is a ubiquitous feature in many liquids and glass formers. The signature of IRO is a prepeak in the structure factor at exchanged wavevector,  $Q$ , values smaller than the main peak. Using QuasiElastic Neutron Scattering, the collective dynamics of the scattering length fluctuation was investigated across length-scales encompassing the intermediate range order, the interparticle distance, and smaller. Results on three representative glass formers will be reported: isopropanol, a hydrogen bonding alcohol, and two ionic glasses, zinc chloride and calcium potassium nitrate.

In the alcohol, the IRO originates from the presence of associates whose dynamics affects the macroscopic properties of the system. Interestingly the temperature dependence of the dynamics of the associates differs from that of the structural relaxation at the main peak, remaining Arrhenius even below the melting temperature. In the two ionic glasses  $\text{ZnCl}_2$  and CKN, the IRO originates from the network molecular structure. Whereas zinc chloride is an intermediate glass-former in the Angell's fragility classification CKN is a fragile one. In both these ionic systems the character of the temperature dependence of the relaxation is the same at the prepeak and at the main peak, Arrhenius for  $\text{ZnCl}_2$  and super-Arrhenius for CKN. However, data collected on the recently commissioned wide angle neutron spin echo spectrometer, WASP, at the Institut Laue Langevin in Grenoble, indicate that at  $Q$  values larger than the main peak, i.e. for length-scales smaller than the nearest nitride-nitride ion distance, the dynamics displays a less fragile behavior than at the main peak.

These results provide nanoscopic experimental evidence of the role played by the microscopic structure in determining the molecular dynamics in the supercooled state.

# The viscosity in supersaturated aqueous sugar solutions and applications in cryopreservation

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While cooling a supersaturated solution of water with polyhydroxy compounds such as sugars and polyols, one encounters a glass transition. The glass transition temperature in this case depends on the concentration of the solute. Since the early 1940s, when Father Basile J. Luyet began experimenting with the cryopreservation of biological systems through the vitrification of these solutions, the behavior of the supersaturated regime has been studied within the framework of the glass transition.

In the case of the glass transition of a supercooled liquid, the study of relaxation processes, gives the main clue of its physical properties through the dependence of its viscosity in terms of temperature.

In this work we present a physical approach for the viscosity of different supersaturated binary aqueous sugar solutions that presents a universal behavior in terms of concentration and temperature based on the result of previous works for the description of the viscosity of supercooled liquids. This universality has been reported in several experimental procedures in cryopreservation.

# Amorphous silica coating of phosphorescent nanoparticles

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The applications of functional nanoparticles often depend on them having properties different to the bulk or being deliverable in environments where larger particles are disadvantageous. In the field of luminescent materials,  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  is recognised for its persistent phosphorescence.<sup>(1)</sup> These materials have many promising applications in various fields, including: in solid state lighting; in display devices; in biomedical fields for biological labelling, drug delivery, bio-sensors and photo-dynamic therapy; in nano-biotechnology; in temperature sensors; etc. However, the phosphorescence is susceptible to degradation by hydrolysis and oxidation, and this is more detrimental for nanoparticles. Inorganic coating of nanoparticles is often conducted to protect nanoparticles, to make them compatible with certain environments (e.g. biocompatible), or to add functionality (e.g. core-shell). A silica coating has advantages of being biologically benign, water-resistant, durable, amorphous, and not inhibiting functionalities, e.g. it is transparent. Therefore, the aim of this work is to protect the phosphor nanoparticles via silica coating.<sup>(2)</sup> The sol-gel technique is indeed adaptable to the coating of nanoparticles.<sup>(3)</sup> There have been limited previous reports of sol-gel coating of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  particles, with sizes ranging from 100s nm to microns. This presentation reports new work on sol-gel silica coating of sub-100 nm  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  nanoparticles. The work has involved preparing nanoparticles by combustion synthesis and applying silica coatings by sol-gel methods. The coated nanoparticles have been characterised using X-ray diffraction, Fourier transform infrared spectroscopy, electron microscopy and fluorimetry to establish the effect of coating on the structure and phosphorescence.

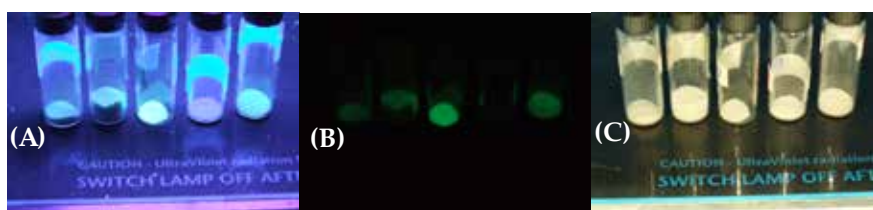


Figure 1: (A) Coated  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  nanoparticles, (B) Phosphorescence in the dark and (C) Fluorescence under UV light

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# A TEM study into helium bubble behaviour in $\text{Gd}_2\text{Ti}_2\text{O}_7$ glass-ceramic composites

