

The Role of Tin in Glass System

Fungsi Timah dalam Sistem Kaca

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Abstract

Tin constitutes a minor component in commercially produced flat and container glasses. Divalent, tetravalent and tin metal diffused into the surface of the glass during production and strengthened the chemical and physical properties of these glasses. Tetravalent tin has a low solubility in any glass system but divalent tin can formed glasses with a high Sn^{2+} content in borate, germanate, phosphate, and silicate glass systems. This paper surveyed past studies of the roles of tin in glass systems that contained tin. The different structural roles of Sn^{2+} and Sn^{4+} in various glass systems surveyed are discussed in term of the structural difference between divalent and tetravalent of tin compounds in the glass systems, which were reflected in the results of spectroscopic and physical properties studies of the glasses. Divalent tin has been shown to fulfill various structural roles as either modifier or intermediate, depending on the type of glass system and composition.

Keyword Glass system, glass structure, glass formation, modifier, intermediate, tin, stannous silicates, stannous borates, stannous germanates, stannous fluorophosphate

Abstrak

Timah adalah komponen minor dalam kaca keping dan kaca bekas komersil. Timah dwivalen, timah tetravalen dan timah logam membaaur ke dalam permukaan kaca semasa proses pengilangannya dan memperkuat sifat kimia dan fizikal kaca tersebut. Timah tetravalen mempunyai keterlarutan yang rendah dalam semua sistem kaca, tetapi timah dwivalen boleh membentuk kaca dengan kandungan Sn^{2+} yang tinggi dalam sistem kaca borat, germanat, fosfat, dan silikat. Kertas ini meninjau kajian-kajian lepas tentang fungsi timah dalam sistem kaca mengandungi timah. Fungsi yang berbeza yang dimainkan oleh Sn^{2+} dan Sn^{4+} dalam beberapa sistem kaca yang ditinjau, dibincangkan dari segi perbezaan struktur diantara sebatian timah dwivalen dan tetravalen dalam sistem kaca dan dikaitkan dengan keputusan kajian spektroskopi dan sifat kaca yang dikaji. Hasil kajian menunjukkan bahawa timah dwivalen berfungsi sama ada sebagai bahan pengubahsuai kaca atau bahan pertengahan kaca, bergantung kepada sistem dan komposisi kaca.

Kata Kunci sistem kaca, struktur kaca, pembentukan kaca, pengubahsuai, pertengahan, timah, stanus silikat, stanus borat, stanus germanat, stanus florofosfat

Introduction

Tin is not a common constituent of glasses. As tin oxide, it is used extensively in very small quantities in making gold, copper and selenium ruby glasses (Dodd, 1964). Tin oxides have also been known to be used as opacifiers and glazes for glasses (Rooksby, 1964). Tin is 'metallophilic'; a term suggested by Weyl (1967) for elements that aid in the introduction of metal bonds into distinctly ionic bonds in glass. Because of this, tin oxide (SnO) is used to increase the adhesion of metal films to glass surfaces e.g. in making silvered mirrors and gilding of glass. In hot end surface coating process to increase the strength of glass containers, a tin compound is applied by chemical vapour deposition or spraying on the glass surface. The diffusion of tin ions into the surface of the containers decreases the size of the damaging Griffith flaws (Sanyal & Mukerji, 1982) and hence strengthens the glass.

Perhaps the most important use of tin in the glass industry is in the production of flat and parallel sheet glass by the float process, invented in 1959 by Pilkington Brothers Limited (Persson, 1969). This glass is commercially known as float glass and is a silicate based glass of basic composition of $\text{Na}_2\text{O} + \text{CaO} + \text{SiO}_2$, referred to as soda-lime-silica glass. In the float glass process, the molten glass is floated on top of a bath of molten tin kept at 1050 °C. The bottom glass surface is supported only by molten tin, whereas the top surface is exposed to the slightly reducing atmosphere of a mixture of hydrogen and nitrogen called forming gas. Gravity allows the glass to flow out, while its surface tension holds it back to an equilibrium thickness of ~7.1 mm. Sheet glass of thicknesses from 1.5 to 2.5 mm can be made by either stretching or compressing the glass ribbon. While in the float bath, heat is applied to both surfaces of the ribbon and this 'fire polishing' gives perfectly flat and parallel surfaces. The glass enters the bath at ~ 1150 °C and with a viscosity 10^3 Pa s and leaves it at ~650 °C. In this condition, tin from the float bath diffuses into the float contact surface and to a lesser extent into the non-contact surface by chemical adsorption of tin vapour. It is found that the tin contact surface has a high concentration of tin in different oxidation states to a depth of 5 – 30 μm (Pilkington, 1969; Colombin, *et al.*, 1977; Sieger, 1975; Jie & Choa, 1990; Chappell & Stoddart, 1974). Therefore the float contact surface has chemical characteristics different in some respects from those of the bulk glass. Although this compositional modification does not extend far into the surface, it does cause the physical and chemical behaviour to differ from that of the bulk glass and the upper surface. For general uses, such as window glass, this is not critical. However for specialized uses such as very thin glass discs used as substrates for optical and magnetic recording, this will affect the planarity of the disc. In addition, the stoichiometry of the tin oxide at the surface affects the tendency of the surface quality to deteriorate (blooming) when the glass is reheated for tempering to produce curved articles like car windscreens (Pilkington, 1969).

