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Lecture 2.
Glass Science
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1. Historical Synopsis

Glass, like all other optically transmitting media, will degrade image performance if not of the highest quality in terms of homogeneity and refractive index. Although there are many references to glass lenses and refraction in ancient history it is a widely held view that **optical glasses** as we know them today began to be developed during the new age of scientific thought and discovery in the seventeenth century. In particular, the crucial *driving* force was the development of the early optical telescopes and microscopes for which there was a dire need for glasses which would enable the correction of known aberrations of optical systems.

One of the most *important* of these was chromatic aberration and correction of this defect became a major concern in scientific circles (NEWTON, CHESTER MOOR HALL, DOLLAND). The development of glass of suitable optical quality was clearly crucial and important work by GUINAND and FRAUNHOFER led to the famous experiments of FARADAY at the Royal Institution in 1827. Faraday's researches went largely unnoticed by the commercial glassmakers, although Chance Brothers did exhibit a high quality *flint* glass disc at the Great Exhibition in 1851, but fortunately it *did* come to the attention of the Rev. VERNON HARCOURT, a gifted amateur scientist and a founder member of the British Association. *Starting* in 1834 he carried out systematic experiments in glass *chemistry* and added many new elements to the list which had previously been used in glassmaking. It is clear that Harcourt was aware of the close relationship between chemical composition and optical properties but was unable to achieve the necessary homogeneity and chemical durability required for commercial production.

The next major development in the understanding of optical glasses occurred in Germany. Carl Zeiss had established himself (1846) as a maker of scientific instruments in the Thuringian town of Jena but soon became dissatisfied with the quality of his instruments and began to collaborate with a young physicist, Ernst Abbe, who was carrying out a programme of research at Jena University on improvements to existing microscopes. Abbe proceeded to formulate a completely new theory of image formation in microscopes but realised from the outset of his work that the available crown and flint glasses could not fulfil the demanding conditions of the new theory and tried to persuade the glass houses to experiment with new types of glasses. Indeed Abbe expressed his *feelings* much later when he wrote: 'For many years I attempted to combine practical optics-with a form of optics in which as yet undiscovered glasses would allow me to discuss future progress in this field. Such progress would require the glassmakers to adapt their methods to the stringent demands of instrumental optics.'

Fortunately for the development of the optical glass industry an exhibition of scientific instruments held in London in 1876 gave Abbe the opportunity to write a review of the Glass Science position of microscope optics at that time in which he pointed out with some regret that an almost perfect microscope could be constructed if the right glasses were available. This review came to the attention of Dr .Otto Schott who, as the son of a plate glass manufacturer, had become interested in the chemistry of glassmaking. Having made a new kind of lithium glass he sent it to Abbe for evaluation in 1879 but this composition did not possess the refractive index and dispersion required. However this early 'failure' was soon followed by a more successful development of borate and phosphate glasses and in 1881 Schott and Abbe began a brilliant collaboration in which Schott prepared a wide range of different compositions and Abbe undertook a critical optical evaluation. An immediate result of this partnership of science and technology was the publication of a catalogue of 44 optical glasses among which were 19 entirely new compositions. The manufacture of optical glass then became a virtual German monopoly until the Great War of 1914-1918.

As a result of this situation there was almost no optical glass industry in the United States and only Chance Brothers in the U.K. made commercial optical glass. Indeed most of the optical glass used in both countries was imported from Germany. The war therefore forced the U.S. Government to appeal for assistance in the manufacture of optical glass. Personnel from the Geophysical Laboratory of the Camegie Institution in Washington were seconded to the Bausch and Lomb Optical Co. of Rochester, New York, which had become interested in optical glasses in 1912. The immediate problem was obviously to reproduce glasses of a standard type which had been produced in Europe viz. ordinary crown, borosilicate crown, light and dense barium crown, light and dense flint. This enormous cooperative effort, including other interested groups, meant that Bausch and Lomb were on a production basis by the end of 1917.