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Disposal of actinides from spent nuclear fuel is an essential problem as around 1390 m<sup>3</sup> high level waste (HLW) is produced in United Kingdom every year. Nuclear wasteforms used to immobilize the actinides must be stored for a long-term geological timescale. During the process, self-irradiation damage caused by  $\alpha$ -decay event (recoil nuclei +  $\alpha$ -particles) from Pu and other minor actinides will result in the accumulation of helium atoms which can, on a macroscale lead to the formation of helium bubbles when reaching the critical concentration, causing mechanical changes such as surface swelling and cracks, therefore giving an enhancement in leaching from ground water, which is detrimental to health and environment. Recently, glass-ceramic nuclear wasteforms have attracted great attention for immobilizing high-level nuclear waste, because they exploit both advantages of glasses and ceramics, while simultaneously overcoming their shortcomings. Besides, since the more stable crystalline ceramic matrix serves as the main host phase to incorporate the radioactive actinides, other processing chemicals can be accommodated in glass matrix, which provides a double barrier to prevent from leaching. In order to understand the He accumulation due to long-term  $\alpha$ -decay, we performed 10 keV *in-situ* TEM He-implantation experiment to study the formation of helium bubbles as a function of He dose. The average bubble sizes inside the ceramic matrix increased from 1.1 nm to 1.5 nm with the increase of fluence. No helium bubbles can be found in glass matrix or glass-ceramic interfaces due to the high helium diffusion coefficient, which allows helium bubbles to escape from these areas. Besides, helium bubbles accumulated along the grain boundaries are significantly larger and prominent compared to others inside the grain, as helium diffusion coefficients of O, Si, K along grain boundaries are significantly higher than in the crystal lattice in similar minerals, increasing the chances for helium to accumulate along grain boundaries. Quantitative results will be discussed during the conference.

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# Thermophysical property measurements of liquid lanthanoid sesquioxides by the electrostatic levitation furnace onboard the ISS

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Investigations of properties at high temperatures liquids are very challenging particularly above around 2000 K, because chemical reactions between samples and containers are unavoidable. In addition, crystallizations from the container makes it difficult to maintain the liquid state. However, the use of levitation techniques can overcome these problems and enable to precisely measure the physical properties over wide temperature range including deep undercooling, owing to the elimination of contamination and extrinsic heterogeneous nucleation. Using Columbo force, our group have been developing an electrostatic levitation furnace (ELF) and installed a facility in the International Space Station (ISS) to allow the investigation of metal oxides which are difficult to levitate under the gravitational force due to insufficient charge amount accumulated on the samples.<sup>(1-3)</sup> In order to demonstrate the capability of the ISS-ELF, thermophysical properties of lanthanoid sesquioxides ( $\text{Ln}_2\text{O}_3$ ) were measured. Firstly, the densities of  $\text{Er}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{Tb}_2\text{O}_3$ , and  $\text{Gd}_2\text{O}_3$  at their melting temperatures ( $T_m$ ) were obtained over the wide temperature range (2700–3200 K),<sup>(2)</sup> and these density values were shown to exhibit a linear correlation with temperature. The molar volumes of these oxides at their  $T_m$  values were calculated and compared with those of other sesquioxides. The volumes of the nonglass-forming sesquioxides ( $\text{Er}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{Tb}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Ga}_2\text{O}_3$ ) exhibit linear correlations with the cubes of their cation radii. In contrast, those of the glass-forming oxide ( $\text{B}_2\text{O}_3$ ,  $\text{As}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3$ ) showed different correlations. Therefore, molar volumes might be a good indicator of the ability of a single component oxide to form glass. Next, surface tension and viscosity of  $\text{Tb}_2\text{O}_3$  were measured using the ISS-ELF and oscillating drop method.<sup>(3)</sup> These values at  $T_m$  showed 27 mPas and 730 mN/m, respectively, which are close to those of  $\text{Al}_2\text{O}_3$ . This talk will discuss the temperature dependence and uncertainty.

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# The influence of fluorides on the luminescence of Eu<sup>3+</sup> doped phosphate glasses

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Factors such as simplicity of execution, low production costs, versatility and durability determine the direction of development of materials used in solid-state lighting, for which demand has increased significantly in the last decade.<sup>(1)</sup> Amorphous materials doped with rare earth ions, in particular phosphate glasses, have high potential in this field. Phosphate glasses stabilized with heavy metal oxides are characterized by exceptional solubility of modifiers and rare earth elements, good chemical durability and low fluorescence linewidths.<sup>(2)</sup> The use of glasses as an optical matrix is an excellent answer to the problem of thermal stability of commercially used encapsulants and phosphors. The addition of fluorides allows to obtain even more suitable optical materials with lower phonon energy, high UV transparency, and high quantum yields, which makes them promising candidates for durable phosphors in LEDs.<sup>(3)</sup> The series of phosphate glass systems of nominal composition P<sub>2</sub>O<sub>5</sub>-Bi<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>-X (X=5, 10, 15 mol% of AlF<sub>3</sub>, KF), doped with 0.5 mol% europium were prepared by conventional melt-quenching technique. The acquired glasses were structurally characterized by XRD and FT-IR measurements. DTA measurements were conducted to determine the thermal properties. The effect of fluorides on Eu<sup>3+</sup> ions luminescence was analyzed on the basis of the luminescence emission spectra under UV excitation and UV-Vis spectroscopy.

On the basis of the conducted research, significant changes in the luminescent properties were observed with the introduction of fluorides in various contents.

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# Combination of neutron techniques for mosaic glasses analysis

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We present a completely non-destructive study of historical mosaic glasses based on the combination of different neutron techniques. The goal of the analysis is to obtain a bulk characterization of the glasses in terms of elemental and mineralogical phase composition in a completely non-destructive way.

We have selected a set of about 20 glass specimens of mosaic tesserae from archaeological excavations or mosaic under restoration, dating from the 6th to the 13th century AD, coming from different archaeological sites and geographical areas (Italy, Greece and Syria). Prompt Gamma Activation Analysis (PGAA – a kind of Neutron Activation Analysis with an external guided cold neutron beam) and Time-of-Flight Neutron Diffraction (ToF-ND) analysis have been applied. PGAA, performed at the Budapest Neutron Centre (BNC, Budapest, Hungary), can be used to quantify almost all the major and minor components (H, Na, K, Mg, Al, Si, Ti, Mn, Fe and Cl) and some trace elements (B is an important one, occasionally also Cr, Sc, V, Nd, Sm and Gd). As neutrons penetrate deep into the sample, PGAA can determine and quantify the bulk glass composition. ToF-ND is used to identify the mineralogical phases, acting as opacifiers, dispersed in the glass matrix. The neutron diffraction analysis has been performed at the ISIS Neutron and Muon Source (UK). Previous non-destructive analyses have been performed on the same samples through Raman Spectroscopy, Particle Induced X-ray and Gamma Emission (PIXE and PIGE) and Neutron Resonance Capture Analysis. However, results are not fully representative of the entire bulk of the glasses as Raman spectroscopy and PIXE/PIGE are spot and superficial analyses (compared to the neutron-based ones) while NRCA returned only qualitative information regarding the presence of Sb, Cu, As, and Pb in some samples. This way, the above mentioned methods are complementary to each other.<sup>(1)</sup>

Moreover, an attempt of extrapolation of the crystalline phases content within the amorphous matrix from the neutron diffraction data is under consideration.