From what has been discussed above, tin constitutes only a minor component in commercially produced glasses but its role is an important one because it can improve the glasses' mechanical, optical, thermal and chemical properties. However its effect on glass properties is not well understood. Past studies have shown that the solubility of SnO_2 in silicate and borate glasses is very low (Min'ko *et al.*, 1973); but the divalent state (Sn^{2+}) of tin in the form of SnO can form stannous silicates (Carbo Nover & Williamson, 1967; Ishikawa & Akagi, 1978), stannous borates (Paul *et al.*, 1977) and stannous germanates

(Silver *et al.*, 1977) glasses with high SnO content. Also, the divalent state (Sn^{2+}) of tin the form of SnF_2 can form stannous fluorophosphate glass with glass formation extending from 0 to 80 mol% SnF_2 (Shaw & Shelby, 1988).

Therefore, apart from commercially produced glasses which contain tin in minor composition; we also see that glass can form with a high Sn^{2+} content in borate, germanate, phosphate, and silicate glass systems. This paper presents a review of some of the work that has been done to study the role of tin in various glass systems mentioned above.

Borate Glass

Binary SnO-B₂O₃ glass

Paul *et al.* (1977) studied binary SnO-B₂O₃ glasses with SnO contents ranging from 12 to 58% by infrared and ¹¹⁹Sn Mössbauer spectroscopies. Glasses were prepared by melting tin(II) oxalate with boric oxide in silica crucibles at melting temperatures between 900° C and 1000°C. The disproportionation of SnO to SnO₂ and Sn metal was minimised by controlling the oxygen partial pressure of the furnace between 10⁻¹⁰ and 10⁻¹⁸ atm. The solubility of SnO₂ in borate is very low. A maximum of 0.2 wt.% (0.1 mol%) SnO₂ dissolved in some of the glasses and such a small SnO₂ contamination was neglected. The changes in infrared results showed that, like alkali borate glasses, a small amount of SnO (less than 20 mol%) produces tetrahedral boron while large amounts result in non-bridging oxygen in addition to tetrahedral boron. The ¹¹⁹Sn Mössbauer spectra, taken at 80 K, showed that the chemical isomer shifts and the quadrupole splittings for Sn^{2+} in all glass samples were larger than in tetragonal SnO. The isomer shift increases with SnO content up to about 20 mol% and thereafter decreases smoothly with increasing SnO, while quadrupole splitting does not change much with SnO content. From this study they concluded that, for SnO contents up to 20 mol%, the Sn—O bonding is mostly ionic and, at higher SnO contents, the non-bridging oxygens are coordinated to Sn^{2+} ions. In other words SnO is acting as modifier at low concentration of SnO and from SnO contents of more than 20 mol%, it starts to make cross-linkages with the glass network.