Just as the work of Abbe and Schott marked a turning point in the development of optical glasses so too was the pioneer research of G.W.Morey in the late 1930's. By introducing rare earth oxides and other expensive oxides into optical glassmaking he was able to extend the glassmakers' map into hitherto uncharted areas and enabled modern optical instrument design to become established.

New optical glasses continue to be in demand and a greater understanding of the chemistry of melting makes it possible for designers of optical systems to make demands on the glassmakers which would have seemed unreasonable only a few years ago.

2.Thermodynamics and Structure

Just as the eighteenth and nineteenth centuries had been important in establishing the obvious link between glass chemistry, homogeneity, and the performance limits of optical instruments, so the twentieth century has seen glass as a material come of age in both a technological and scientific sense. It would be impractical here to select all the major factors contributing to this situation but at least in the early years of the century two important developments are now recognised:

1. a renewed interest in glasses as a result of an apparent contradiction of the Third Law of Thermodynamics,
2. the pioneering work of ZACHARIASEN (1932) on glass structure.

Let us briefly consider these two factors in turn.

As cryogenic techniques developed it became important to establish that materials would behave thermodynamically as predicted. One of the easiest (but not easy!) thermodynamic parameters to consider was that of enthalpy H or its derivative, specific heat C, and many measurements were made on organic substances such as ethyl alcohol and glycerol. It was well-known that these substances did not recrystallise on cooling from the melt and readily formed 'glasses' in the popular sense. However, there was much consternation when calculations showed that the entropy S of the crystalline state at absolute zero of temperature appeared to be less than that of the 'glassy state' at the same temperature, in clear violation of the Nernst Heat Theorem or the Third Law of Thermodynamics. The entropy difference between supercooled liquid and the corresponding crystalline phase at any (absolute) temperature T is given by:

$$\Delta S = \frac{[\Delta H(fusion)]}{T_{MP}} - \int_{T}^{MP} [C_p(glass) - C_p(crystal)] dT/T$$

where ΔH(fusion) is the heat of fusion (J/mole), T_{MP} is the melting point of the crystal, and C_p is the heat capacity at constant pressure. ΔS should vanish as T approaches O°K but in fact remains finite at the lowest temperatures reached. In 1920 LEWIS and GIBSON suggested that the entropy difference was due to entropy of mixing but we now know that the difference is due to configurational changes. The importance of this early work was largely overlooked in the field of glass science until taken up later by DAVIES and JONES (1953). It is now agreed that the anomaly is a result of the experimental method and that since the glassy state is a non-equilibrium one it is not expected that equilibrium laws should apply. Nevertheless this work on the thermodynamic aspects of the glass transformation was vital in establishing glasses as materials worthy of serious scientific study.

The second factor mentioned above has probably led to more debate than any other topic in glass science. What precisely is the structure of glass and indeed what precisely is a glass? Perhaps it is worth quoting the first paragraph of Zachariasen's classic paper written in 1932: 'It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses. Glasses are described as supercooled liquids or as solids. The former term is justifiable from the point of view of physical chemistry, the latter from the theory of elasticity. It seems rather futile, however, to try to decide which of the two descriptions is the proper one to use when we are ignorant about the characteristic properties of the atomic arrangement.'

How much less ignorant are we now? It is interesting to note that Zachariasen never mentions the terms network-former, network-modifier or intermediate oxide although he does express his ideas in terms of an extended three-dimensional network of oxygen polyhedra. As for his so-called 'rules' viz.

(1) an oxygen atom is linked to not more than two atoms A

(2) the number of oxygen atoms surrounding A must be small

(3) the oxygen polyhedra share corners with each other, not edges or faces,

it is again helpful to recall the author's own words:

'It must be remembered that the conditions which we have given for glass formation are not the only ones.

Whether a substance will form a glass or not will depend also on the conditions under which the melt is cooled down. We have stated therefore that certain substances may form glass, namely, when the melt is cooled under conditions favourable for glass formation.'

It has not been helpful when subsequent authors have either cited Zachariasen out of context or have implied that the 'rules' of glass formation have been broken.