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# Structural study of ZnO–B<sub>2</sub>O<sub>3</sub>–WO<sub>3</sub> glasses modified with Nb<sub>2</sub>O<sub>5</sub>

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The effect of addition of Nb<sub>2</sub>O<sub>5</sub> on the structure, thermal stability and optical properties of ZnO–B<sub>2</sub>O<sub>3</sub>–WO<sub>3</sub> glass matrix has been investigated by infrared (IR) and Raman spectroscopy, density measurement, DTA analysis and optical transmission spectroscopy. Homogeneous bulk glasses were obtained from the compositions containing 5 mol% Nb<sub>2</sub>O<sub>5</sub>, while partially crystallized sample was developed from the compositions having 10 mol% Nb<sub>2</sub>O<sub>5</sub>. The glasses obtained are highly transparent (85–90 %) and colorless in the visible light region and give the optical band gap energy of 3.64–3.68 eV. IR spectroscopy confirmed the presence of trigonal BØ<sub>3</sub> units in boroxol rings, tetrahedral BØ<sub>4</sub><sup>–</sup> units in tetraborate groups (Ø=bridging oxygen atom), and borate triangles with non-bridging oxygen atoms. The combination of Raman and IR spectroscopy indicate the presence of tungstate species mainly in the form of WO<sub>4</sub> tetrahedra without excluding the formation of WO<sub>6</sub> octahedra in the glass matrix. Also, Raman and IR spectra suggest that niobium ions incorporate into base glass matrix as isolated and distorted NbO<sub>6</sub> octahedra, with W<sup>6+</sup> ions creating new W–O–Nb bonds. The density, molar volume and oxygen packing density of glasses have been found to increase with the introduction of Nb<sub>2</sub>O<sub>5</sub>, while oxygen molar volume decreases and indicates higher cross-linking within glass network. Glass transition temperature increases with Nb<sub>2</sub>O<sub>5</sub> addition, whereas thermal stability against devitrification decreases due to the formation of new strong bonds with participation of niobium.

**Acknowledgments:** The study was performed with financial support of Bulgarian National Science Fund at the Ministry of Education and Science, Contract KII-06-H29/7.

# Structure and luminescent properties of borate-bismuth glass and glass-ceramics doped with Ag nanoparticles

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Nowadays, a lot of interest is focused on optoelectronics materials, due to their wide range of applications, such as light-emitting diodes (LEDs), non-linear photonic materials, and optical waveguides. A significant part of them are glasses doped with metal nanoparticles, due to the possibility of localized surface plasmon resonance (LSPR) occurrence. It is known, that LSPR can increase the intensity of rare-earth ions emission, by creating so called “hot-spots”.<sup>(1)</sup> Electron excitations under specific wavelengths can lead to charge oscillations at the metal-insulator boundary, resulting in electric field enhancement around metal nanoparticles. Crucial for such a purpose is an appropriate glass matrix, which should provide transparency in a wide range of frequencies, good chemical, and thermal stability, and low phonon energy. Borate-bismuth glasses doped with Ag nanoparticles and Ln<sup>3+</sup> ions dispersed inside could meet these requirements.

In this work, the results of the investigation of structure and optical properties of B<sub>2</sub>O<sub>3</sub>–Bi<sub>2</sub>O<sub>3</sub> glasses and glass-ceramics doped with Ag and Eu<sup>3+</sup> ions are presented. Glasses were prepared by the conventional melt quenching technique. Ag nanoparticles were synthesized during the heat-treatment process. The structure of the samples was examined by XRD, DTA, FTIR and XPS methods. The optical properties were studied by UV-Vis spectroscopy. To examine the luminescent properties, prepared samples were excited by UV radiation.

Based on the obtained results, borate-bismuth glass and glass-ceramics could be considered as a promising plasmonic materials. Moreover, they can find application as phosphors in light-emitting diodes.

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# Structure and properties of boron oxide-doped sodium niobate-phosphate glasses

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Niobium is one of the elements used to modify the structure and properties of phosphate glasses. It was found that niobium containing phosphate glasses show good chemical durability, good VIS to near IR transparency, high transition temperature and high refractive index. These properties contribute to their prospective applicability for various optical devices or as potential candidates for the nuclear waste immobilization. Moreover, niobate-phosphate glasses show also promising biological response with stimulation of alkaline phosphatase activity of osteoblast-like cells, which can be used to improve the performance of biomaterials. Doping of phosphate glasses by boron oxide is generally known to improve their mechanical properties and chemical resistance against atmospheric moisture. The reason for the improvements in the properties of borophosphate glasses is ascribed to the transformation of linear-chain structure into three-dimensional structure.