Alkali Tin Borate glass

Eissa *et al.* (1974) studied borate glass containing SnO₂ in minor amounts by the Mössbauer effect. The general composition formula of the glasses is (100-X) mol% B₂O₃ + X mol% Me₂O + Y mol% SnO₂, where Me = Li, Na or K, X = 10, 20 or 30 and Y is the quantity of SnO₂ introduced. Under an oxidizing atmosphere, the amounts of SnO₂ dissolved in the glasses containing 10, 20 or 30 mol% alkali oxide were not more than 2, 4 or 5 mol% respectively, while the composition with 30 mol% Li₂O did not form glass under any condition. The room temperature isomer shifts of ¹¹⁹Sn Mössbauer spectra of the glasses were considerably different from that of the crystalline SnO₂. This shows that tin in small amounts can effect the glass structure and the γ resonance of ¹¹⁹Sn was sensitive to structural changes of the glass. This conclusion is in agreement with an earlier study of Mitrofanov & Sidorov (1967) who investigated the same series of glasses. Both studies found that the difference in the values of the isomer shift between the SnO₂ in glasses and crystalline

SnO_2 indicates that the ionic nature of the Sn—O bond is stronger in the glasses than in SnO_2 crystal. The increase of the absolute value of the isomer shift with the increase of the alkali content was interpreted as being due to the increase of ionicity of the Sn—O bond in glass. The absolute value of isomer shift decreases on going along the Li-Na-K series, which indicates that the ionicity of the Sn—O bond decreases with increasing ionic radius of the alkali ion. The quadrupole splitting and line width decrease with the increase of alkali content and on going along the Li-Na-K series but the line width in glasses is only slightly greater than the line width in crystalline SnO_2 . The general conclusion of both studies is that tin in the glass is in the quadrivalent state having a structure in which oxygen forms a highly distorted octahedron around the tin atom.

Germanate Glass

Binary SnO-GeO₂ glass

The binary SnO-GeO₂ glasses were studied by Silver *et al.* (1977), motivated by the fact that the binary PbO-GeO₂ were reported by Phillip & Scorger (1965), Topping *et al.*, (1974) and Topping & Murthy (1974) to have two interesting features. Namely; that the $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ glass ceramic is an important ferroelectric material and PbO-GeO₂ glasses have extremely high refractive indices. They studied three glass compositions: (i) Opaque yellow glass of composition $\text{Sn}_5\text{Ge}_3\text{O}_{11}$ melted in open carbon crucibles under oxidising conditions at 800° C, resulted in some metallic Sn and SnO_2 from the disproportionation of SnO in the glass and on its surface respectively. (ii & iii) Glasses of composition SnGeO_3 and $\text{Sn}_6\text{Ge}_3\text{O}_{20}$ melted between 700 and 800° C in vacuum out-gassed sealed silica ampoules, giving yellow-green SnGeO_3 glass and orange-yellow $\text{Sn}_6\text{Ge}_7\text{O}_{20}$ glass. The Mössbauer spectra of these glasses showed only a Sn^{2+} peak, indicating that the specimens were free from Sn^{4+} . The chemical shifts and the quadrupole splittings are higher than those of the tetragonal SnO. This shows that the Sn—O bond in the glass is more ionic and distorted than in crystalline SnO. The refractive indices of the glasses are very high and are of the order of those found for the PbO-GeO₂ glasses (Bansal & Doremus, 1986).

Phosphate Glass

Binary SnF₂-P₂O₅ glass

Binary SnF₂-P₂O₅ glass was studied by Shaw & Shelby (1988), motivated by the quest of finding glasses with properties of low melting temperature, high chemical durability and high thermal expansion. These properties are desirable for many applications which include the moulding of optical elements using standard equipment normally used for plastics, low temperature glass to metal seals and the incorporation of optically active organic molecules into inorganic glass matrix used in dye lasers. They succeeded in making stannous fluorophosphate glass with glass formation extending over a relatively large (0 to 80 mol% SnF₂) composition region and melting temperatures between 400 to 500° C. But only glasses with SnF₂ contents between 55-77 mol% were durable enough to moisture attack and they exhibited a very high thermal expansion. A structural model was proposed

by Tick (1984) for these glasses, suggesting a basic structural unit of Sn—O—P—O bonds. The divalent tin plays the role of a network former, in tetrahedral coordination, bonding with phosphorus via oxygen (Sn—O—P), shown in Figure 1.

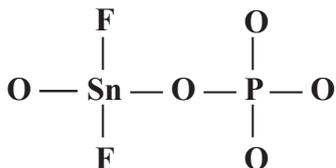


Figure 1 Structural model of the binary SnF₂-P₂O₅ glass

The network is extended in three dimensions by corner sharing of tin and phosphorous polyhedra, assuming no P—F bonding. The density composition relationship of this glass shows a sharp change at approximately 60 mol% SnF₂, the composition at which the glass exhibits the best resistance to water attack. This suggests that a structural change in the glass network occurs at this composition. As SnF₂ (Sn²⁺) content increase, there is an increase in the linkage of the glass network as the formation of Sn—O—P—O bridges decreases the number of weak P—O—P bonds. At around 60 to 65 mol% SnF₂, the number of Sn—O—P—O bonds is at a maximum. Further increase of SnF₂ content eventually results in the formation of Sn—F—Sn bonds, which are weak to water attack.