3. Definition of the Glassy State

On examining the literature on glasses it is evident that many authors have been challenged to find a unique definition of the 'glassy' state. Definitions have ranged from the concept of glass as a fourth state of matter to descriptions which are almost too abstract to be meaningful. It is probably simplest to start with a more or less 'conventional' definition and to indicate situations and materials where the experimental evidence is much less unequivocal.

A **glass**, or a substance in the glassy or vitreous state, is a material formed by cooling from the normal liquid state, which has shown no discontinuous change (such as crystallization or separation into more than one phase) at any temperature, but has become more or less rigid through a progressive increase in its viscosity.

It is convenient to regard a certain value of the viscosity as defining a natural boundary to the glassy state, and any material formed similarly whose viscosity has not reached this limiting value is simply called a liquid or supercooled liquid. In familiar usage glasses are mixtures of inorganic oxides and / or fluorides but many polymers and amorphous forms of elements such as sulphur and selenium are covered by the preceding definition. As a material, glass behaves like a typical solid in certain respects (mechanical properties) but has a non-crystalline (liquid like) atomic structure.

We could define a glass in a more graphic way using the language of MALONEY. A glass is a rigid liquid. Is this a contradiction in terms? Not really since all liquids (except superfluids) have measurable viscosity, or resistance to flow, and if we apply a stress fast enough the liquid can behave as an elastic solid. The system has no time to flow in order to relieve the stress. Common glass at room temperature cannot really be given any meaningful viscosity, and yet when examined by diffraction techniques it has all the structural properties of a liquid.

Glasses do not have freezing points like 0°C for water or 850°C for sodium chloride. However, the liquid from which the glass is formed may freeze, a process we call devitrification. This could happen at temperatures just below the **liquidus temperature**, the temperature above which no crystals may form. At room temperature devitrification is impossible because the liquid is too cold to freeze.

Undercooling or supercooling of liquids is not uncommon but clearly the liquids are metastable and this metastability is related to viscosity. Thus even if a small unstable crystal is formed its growth may be slow if the viscosity is high. The formation of nuclei is also dependent on the viscosity. In the case of NaCI at the freezing point both the rate of nucleation and the rate of crystal growth are very fast relative to the rate of cooling and so the liquid crystallizes. In glasses on the other hand the viscosity becomes so great that even when the thermodynamic probability for nucleation and growth is high the material refuses to freeze.

As mentioned above these comments on glass formation apply widely but current research reveals other definitions viz.

a) A glass is a random arrangement of 'local structural units' such as SiO_4 tetrahedra,

b) A glass is a collection of very small (1.5-2.0nm) crystals of a compositionally equivalent phase which is randomly packed with an undefined interface. This definition is often known as the microcrystallite hypothesis.

c) Glasses contain clusters of atoms with defect regions between them, but having non-crystallographic order.

There are protagonists for each of these views and selective evidence can be produced to support them. For example, the microcrystalline model may be a good description of some elemental semiconductors and model a) has been used for amorphous alloys. For amorphous metals there appears to be no consensus view as yet but random network models are still believed to be at least a good approximation to conventional glass forming systems.

4. Comments on Criteria for Glass Formation

Many authors have discoursed on the necessary and .sufficient conditions for glass formation taking into account many aspects such as thermodynamic conditions, kinetic factors and the topology of atomic arrangements. All agree, however, that there should be no crystallisation on cooling from the liquid. Above the melting point or liquidus temperature the liquid is by definition thermodynamically stable but below the transformation temperature the amorphous state is thermodynamically unstable (although kinetically stable). It also seems to be obvious that in order to allow the necessary extraction of energy from the liquid to prevent crystallisation we must reach a critical quench rate Rc. For silica this is about 10^{-3} Ks^{-1} but for many materials Rc > 10^{12} Ks^{-1}. Crystallisation depends on both the rate of nucleation RN and the rate of crystal growth RCG For low viscosity melts RN is very high and this is the determining factor near the freezing point. On the other hand although in glass forming liquids both RN and RCG may become significant near $0.8T_m$ high viscosities at this temperature will inhibit both nucleation and crystal growth to such an extent that a glass is formed. Another parameter which is sometimes considered is the ratio of T_G $/T_m$ and it is found that when it exceeds 0.6 glasses may be formed by quenching from the melt, with glass formation particularly easy at a value of *2/3.* Below 0.55 very high Rc's are essential. In another sense we could define a glass as a disordered arrangement of atoms in which the local network leads to a high viscosity and a large temperature coefficient of viscosity ($d\eta/dT$) at critical temperatures such that nucleation, and hence crystal growth, is suppressed.