In the present study we report a description of changes in the structure and properties of sodium niobate-phosphate glasses where starting  $40\text{Na}_2\text{O}-40\text{P}_2\text{O}_5-20\text{Nb}_2\text{O}_5$  composition was modified by  $\text{B}_2\text{O}_3$  in the compositional series  $(100-x)(0.4\text{Na}_2\text{O}-0.4\text{P}_2\text{O}_5-0.2\text{Nb}_2\text{O}_5)-x\text{B}_2\text{O}_3$  within the concentration range of  $x=0-48$  mol%  $\text{B}_2\text{O}_3$ . Glasses were characterized by the measurements of density, molar volume, index of refraction and chemical durability. The structure of glasses was investigated by Raman and MAS NMR spectroscopy, their thermal properties were studied by DSC, thermodilatometry and hot stage microscopy. Crystalline phases were identified by X-ray powder diffraction analysis. Raman and NMR spectra showed that the structure of starting  $40\text{Na}_2\text{O}-40\text{P}_2\text{O}_5-20\text{Nb}_2\text{O}_5$  glass is formed mainly by metaphosphate ( $\text{Q}^2$ ) and diphosphate ( $\text{Q}^1$ ) structural units interconnected by P-O-P bonds.  $\text{Nb}_2\text{O}_5$  is incorporated in the structural network in the form of  $\text{NbO}_6$  octahedral units. Introducing and gradually increasing of  $\text{B}_2\text{O}_3$  content causes a slow depolymerization of the phosphate structural network and the development of  $\text{BO}_4$  and  $\text{BO}_3$  units in the local structure of the glass matrix. The substitution of  $40\text{Na}_2\text{O}-40\text{P}_2\text{O}_5-20\text{Nb}_2\text{O}_5$  composition for  $\text{B}_2\text{O}_3$  led to a gradual decrease in density and molar volume of glasses, whereas glass transition temperature, dilatometric softening temperature and index of refraction reach maximum values within the range of  $x=8-12$  mol%  $\text{B}_2\text{O}_3$ .

# Similarities and differences between homo- and hetero-connectivity in crystals and glasses of the BaO–SiO<sub>2</sub> system

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The seminal work of Brawer & White<sup>(1)</sup> remains a motivational work that links the vibrational modes of crystals to glasses in silicate systems. At the time the central force model was predominant, however, it has been displaced by *ab initio* methods which are revealing new insights. The tetrahedra which form the structural units in crystalline phases persist into the melt, and therefore, their signatures in the vibrational modes recorded in Raman spectra are comparable. This has led to a various interpretations of glass spectra based on group theory arguments. In this poster, the Raman spectra of crystals<sup>2,3</sup> for phases from Ba<sub>2</sub>SiO<sub>4</sub> to BaSi<sub>2</sub>O<sub>5</sub> versus those of glasses<sup>4,5</sup> from the compositions range  $x\text{BaO} \cdot (1-x)\text{SiO}_2$ ,  $0.28 \leq x \leq 0.45$  will be compared.

Hetero-connectivity, where a Q<sup>n</sup> species is linked to a Q<sup>n±1</sup> unit, is the norm in silicate glasses and melts whereas it is uncommon to most crystals, which are generally homo-connected, e.g. Q<sup>n</sup>–Q<sup>n</sup> structures. The BaO–SiO<sub>2</sub> system contains three crystalline phases, Ba<sub>4</sub>Si<sub>6</sub>O<sub>16</sub>, Ba<sub>5</sub>Si<sub>8</sub>O<sub>21</sub>, and Ba<sub>6</sub>Si<sub>10</sub>O<sub>26</sub>, which are hetero-connected having Q<sup>2</sup>:Q<sup>3</sup> ratios of 1:2, 1:3 and 1:4, respectively. Recent work has simulated the Raman spectra of these crystalline phases and reproduce the vibrational modes within a mean absolute of  $\pm 7 \text{ cm}^{-1}$ . The structural origin of these modes, their splitting and the range of frequencies possible for these modes is evaluated as a function of mean polymerization. The structural origin is discussed in detail and framed by comparison to ~140 crystalline silicate spectra. The implications for the structural origin of the peaks in the Raman spectra of the barium silicate glasses is then evaluated in detail to reveal new directions for their interpretation with implications for (de-) polymerization during crystallization.

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# Silver photochemical reactivity under electronic irradiation analysis of gallo-phosphate glasses

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Nowadays photonics is becoming a key enable technology for the future thanks to its ubiquity in a vast spectrum of disciplines. The development of new functionalities in integrated phonic circuits remains highly challenging in order to push photonics technology out of its limit, up to a mature level for industrial transfer. In this framework, the development of innovative materials suitable for integrated circuits as well as laser processing facility are of crucial importance. Indeed, the ability to use direct laser writing for shaping and inscribing functionality in glass material has open a way for the versatile production of multi-scale subwavelength photonic architectures. Recently we demonstrated the possibility to create multi-scale 3D architecture with highly localized fluorescence contrast in photosensitive silver-containing Gallo-phosphate glasses by means of all-optical femto-second laser writing<sup>(1)</sup> However, the understanding of the photochemical phenomena allowing the formation of the silver clusters, which are at the origin of the fluorescence in the Gallo-phosphate glass remains unclear. Indeed, femtosecond laser interaction with glass creates highly out-of-equilibrium free electrons that allow for the activation of silver-based photo-chemistry and associated local material modifications at the root of high optical contrasts both for linear and nonlinear optical proprieties. In this framework, it is highly interesting to perform high-energy ionizing irradiation to access the initial mechanisms of material modification, and thus to provide the fundamental understanding of the material parameters that play a role in glass photosensitivity.

In the present work, we performed electronic irradiations followed by EPR spectroscopy. This allowed us to demonstrate the process involved in the interaction of electron beam with both the silver-containing and silver-free glass matrices. This allowed understanding the initial phenomena of electron deposition and charge trapping that support the photosensitivity of these glasses by identifying the point defects and the Ag species, which are formed. The in-situ cathodoluminescence measurements gives additional valuable information about the cascade of chemical reactions in the formation of new silver species, namely from the initial silver ions to the molecular silver clusters.