Ternary SnO-SnF₂-P₂O₅ glass

Shaw & Shelby (1988) extended their studies to the ternary SnO-SnF₂-P₂O₅ glass system as a logical extension to the binary SnF₂-P₂O₅ glass. The addition of SnO to binary stannous fluorophosphate glasses resulted in a decrease in the volatility of the melt and dramatic improvements in the chemical durability of the glass. In binary SnF₂-P₂O₅ glasses with 60 to 65 mol% SnF₂ exhibited the best durabilities but these glasses were still susceptible to water attack. The substitution of SnO for SnF₂ dramatically reduced the dissolution rates and glass samples containing 30 mol% SnO showed dissolution rates comparables to soda-lime-silica glasses. Thus glasses with 30 mol% SnO and containing less than 50 mol% P₂O₅ are chemically very durable. According to Zachariasen's model, (Zachariasen, 1993) glass formation would be impossible for a P₂O₅ content less than 50 mol% and if the Sn²⁺ act as network modifiers. It is evident from these studies that some fraction of Sn²⁺ act as network forming cations. Later Xu & Day (1990) studied the same system and made the same finding as Shaw & Shelby (1988). They concluded that the decrease in either the P₂O₅ contents of F/O ratio causes the major improvement in the chemical durability. In glasses containing 30 to 50 mol% P₂O₅, the infrared studies showed that Sn cations act as network formers, thereby forming an orthophosphate like structure. The infrared spectra of these glasses also showed that Tick's assumption that no P—F bonds are present in these glasses is incorrect. Therefore, Xu & Day (1990) proposed a different structural unit shown in Figure 2.

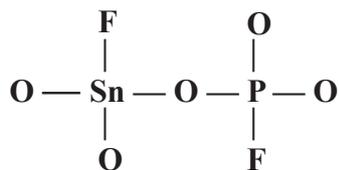


Figure 2 Structural model of the ternary SnO-SnF₂-P₂O₅ glass

The increase in chemical durability through the increase of SnO content is due to the fact that the weaker linkages of Sn—F—Sn, Sn—F—P and P—F—P are gradually replaced by stronger Sn—O—Sn, Sn—O—P and P—O—P linkages.

Silicate Glass

Binary SnO-SiO₂ glass

Early studies on the binary SnO-SiO₂ glass system were focussed on the preparation of glass in order to establish the phase relations in the system. Keysselitz and Kohlmeyer (1933) first reported the preparation of glass in this system by heating compressed pellets of mixtures of stannous oxalate and silica. On heating the pellet, the oxalate decomposed to give Sn, SnO, CO and CO₂. The evolution of CO and CO₂ gases expelled the air from the crucible and the low oxygen partial pressure of the gas mixture minimised oxidation of the melt. Spandau & Kohlmeyer (1947) melted mixtures of SnO + SiO₂, and obtained a yellow glass. Slonimskii & Tseidler (1959) improved this technique by heating mixtures of SnO + SiO₂ in hermitically sealed alumina crucibles. The resulting glass showed that up to 3 wt% Al₂O₃ had dissolved in the melt. They also found that the glasses decomposed to metallic Sn, SnO₂ and quartz on heat treatment. Chizhikov *et al.* (1962) prepared this glass by reducing mixtures of SnO + SiO₂ with carbon in a nitrogen filled Tammann furnace. All the above researchers concluded that there are no binary compounds, stable or metastable in the phase relations of SnO + SiO₂ glass system.