Finally we come to ask the almost metaphysical questions: 'Is randomness a well-defined concept? Can we have constrained randomness in which there might be an element of preference such as chemical ordering or correlated domains? Would it not be easier to suggest that disorder is not mere chaos but implies defective order? It therefore does not seem reasonable to expect **unique definitions** of structure and/or glassy state since so many factors are involved in the formation of the material we commonly call glass. There may be topological constraints imposed as the 'structure' is built up as well as kinetic constraints on the rate of nucleation and crystal growth. With the added confusion of randomness it would appear that there is no wider consensus on the definition of a glass than there was 60 years ago.

5. Structural Aspects

The structure of silica consists of SiO_4 tetrahedra linked at the corners. The resulting bond angle Si-O-Si can take a range of values near 150° without causing a large increase in strain energy and the tetrahedral units can also twist relative to each other. This flexibility gives rise to an essentially random network structure as recognized by ZACHARIASEN. There is a very high energetic barrier to structural re-arrangement and hence a low probability of crystallisation. The tetrahedral units link together to make 5,6,7-membered rings and the packing density is low. The most important result of these structural considerations is that fused silica has an extremely low coefficient of thermal expansion and low density and hence the material has many important applications.

The structure of silicate glasses is also based on linked silica tetrahedral units. The modifying alkali ions are inserted into the interstices already available while the extra oxygens in effect break down the network since there are too many for them all to be shared between two tetrahedra. The presence of **non-bridging oxygens** has many consequences, not least in significantly affecting thermal expansion, density, refractive index and UV transmission. The number of non-bridging oxygens can be reduced by selective substitution of Si by Al and other changes in physical properties may depend on the precise $Na_2O:Al_2O_3$ ratio. The coordination around alkali ions is much less well-defined than in the case of a network forming ion such as silicon (coordination number 4) and indeed different configurations may be possible at room temperature. The existence of these different coordinations may be inferred from experiments on internal friction and the thermometer effect.

Structural studies show that the boric oxide structure consists of linked BO_3 triangular units. The addition of alkali does not break up the network in the same way as for silica. Instead, triangular units are converted to BO_4 units, a process which continues up to about 35 mole% added alkali. Above this concentration there is a rapid breakdown to all triangular units and the formation of non-bridging oxygens. No simple relationship exists between structural trends and properties hence the debate in the literature on the so-called **boric oxide anomaly** but the underlying complexity of behaviour is clearly related to coordination changes.

In phosphate glasses each phosphorus atom is surrounded by four oxygens as in silicates but one is non-bridging because of the stoichiometry. The introduction of alkaline earths and alkalis tends to encourage crosslinking and so stiffen the network. Oxides such as Al_2O_3 which can also adopt tetrahedral coordination but are deficient in oxygen allow fully connected structures to develop and give very stable P_2O_5 -rich ultraphosphates. At higher concentrations of added alkalis phosphate glasses have structures based on rings and chains although the average chain length (or degree of crosslinking) depends on the alkali to P_2O_5 ratio.

These glasses are termed metaphosphates or polyphosphates. The structures of more recently developed glass systems including chalcogenides, halides and amorphous metals are in general more complex than the oxides and will not be dealt with here.

6. Commercial Glass Systems

6.1 Vitreous Silica

Vitreous silica SiO_2 is the only single oxide glass which finds commercial application. Silicon dioxide has a melting point of 1730°C but temperatures in excess of 2000°C are needed to render the melt workable and even higher temperatures are required to give glass of optical quality.