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# Use of glass from smartphone touch screen for radiological accident dosimetry by EPR spectroscopy

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In the context of malevolent or accidental use of radioactive materials, there is an identified need for a fast and reliable method to sort out the individuals actually exposed to ionizing radiation and needed immediate medical cares. A proposed method by IRSN uses the smartphone touchscreens as a radiation dosimeter in order to determine the dose of exposure to a person. Touchscreen glasses are analyzed by Electron paramagnetic resonance spectroscopy (EPR).<sup>(1)</sup> EPR has been used to estimate dose of exposure to radiation with a wide variety of materials collected on exposed individuals.<sup>(2)</sup> However, the huge advantage of tempered glass of touchscreen is that everyone has currently a smartphone and therefore a fortuitous dosimeter in their pocket. The work here presented is focused on the study of the seven generations of Corning® Gorilla® Glass. Gorilla® glasses are known to be made of aluminosilicate glasses but the specific concentrations are not published. By being able to identify in the glass of the touch screen, the stable induced defects caused by irradiation along with the detection of the type of glass generation, the exposure dose can be quantified. The EPR spectra are complex in their analysis as radio induced defects could overlap with defects present already in the glass or during their manufacturing process or even due to exposure to UV irradiation. As shown in Figure 1, the evolution of the EPR spectra for Gorilla Glass generation 4 according to the irradiation dose.

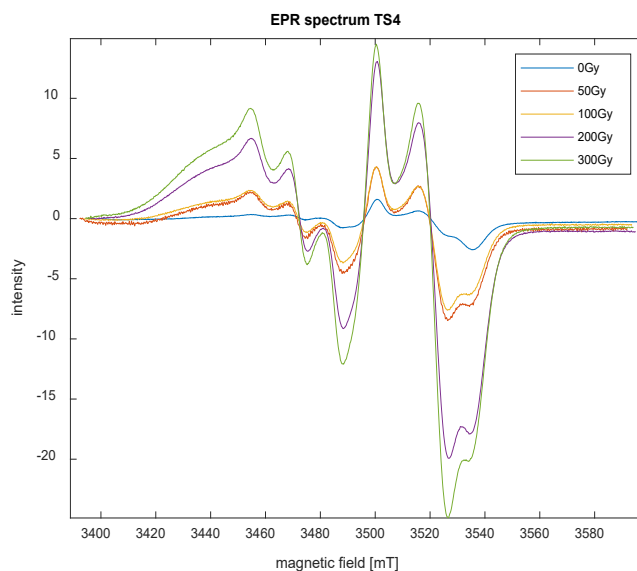


Figure 1. EPR spectra of Gorilla® Glass 4<sup>th</sup> generation according to the irradiation dose

Consequently, our goal is to propose an operational protocol for quantification of defects induced by radiation and related radiation doses in the touch screen glass. This technique is non-destructive and requires for the moment to collect on the phone a few tens mg of the touch screen.

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# Unveiling the depolymerization of densified lead metasilicate glass: an *in-situ* high-pressure vibrational spectroscopy investigation

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Lead-bearing glasses are known for their high-density and high-refractive index, enhanced by specific pressure treatment.<sup>(1)</sup> Raman investigation performed on densified glass appoints to an unusual decrease of non-bridging oxygens (NBO), suggesting the consumption of free-oxygens among the mechanisms leading to the glass densification.<sup>(2)</sup> In this work, lead metasilicate glass was submitted to high-pressure in a Diamond Anvil Cell (DAC) and investigated *in-situ* by Raman spectroscopy to shed further light on the structural mechanisms of compression and decompression. Vibrational spectra were acquired in complete pressure cycles applying independently as pressure transmitting media in the DAC: alcohol solution, nitrogen gas, and argon gas. A stepwise behavior was observed during the compression path, as depicted by the barycenter evolution of the high-frequency Raman region, assigned to symmetric Si–O stretching vibrations. The progression of this spectral region suggests the depolymerization in densified PS glass occurring through mechanisms of polymerization, intermediated by a more-polymerized state under high pressure. Such modifications are accompanied by a change in the lead environment possibly extending from deformation within the tetragonal pyramids to the formation of highly coordinated PbO<sub>n</sub> polyhedra, as indicated by the *in-situ* modifications in the low-frequency Raman region.<sup>(3)</sup>

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# Microstructure and characterization of coloured zirconia ceramics

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The zirconia-based ceramics are widely used due to their excellent mechanical properties and for widely industrial applications like sensors, refractory materials, biomaterials, pigments and fuel cells. Many challenges were done for the optimization of the synthesis methods of these ceramics because zirconia has three patterns: monoclinic (remains stable up to 1170°C), (between 1170 and 2370°C) and cubic (>2370°C). During cooling, the transitions between these crystalline phases back to monoclinic phase which involve a large volume expansion, micro-cracks, inclusions and catastrophic failure.

In this work the addition of MgO can produce the stabilized zirconia of high temperature to exist at room temperature after sintering and the higher levels of Fe<sub>2</sub>O<sub>3</sub> contents in the host matrix make a colored zirconia. The samples in the xFe<sub>2</sub>O<sub>3</sub>·(100-x)[ZrO<sub>2</sub>·MgO] composition where x=0–40 mol% Fe<sub>2</sub>O<sub>3</sub> were prepared by a solid state reaction method using as starting materials their metallic oxides.

The structural, spectroscopic, magnetic and optic properties were evaluated using the following investigations: the analysis of X-ray diffraction (XRD), scanning electron microscopy (SEM), Small Angle Neutron Scattering (SANS), Fourier transform infrared (FTIR), UltraViolet-Visible (UV-Vis), Photoluminescence (PL) and Electron Paramagnetic Resonance (EPR) spectroscopy.