Carbo Nover & Williamson (1967) studied the crystallisation and decomposition of SnO-SiO₂ glasses ranging in composition from 28 to 59 mol% SnO. Their method of glass preparation was based on that used by Keysselitz & Kohlmeyer (1933) where compressed pellets of mixtures of stannous oxalate and quartz were melted in alumina crucibles. Glasses containing 42 mol% SnO or more crystallised to give a new metastable compound, designated stannous metasilicate (SnSiO₃). This phase grows at subsolidus temperatures as polycrystalline spherulites. The ease with which these crystalline spherulites grow depends on the composition of the glass. They grew most readily from glass compositions on either side of the 1:1 composition. This phase decomposes at 700° C to give SnO + silica and to SnO₂, Sn + silica at higher temperatures. They conclude that the structure of SnSiO₃ is thought to be related with SnO. Ishikawa & Akagi (1978) studied the structure of SnO-SiO₂ glasses with SnO contents ranging from 32 to 57 mol % SnO. Glass samples were prepared from mixtures of stannous oxalate and silicon dioxide melted in alumina crucibles. The information they obtained both from infrared spectra and radial distribution studies of x-ray diffraction data of the glasses, supports the suggestion of Carbo Nover & Williamson (1967) that the structures of the glasses resembles that of the crystalline metastable SnSiO₃.

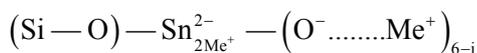
From radial distribution studies, they also found that there is a structural contraction in the glasses with SnO contents greater than 35 mol %. Neither paper proposed atomic models of the glass structure since the structure of SnSiO₃ crystals has yet to be determined. Itoh & Mori (1977) studied the electrical resistance as a function of temperature of SnO-SiO₂ glass containing 47.42 mol % SnO and found that the electrical resistance began to decrease at 450° C; corresponding to the glass transition temperature.

Sodium Tin Silicate glass

The solubility of SnO₂ in silicate glass is very low. A maximum of 0.8 mol% SnO₂ can be dissolved in SiO₂ (quartz) in making the stannosil glass (Maddock, 1939). However, the presence of alkali oxide, can increase the solubility of SnO₂ in a silicate melt. Zorina and Vakhrammev (1969) studied the incorporation of SnO₂ in the following ternary system of sodium tin silicate glasses:

15Na₂O.xSnO₂.(85-x)SiO₂ ; 20Na₂O.xSnO₂.(80-x)SiO₂ ; 25Na₂O.xSnO₂.(75-x)SiO₂ ;
 30Na₂O.xSnO₂.(70-x)SiO₂ ; where x = 0; 2.5; 5; 7.5; 10 mol%.

Their attempt to prepare transparent glass with SnO₂ content greater than 15 mol% failed owing to the sharp increase in the viscosity of the melt. Infrared spectra of the glasses showed that some of the octahedral coordination of tin began to change to tetrahedral coordination for SnO₂ contents greater than 5 mol% but the octahedral coordination of tin predominated. Danheim *et al.* (1976) studied the Mössbauer effect of tin in the glass system Na₂O-SiO₂. By adding varying amounts of SnO₂ or SnO to the system and melting the glass in oxidizing or reducing atmosphere, they were able to vary the tin valence ratio (Sn⁴⁺/Sn²⁺) over a wide range in the glass. By comparing the values of the isomeric shift with that of known crystalline tin compounds, the coordination numbers of the Sn⁴⁺ and Sn²⁺ ions were determined and, depending on the glass composition and the valence ratio, both ions can undergo a transition from 4 to 6 coordination or vice versa. For both ions a change from 6 to 4 coordination indicates that the ion is changing from modifier to network former. Danheim *et al.* (1976) concluded their studies by saying that tin in the glass is in a distorted lattice. Mitrofanov & Sidorov (1967) studied the Mössbauer effect of tin in the ternary system of Me₂O-SnO₂-SiO₂, where Me = Li, Na, K and found that the tin chemical shift for each alkali in tin silicate glass did not change with composition and the spectral line width was only slightly greater than the line width of crystalline SnO₂. They added that in this glass system tin atoms were surrounded by oxygen atoms and had six-fold coordination in the form of a group,



whose structure remained constant when quantitative changes were made in the composition of the glass. They concluded that the glass structure was not in agreement with the Zachariasen's disordered lattice hypothesis (Zachariasen, 1932) and indicated the existence of definite chemical compounds in glasses.

Tin in Soda-Lime-Silica (Float) glass

Almost 85 % of the flat sheet soda-lime-silica glass produced in the world is made by the float process in which a ribbon of molten glass flows out of the melting furnace and solidifies while floating on a bath of molten tin enclosed in a float chamber filled with an inert gas mixture of nitrogen and hydrogen. Some tin diffuses into the lower surface that is in contact with the molten tin. A smaller amount diffuses into the upper surface by chemical adsorption from tin vapour in the float chamber. Figure 3 shows the typical tin diffusion profiles in the underside of float glass taken from Pantano *et al.* (1993) It shows that the depth of tin penetration is about 16 μm and the tin oxide concentration at the surface is about 15 wt% (~ 4 mol %).