Since it has a very high degree of chemical stability vitreous *silica is* virtually insoluble in water and in all mineral acids except hydrofluoric, but is slowly dissolved by alkali hydroxides. With a high softening point and low expansion coefficient it is an ideal material for crucibles and high temperature chemical apparatus. There are also many applications in optical technology on account of an unusually wide range of spectral transmission.

The open structure of silica, with oxygen atoms occupying less than 50% of available space, means that the packing density is low and small gas molecules like He and H_2 can permeate through the structure with finite diffusion rates. This property has been a disadvantage in telecommunication fibres used in marine environments because H_2 has diffused into the core and increased the optical loss For a similar reason fused silica tubes would be unsuitable in ultra high vacuum systems.

Although infrared transmission is not exceptional ultrapure silica fibres are now well established in telephone networks with low signal loss over commercially viable distances. These high transmission glasses are generally prepared by several techniques essentially based on chemical vapour deposition and control of refractive index is achieved by using dopants such as B_2O_3, P_2O_5, GeO_2 and F.

There are many technically interesting ways of making vitreous silica from the melt or vapour phase and commercial production forms a very specialized sector of the glass industry. An acceptable grade of silica may be produced by the Vycor process in which a borosilicate glass of special composition is heat treated at 600°C to induce separation into an alkali borate phase and silica.

The borate phase is easily leached out and the remaining porous silica rich phase can be densified by sintering at temperatures only a little above Tg. Sol-gel processing is also possible and if TiO_2 is incorporated into the structure the resulting glass may have a practically zero thermal expansion coefficient near room temperature. If drawn into fibre the density of fused silica may be 2% less than bulk material but extremely high pressures can 'densify' the structure by a similar amount.

Some typical values of physical properties are:

Tg =1100°C; thermal expansion coefficient=$0.5*10^{-7}$; liquidus temperature=1723°C; Young's modulus=700GPa; Vickers microhardness=71 *O* kg/mm^2

6.2 Two-component Glasses

In general two-component silicate glasses are of little interest commercially but it is perhaps worth mentioning why this is so.

The most common two-component systems are the alkali silicates of generic type R_2O-SiO_2 where R may be Li, Na, K, Rb, and Cs. The glass forming region is large, extending in the case of sodium glasses to the metasilicate composition $Na_2O.SiO_2$.

At higher concentrations of alkali the melt viscosity at the liquidus is low and crystal growth is rapid. The addition of basic sodium oxide to the acidic silica gives a dramatic decrease in the liquidus temperature and an examination of the phase diagram of the Na_2O-SiO_2 system reveals two deep eutectics at about 74% and 61% silica by weight. At the former eutectic the liquidus temperature has fallen from over 1700°C for all silica to less than 800°C. Stable glasses could be produced over the range 60-80%SiO_2 without exceeding a melting temperature of 1500°C but such sodium silicate glasses are so poor in chemical durability that their commercial exploitation is impossible. The only commercial application of note is in the detergent industry which uses liquids based on the H_2O-Na_2O-SiO_2 system.

Not all oxides are completely miscible with silica and many two-component systems either separate into two immiscible liquids on cooling or have such high liquidus temperatures that the melt viscosity is too low to inhibit devitrification. Thus CaO-SiO_2 is not a glass forming system under usual conditions and has quite a large two-liquid region. The systems R_2O-SiO_2, PbO-SiO_2 and BaO-SiO_2 do not have two-liquid regions but may show sub-liquidus phase separation. Perhaps only glasses in the PbO-SiO_2 system are of commercial significance.

6.3 Silicates

It is extremely fortunate for the glass industry that the addition of calcium oxide to the soda-silica system not only increases the chemical durability of the glass to the extent that commercial glasses are possible but that the phase diagram retains a deep eutectic, allowing acceptable temperatures for industrial production. Most bulk commercial glasses are based on the soda-lime-silica system within a relatively narrow range of compositions near the primary eutectic. The range of optimum compositions is therefore small but most manufacturers have to add minor constituents (Al_2O_3, K_2O, MgO) in order to meet a required product specification.