X-ray diffraction patterns confirm the presence of four crystalline phases, namely tetragonal and monoclinic ZrO<sub>2</sub>, MgO and Fe<sub>3</sub>O<sub>4</sub> crystalline phases with cubic structures, respectively. The scanning electron images show irregular shapes and aggregations with the presence of grains having polyhedral shapes with different sizes. The IR data demonstrate that the addition of Fe<sub>2</sub>O<sub>3</sub> improves the tetragonal /cubic ZrO<sub>2</sub> content by decreasing of monoclinic ZrO<sub>2</sub> phase but appear new IR bands corresponding to the stretching vibrations of the Fe–O bonds from [FeO<sub>4</sub>] and [FeO<sub>6</sub>] structural units. UV-Vis and PL data indicate larger concentrations of oxygen vacancies with addition of higher Fe<sub>2</sub>O<sub>3</sub> concentrations. The EPR spectra are due to the presence of Fe<sup>3+</sup> ions and depend on the Fe<sub>2</sub>O<sub>3</sub> content of samples. The increase of the Fe<sub>2</sub>O<sub>3</sub> content leads to the increase of the resonance line centered at g~2.36 and the appearance of a broad line characteristic of clustered ions can be observed. Broadening of the absorption line width centered at about g~2.36 as a function x indicates the presence of Fe<sup>2+</sup> ions (do not give EPR signal) along with Fe<sup>3+</sup> ions in the ceramics.

# Polaronic transport in vanadium phosphate glasses containing transition metal oxides

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Oxide glasses containing transition metal oxides (TMO) such as  $V_2O_5$ ,  $MoO_3$ ,  $WO_3$ , and  $Fe_2O_3$  exhibit electronic conductivity with a small polaron hopping mechanism. The polaronic conductivity in these glasses arises from the transfer of electrons between TM ions in different oxidation states and depends on the amount of TMO, the fraction of reduced TM ions, and the average distance between TM ions. In this study, we investigate the influence of the addition of a second TMO on the polaronic conductivity of vanadium phosphate glasses. For that purpose, three series of ternary  $xTMO-(60-x)V_2O_5-40P_2O_5$  glasses with a wide range of compositions,  $x=10-60$  mol% for  $TMO=WO_3$  and  $MoO_3$  and  $x=10-45$  mol% for  $TMO=Fe_2O_3$ , were prepared by the melt quenching method. The structure and electrical properties of the prepared glasses were studied by Raman and impedance spectroscopy, whereas Differential Thermal Analysis investigated thermal properties. The sum fraction of transition metal ions in a lower oxidation state was determined from the temperature dependence of magnetization measured using SQUID magnetometer. Each glass series shows different electrical behavior upon gradual substitution of  $V_2O_5$  by TMO. While with the addition of  $MoO_3$ , conductivity continuously decreases over three orders of magnitude, it shows a deep minimum at ~53 mol% of  $WO_3$  and ~27 mol% of  $Fe_2O_3$ . The observed decrease in conductivity over the entire range of mixed  $MoO_3-V_2O_5-P_2O_5$  and  $WO_3-V_2O_5-P_2O_5$  compositions is directly related to a decrease in the concentration of vanadium ions which have a determining role in the electrical processes. It seems that molybdenum and tungsten ions do not participate in the polaron transport in these glasses and hence cannot compensate for the decrease in  $V_2O_5$  content. However, the high conductivity of binary  $40WO_3-60P_2O_5$  glass is related to the structural peculiarities of this glass system manifested by the tendency of tungsten units to form clusters within which the transport of polarons is facilitated. On the other hand, a substantial increase in conductivity above 27 mol% of  $Fe_2O_3$  suggests that iron ions actively contribute to the conduction process. Since the binary  $Fe_2O_3-P_2O_5$  glasses exhibit significantly lower polaronic conductivity ( $<10^{-9} (\Omega \text{ cm})^{-1}$ ) than our mixed  $Fe_2O_3-V_2O_5-P_2O_5$  compositions, it can be inferred that a high conductivity of the latter glasses originates from the polaron hopping between various transition metal ions ( $V^{4+}-V^{5+}$ ,  $Fe^{2+}-Fe^{3+}$ ,  $Fe^{2+}-V^{5+}$  and  $V^{4+}-Fe^{3+}$ ).

# Synthesis and characterisation of magnetic iron oxide nanoparticles coated in a silica shell

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Magnetic nanoparticles have been a popular field of study due to their wide variety of applications, including batteries, bio-medicine, and storage media. Among those  $\text{Fe}_3\text{O}_4$  (magnetite) nanoparticles are widely studied, but suffer from being prone to oxidise into  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite). In order to overcome this problem, a core of  $\text{Fe}_3\text{O}_4$  nanoparticles can be coated with a protective layer such as amorphous silica.

In this study, magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesised using the co-precipitation method, due to its high yield and use of inexpensive materials. The particles were then coated with silica using a 'sol-gel' method. Both bare and coated nanoparticles displayed magnetic properties. Characterisation was done using Powder XRD analysis. All samples displayed characteristic  $\text{Fe}_3\text{O}_4$  peaks, with coated samples also showing evidence of the presence of amorphous silica which produces a broad halo in the region of  $20\text{--}30^\circ 2\theta$ . The average size of the  $\text{Fe}_3\text{O}_4$  nanocrystals was calculated with the Scherrer equation, showing nanoparticles to be in the 13–16 nm range, in both bare and coated samples.

The effect of different methods of nanoparticle synthesis (to achieve a product that is monodisperse in size and shape), and different coating methods (to achieve an even coating of individual nanoparticles) will also be discussed. The possibility of dispersing the coated samples into a glass matrix will be explored.