There have been a few studies done on float glass, concentrating on the determination of tin oxidation states and quantifying these oxidation states as a function of depth in the glass. Chappel & Stoddart (1974) studied the underside, top and air fracture surfaces of an unweathered float glass by Auger electron spectroscopy to compare compositions of the exterior surfaces with that of the bulk. Calcium, magnesium, potassium, silicon and

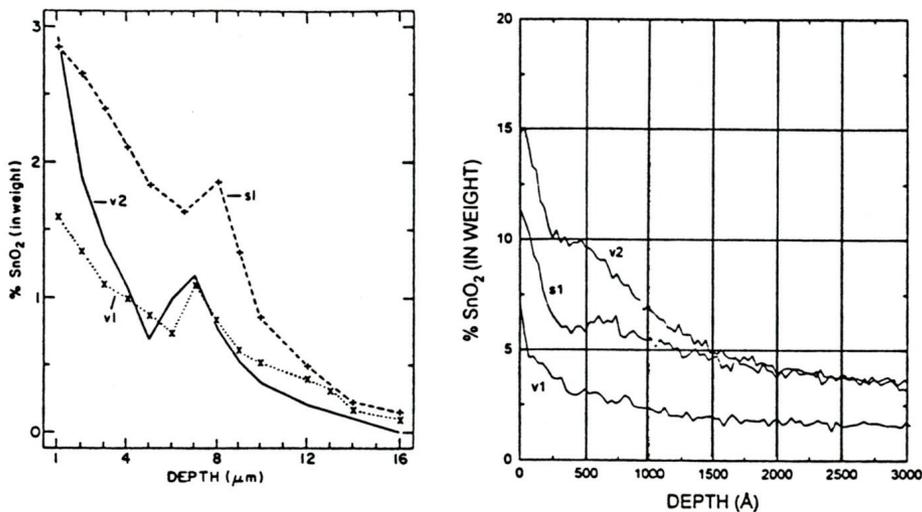


Figure 3 Typical tin diffusion profiles in the underside of float glass specimens taken from Pantano *et al.* (1993). The in-depth and near-surface profiles for three different 6 mm clear float glasses: by EPMA (left) and by SIMS (right). For simplicity the tin oxide concentration is expressed in wt.% SnO_2 even though it has been shown that tin in both valence states of +2 and +4 coexist in the glass. All the three samples exhibit what Sieger (1975) described as an anomalous 'hump' or satellite peak at about half the effective depth of penetration.

oxygen were detected in all surfaces in qualitatively similar amounts to that in the bulk but contaminants (carbon, nitrogen and sulphur) were also found on the exterior surfaces. On the underside, tin and iron were present but, on the top, tin was found at about only one tenth of the underside concentration. Sodium could not be detected because of its rapid migration from the surface along the field gradient induced by the electron beam.

Sieger (1975) studied the tin profiles of float glass surfaces by a method that involved electron-microprobe analysis of the edges of the samples and etching of a layer from the surface and chemically analyzing it for stannous and stannic tin. The depth of tin penetration through the underside varies with glass thickness and cleanliness of tin bath. Glass near equilibrium thickness (6 mm) shows deeper in penetration than either 3 or 12 mm. Stannous and stannic tin are present near the bottom surface with the former predominating. The tin penetration profile also exhibits a 'hump' located at about half the effective depth of tin penetration. Colombin *et al.* (1977) measured the penetration depth of tin in float glass using ESCA [Electron Spectroscopy for Chemical Analysis (= XPS)], photo emission induced by ion bombardment and ellipsometry. Their studies concluded that the concentration of tin in the first 100 nm of the underside of float glass decreases very rapidly as a function of depth and the concentration of tin at the surface (10 nm) of the underside is very high. Jie & Choa (1990) studied the underside of float by XPS (X-ray Photoelectron Spectroscopy) to determine the oxidation states of tin. A detailed scan for tin was made on the underside of the float glass sample, measured in the as-received state and after argon ion etching. The depth of tin scanning was about 10 nm. XPS spectra of pure Sn, SnO and SnO₂ were fitted to the spectra of the glass samples. The fit in all cases was excellent and they concluded that,

- (i) In the underside of float glass, tin is present in Sn⁴⁺, Sn²⁺ and Sn⁰, with Sn⁴⁺ having the largest fraction.
- (ii) Deeper into the glass, the fraction of Sn⁴⁺ decreases gradually, while Sn²⁺ and Sn⁰ increases.