When considering the behaviour of other component oxides on commercial silicates itis important to remember that the result may depend on the other oxides already present. Further, a given percentage change in the weight of a light oxide may give a large effect relative to the same percentage for a much heavier oxide.

CaO is an alkaline earth oxide and oxides of the same chemical character (MgO, BaO, SrO) may be added to soda-lime-silica glasses to give particular changes on physical properties. The data on such glasses is now extensive and well documented.

Zinc oxide has some affinity with the alkaline earths and is almost the classic intermediate element. having both network former and network modifier character. Added to *silicate* glasses *it gives* only a small *increase in expansion coefficient* but a relatively large increase in density, and hence refractive index. ZnO also enhances chemical durability and thus is especially valuable in the optical glass *industry.*

Oxides such as PbO, B_2O_3 and Al_2O_3 when added in significant amounts to traditional silicate melts effectively alter the composition (and properties) so much that they form well-defined glass systems which are best dealt with under other headings.

6.4 Borates

Borate glasses are formed at much lower temperatures than silicates and B_2O_3 is an important constituent of glazes, together perhaps with other oxides like lead oxide. Very durable and high electrical resistance glasses are possible in the $CaO-B_2O_3-Al_2O_3$ system (CABAL glasses) and barium aluminoborate glasses are resistant to alkali vapour attack. They can therefore be used to coat the inside of high pressure sodium discharge lamps. Boric oxide is a useful component in many glasses since it reduces melt viscosities and liquidus temperatures but does not impair chemical durability if present in modest amounts.

6.5 Borosilicates

This family of glasses is generally based on the composition field $Na_2O-B_2O_3-Al_2O_3-SiO_2$ and are characterized by a high content of network forming oxides. Indeed, since tetrahedra based on boron, aluminium and silica are all compatible it is possible to have alkali borosilicate glasses which contain alkali cations but no non-bridging oxygens. They are therefore of high chemical durability and low expansion coefficient due to the high proportion of Si-O and B-O bonds. The best known commercial borosilicate is the Pyrex type with an expansion coefficient of say $3.3*10^{-6}$ per °C (one third that of container glass) and yet melting temperatures are only about 1000°C higher than for soda-lime-silica. Borosilicates are widely used as laboratory ware and cooking ware, and as a cheaper alternative to silica in chemical pipelines. They can also be made into fire resistant windows. It is interesting that the intermediate products formed in the Vycor process have very precisely defined, small pores and have uses in filtration and catalysis.

6.6 Aluminosilicates

Aluminium oxide is not a glass former but may form tetrahedral AlO_4 groups and reduce the number of non-bridging oxygens. Therefore alumina is often added to silicate glasses in small amounts in order to improve chemical resistance. However, alumina is highly refractory and too much will increase both viscosity and liquidus temperature. Alkaline earth aluminosilicates based on $RO-Al_2O_3-SiO_2$ are used as special glasses for glass fibres, halogen lamp bulbs and electronic substrates. Boron may be added to reduce processing temperatures but care must be taken not to affect the chemical durability. In alkali alumino-silicates where the ratio Na_2O:Al_2O_3 is unity there are no non-bridging oxygens and cationic mobilities of the alkalis are high. This property is useful in ion exchange strengthening in which potassium ions from a molten potassium salt easily replace the smaller sodium ions near the surface of the glass. Excellent ion exchanged layers up to 100 µm in depth may be obtained after only a few hours and high surface stresses are possible with difficult shapes.

Aluminosilicates with high levels of Al_2O_3 are also used in making glass ceramics. For example, glasses in the Li_2O-Al_2O_3-SiO_2 system have been used for mundane applications in cooking ware and glass hobs, as well as exotic applications such as telescope mirror substrates and laser gyroscopes. Other aluminosilicate glass ceramics may allow photomachining techniques to be applied or have high electrical resistance.