# Effects of thermal history on UK radioactive waste glasses

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Whether for environmental concerns and the reduction of CO<sub>2</sub> or in the pursuit of energy independence, decreasing reliance on, and consumption of, fossil fuels is on the agenda for many, if not all, developed nations. Renewable energies that generate electricity from wind, solar or tidal sources, for example, can all be used to varying degrees in certain areas, but the Titan of low CO<sub>2</sub> energy producers is nuclear fission. The most significant outstanding concern in its use is the long-term solution for the radioactive waste that is produced from spent fuels and their reprocessing. In the UK, the high activity liquor that is produced from the reprocessing of spent fuels is converted at the Sellafield Waste Vitrification Plant (WVP) into borosilicate glasses. The long-term chemical and thermal stability of these waste-loaded glasses are paramount, and as new formulations are developed with suitable waste loading capabilities, these critical properties must be fully understood. In particular for UK glasses, the effects of high temperature, resulting from a combination of cooling from molten within waste canisters, and radiogenic heating by wastes therein, are poorly understood in the context of long-term chemical and thermal stability. In this work, time-temperature-transformation (TTT) curves were produced for UK borosilicate glass systems, MW (Li<sub>2</sub>O–Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>) and CaZn (Li<sub>2</sub>O–Na<sub>2</sub>O–CaO–Al<sub>2</sub>O<sub>3</sub>–ZnO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>). Zero-waste base glasses were studied, in addition to glasses with increasingly complex waste forms representative of UK waste blends. These systems were confirmed chemically by XRF and ICP-MS and structurally by XRD, with thermal and optical property measurements. The chemical durability of these systems will be confirmed using PCT-B testing and vibrational structures explored by Raman spectroscopy. The TTT curves were produced by determining the average  $T_x$  of these systems ( $\approx 650^\circ\text{C}$ ) and conducting isothermal heat treatments for up to 100,000 seconds at  $50^\circ\text{C}$  intervals above and below this average. XRD was used to confirm the presence of crystalline phases for each time-temperature interval. The use of increasingly complex waste forms will allow for effects caused by specific components to be better understood and modelled, particularly with respect to radiation induced defects which are also to be studied within these systems.

# Effect of sulfur on the structure of silicate–phosphate glasses

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Sulfur is a poorly glass-compatible element. Sulfur can be incorporated into silicate and borosilicate glass structures at up to 1 wt% of SO<sub>3</sub> equivalent. More than 1 wt% SO<sub>3</sub> causes the formation of a separate water-soluble (yellow) phase that contains alkali sulfates.<sup>(1)</sup> According to the literature,<sup>(2)</sup> the solubility of sulfur in the structure of phosphate glasses is higher than that in silicate or borosilicate glasses. The volatilization of SO<sub>2</sub> gas due to the synthesis of sulfate glasses is the largest problem.

The aim of this study was to determine the role of sulfur in the structure of silicate–phosphate glasses from the SiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub>–K<sub>2</sub>O–MgO system with varying content of glass formers (SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>) as well as their sulfur free counterparts. All glasses were synthesized by traditional melting raw materials mixture but sulfur containing glasses obtained under reducing conditions. Such glasses could find application as glassy carriers of sulfur for soil environments which is essential element for plants. Thus, we can try to solve the problem of sulfur deficiency in soil.

The amorphous nature of the samples was verified using XRD analysis. The bulk composition of glasses was confirmed with XRF technique. The homogeneity of the glasses was confirmed by SEM EDS measurements. We employed spectroscopic techniques (MIR, Raman and MAS NMR) to investigate the structure of such sulfur-containing glasses. This work also referred to the density and molar volume of the glasses.

The addition of sulfur increased the abilities of glasses with higher amounts of P<sub>2</sub>O<sub>5</sub> to form. The sulfur-doped glasses were characterized by a lower density value than that of their sulfur-free counterparts. The lower density of the sulfur-doped glasses was probably related to the presence of large sulfur-containing anions in their structure. The addition of sulfur showed changes in the silicate–phosphate networks, making them more polymerized, which was probably related to the concentration of potassium ions in the vicinity of the sulfur ions.

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# Ultrafast pulsed lasers – shining light on bone and dental tissue scaffold engineering

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The physics of molecular-scale interaction in rare-earth-ion doped calcium phosphate, calcium-iron-phosphate, and their mixtures with chitosan has been analyzed using the vibrational spectroscopy, X-ray diffraction, X-ray Photoelectron spectroscopy, zeta potential, and scanning electron microscopic techniques. Although the phosphate minerals without chitosan tend to form a mixture of nano-crystalline and amorphous phase, dominated by brushite when pH is less than 7, the nucleation and crystal growth of phosphate phases rapidly diminish in the presence of chitosan (a polysaccharide). We have investigated the semi-crystalline to amorphous phase transition in such phosphate-chitosan mixtures for processing phosphate-mineral base soft and hard scaffolds, which may be used for manufacturing both the materials for restoring the damaged bones<sup>(1)</sup> and tooth surfaces.

<sup>(2)</sup> The effect of resonant absorption of ultra-fast pulsed (100 femtosecond, 100 MHz repetition rate) near-IR laser at 1040 nm into the mineral chitosan phase mixture is also examined for determining the material ablation threshold for designing scaffolds with large surface area for osteogenesis (cell viability and proliferation). In this presentation, applications of laser-machined and laser-surface treated materials in damaged tissue restoration are discussed with selected examples of enamel restoration, infection-induced periodontal damage,<sup>(3)</sup> and healing of critical bone defects.<sup>(4)</sup>

1. Alshubhe, E., Anastasiou, A. D., Mehrabi, M., El Mostafa Raif, Hassanpour, A., Giannoudis, P. & Jha, A. *Mater. Sci. Eng.: C*, 2020, **115**, 111053.
2. A.D.Anastasiou, A. D., Strafford, S., Thomson, C. L., Gardy, J., Edwards, T. J., Malinowski, M., Hussain, S. A., Metzger, N. K., Hassanpour, A., Brown, C. T. A., Brown, A. P., Duggal, M. S. & Jha, A. *Acta Biomater.*, 2018, **71**, 86–95.
3. Anastasiou, A. D., Nerantzaki, M., Gounari, E., Duggal, M. S., Giannoudis, P. V., Jha, A. & Bikiaris, D. *Sci. Rep.*, 2019, **9** (1), 1–11.
4. Anastasiou, A., Edwards, T., Addis, J. G., Thompson, C., Amorese, C., Ireson, R., Strafford, S., Malinowski, M., Routledge, M. N., Brown, A., Hondow, N., Bain, J., Brown, T., Kalmej, Z., Petrucci, M., Grassi, R., Duggal, M. S., Giannoudis, P. V. & Jha, A. 19th International Conference on Transparent Optical Networks (ICTON), 2–6 July 2017, 1–4 .