6.7 Phosphates

Phosphorus pentoxide is an excellent glass former and an extensive range of phosphate based glasses exists. Alkali phosphate glasses are soluble in aqueous media and therefore have low chemical durability. However, this property actually makes them very useful as slow release agents in agriculture to provide trace elements to livestock where grazing conditions are poor. Alkaline earth phosphates are more stable and certain compositions are important in spectroscopy as infrared filters. *Aluminium* orthophosphate *is* iso-structural *with silica* but the range of aluminophosphate glasses is not as extensive as in the aluminosilicate system. Phosphorus is not easily incorporated into silicate glasses and mixed phosphate-silicate glasses often phase separate.

Phosphate glasses have much higher expansion coefficients than silicates and generally durability is low. However, there are glasses within the field ZnO-La_2O_3-Al_2O_3-P_2O_5 where the durability can match that of most commercial soda-lime-silica glasses.

Phosphorus pentoxide, when mixed with high concentrations of fluorides, is useful in producing glasses with favorable optical properties such as excellent transparency in the UV and phosphate based glasses also make good laser materials when doped with suitable active ions. As might be expected, glass ceramics which incorporate phosphorus are of considerable interest as bioactive materials for artificial bones.

6.8 Lead silicates

Of the heavy elements lead is undoubtedly the most important of those used in glass technology. Indeed high lead glasses, with potash as the alkali, were at one time serious competitors to soda-lime-silica glasses. In its divalent form lead is a modifier and is easily polarized giving silicates great structural stability over a wide range of compositions. With a good effect on both the liquidus temperature and the viscosity curve lead makes processing of ware by hand relatively easy. The glasses are soft, easily cut and polished, and the inherent high refractive index gives cut glass tableware the aesthetic accolade it so richly deserves. It is rather sad that international legislation may succeed in damaging this important sector of the glass industry more effectively than any commercial competitiveness.

As a result of their desirable refractive index and dispersion characteristics lead glasses have been extremely important in the development of current optical glasses and in initiating research into new glass forming systems. There are still many sophisticated applications for lead based glasses including radiation shielding windows for nuclear radiation and X-rays, electronic tubes, lamp assemblies and cathode ray tubes.

7. Other Elements used in Glass Manufacture

Like lead, heavy elements such as thallium and bismuth are often polyvalent but in their lower valency states form ionic bonds and the cations take the role of modifiers.

Lanthanum in its trivalent state also appears to behave as a modifier.

The group four element germanium is a glass former and germanium dioxide can be cooled from the melt to give stable glasses. However it is too expensive for commercial production in high volumes. Another group four element, titanium, is not a glass former in its own right but acts as a network former in silicate glasses and hence improves chemical durability. More importantly, titanium dioxide gives a high refractive index without a corresponding high density and is used in the opthalmic industry where weight saving is paramount.

Zirconium oxide can also enter the silica network but is generally only used in small proportions to avoid a consequent increase in liquidus temperature, particularly in the presence of alumina. Like titania, zirconia has some useful optical properties including relatively low dispersions combined with modestly high refractive indices. Of much more significant commercial importance is the outstanding chemical resistance of alkali zirconia silicate glasses to alkaline solutions. In this context alkali resistant glass fibre (CemFIL) contains up to 9.0 mole% ZrO_2.

Tin is also a group 4 metal and exists in glass in both divalent and tetravalent form. At high temperatures the former is the most stable but on cooling Sn^{2+} is oxidized to Sn^{4+}. Hence metallic tin is a powerful reducing agent in glass melts. Tin oxide has a beneficial effect on chemical durability.

Many other elements are important in glass technology and we just note a few of them here:

1) arsenic and antimony, although glass formers if cooled rapidly, act as refining agents with a strong tendency to dissolve oxygen bubbles, 2) sulphur, in the form of its oxides, as a melt refining agent, 3) selenium as a decoloriser, 4) transition metal oxides as primary colorants, 5) rare earth lanthanides as colorants.

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