# The 16<sup>th</sup> International Conference on the Physics of Non-Crystalline Solids, PNCS16

## Oral Sessions

Monday 11 July	Tuesday 12 July		Wednesday 13 July		Thursday 14 July	Friday 15 July
<b>Opening</b>	<b>Glass Formation</b>		<b>Structure - NMR</b>		<b>Heavy Metal Ions</b>	<b>Bioactive Glasses</b>
09:00 Opening (Hannon)	09:00 <u>Alderman</u>	<b>Physical Properties <i>LT1</i></b>	09:00 <u>Zwanziger</u>	<b>Optical Properties1 <i>LT1</i></b>	09:00 <u>Hoppe</u>	09:00 <u>Brauer</u>
09:15 <u>Zhang</u>	09:30 Cormack	Prnová	09:30 Kroeker	Volotinen	09:30 Santic	09:30 Fallah
09:45 <u>de Camargo</u>	09:45 Trachenko	Renka	09:45 Skerratt-Love	Colmenares Calderon	09:45 Calzavara	09:45 Tiskaya
<b>Theory &amp; Simulation1</b>	10:00 Nabahat	Eales	10:00 Ridouard	Heo	10:00 Koudelka	10:00 Hill
10:15 <u>Berthier</u>	<b>Densification &amp; Phase Change1</b>		10:15	Carbonaro	10:15 Marijan	10:15 Coffee
	10:15 Kohara		10:30 Coffee		10:30 Coffee	<b>Applications</b>
10:45 Coffee	10:45 Coffee		<b>Structure - Diffraction1</b>		<b>Structure - Diffraction2</b>	10:45 <u>Seddon</u>
<b>Theory &amp; Simulation2</b>	<b>Dens. &amp; Ph. Change2</b>	<b>Nuclear Waste Storage <i>LT1</i></b>	11:00 <u>Benmore</u>	<b>Optical Properties2 <i>LT1</i></b>	11:00 <u>Bychkov</u>	11:15 Rashwan
11:15 Elliott	11:15 Ollier	Harrison	11:30 Haddad	Galoisy	11:30 Jóvári	11:30 Bouty
11:30 Du	11:30 Martinet	Harnett	<b>Metallic Glasses</b>		11:45 Pethes	11:45 Jose
11:45 Stephens	11:45 Bertholet	Laplace	11:45 Mehrer	Fakhraai/Stephens	12:00 Mohammadi	12:00 Corrias
12:00 Konstantinou	12:00 Cornet	Stone	12:00 Firlus	McGann	<b>Fundamental Studies</b>	
12:15 Weitzel	12:15 Shekhawat	Sánchez	12:15 Duan	Hollis	12:15 Gutwirth	12:15 Bingham
12:30 Longo	12:30 Kotrla	Rigby	12:30		12:30 Holubová	12:30 Closing (Mountjoy)
12:45 Raghvender	12:45 Roggendorf				12:45 Jug	
13:00 Lunch	13:00 Lunch		13:00 Lunch		13:00 Lunch	13:00 Packed Lunch
<b>Angell session1</b>	<b>Greaves session1</b>		<b>14:15 Excursion to Leeds Castle</b>		<b>Chalcogenide Glasses</b>	
14:30 <u>Alba-Simionesco</u>	14:30 <u>Sen</u>		<b>19:00 for 19:30 Conference Banquet</b>		14:30 <u>Barney</u>	
15:00 Lucas	15:00 Weber		<div> <p>The conference Banquet will be held at the Darwin Conference Centre, Darwin College, University of Kent.</p>  </div>		15:00 Bokova	
15:15 Wei	15:15 Sankar				15:15 Chahal	
15:30 Kieffer	15:30 Hannon				15:30 Kassem	
15:45 Coffee	15:45 Coffee				15:45 Coffee	
<b>Angell session2</b>	<b>Greaves session2</b>				<b>Silicate Glasses</b>	
16:15 <u>Yue</u>	16:15 <u>Wilding</u>				16:15 <u>Salmon</u>	
16:45 Wynne	16:45 Moulton				16:45 Henderson	
17:00 Mocanu	17:00 Mountjoy				17:00 Brow	
17:15 Wilke	17:15 Okoczuk				<b>Theory &amp; Simulation4</b>	
<b>Theory &amp; Simulation3</b>	<b>Crystallisation</b>				17:15 Fusco	
17:30 Drabold	17:30 Stanko				17:30 Ghardi	
17:45 ALHasni	17:45				17:45 Kerner	
18:00 End	18:00 End				18:00 End	
	<b>18:30 Poster Session and Buffet <i>Seminar Room1</i></b>					
	20:00 End					

Invited speaker names are underlined.

All talks and posters will be presented in the Sibson Building, University of Kent.

Talks will be presented in the main lecture theatre (LT3), or lecture theatre 1 where indicated: *LT1*

The poster session will take place in Sibson Seminar Room 1.

At 13:15 on Monday, Tuesday, Wednesday and Thursday, a two-course lunch will be provided at Rutherford College, University of Kent