Principi *et al.* (1993) studied the oxidation state of surface tin in float glass using Conversion Electron Mössbauer Spectroscopy (CEMS). The room temperature CEMS spectra show that the surface contains mixture of Sn²⁺ and Sn⁴⁺ oxides. This result excludes the presence of metallic tin, contrary to the results reported by Jie & Chao (1990). By taking into account the fact that the room temperature *f* factor of Sn⁴⁺ is approximately twice that of Sn²⁺, they concluded that Sn²⁺ is the predominant oxide species at the surface of the float glass. The isomer shift and quadrupole splitting are higher than those of the corresponding crystalline phases. By heating the glass for 10 minutes at 730° C, thus simulating the industrial process which produces blooming (deterioration of glass surface quality), the Sn⁴⁺/Sn²⁺ area ratio of the CEMS spectra was found to decrease. Therefore, from this experiment they have shown that the blooming is caused by the oxidation of some of the Sn²⁺ tin species to Sn⁴⁺ when the glass is reheated for tempering or to produce curved glass. This findings supported in some way the mechanism for bloom suggested by Deubener *et al.* (1992) whereby an oxidation of Sn²⁺ in the outer layers alters both their viscosity and expansion coefficients by changing the chemical make up of the surface. Pantano *et al.* (1993) compared the tin profiles at the bottom surface of float glass due to heat treatment with that of the untreated float glass. The concentration profiles of tin in the near surface (0 to 0.5 μm) were obtained using Secondary Ion Mass Spectroscopy (SIMS), while the depth profiles (0.5 to 30 μm) were determined with Electron Probe Microanalysis (EPMA). The heat treatment schedule simulated the industrial process which produces blooming. Their results showed that after heat treatment there was a large tin concentration build-up near the surface and tin concentration depletion at greater depth. In another

words there was a pronounced out-diffusion of tin to the surface due to heat treatment and this process changed the tin profiles as compared to the unheat treated float glass. Their findings supplement the mechanism for the process of blooming forwarded by Deubener *et al.* (1992) above. The studies concluded that surface enrichment of Sn^{4+} species due to heat treatment can only exaggerate those physical and chemical property changes, while the abruptness of the decrease of tin concentration profiles magnifies their effect upon the surface wrinkling.

The above mentioned studies concentrated on quantitative characterization of profiles of tin species that have diffused into the surfaces of float glass and try to account for the blooming of the glass due to heat treatment. There have been few studies carried out to try to make glass having the same chemical composition as the bottom part of float glass that has been in contact with the molten tin and studying the effect of tin upon the physical and structural properties of the glass. Studies by Min'ko *et al.* (1973) and Min'ko (1973) have concentrated on the synthesis of glass of float glass composition with varying amounts of Sn^{2+} and Sn^{4+} . Depending on the synthesis conditions, the equilibrium of $\text{Sn}^{4+} \leftrightarrow \text{Sn}^{2+}$ is established in the glass. This can be displaced almost completely to the left, but only 70% to the right. Min'ko *et al.* (1973) added that the improvement in the physicochemical properties of glasses synthesized under oxidizing compared with those under reducing conditions is due to the differing valence state of the tin in the glass structure. Owing to the different roles played in the glass by the different valence of tin, Sn^{4+} is assimilated by the soda-lime-silica melt only in an amount not exceeding the alkali content of the glass, whereas this is not the limit for Sn^{2+} .

Chemistry of tin in glass

The study on the effect of tin on glass properties is not well understood, because the chemistry of tin in glasses is complicated by the two different valencies available to it and therefore synthesis and analysis of glass containing tin poses some problems. The tetravalent (Sn^{4+}) state is the most stable and, by extrapolation from Si & Ge (higher in Group IVA), it is expected that Sn^{4+} would act as an intermediate in silicate glasses. Past studies have shown that the solubility of SnO_2 in silicate and borate glasses is very low (Volf, 1984). For example about 0.2-2 wt.% of SnO_2 can be dissolved in SiO_2 (quartz) in making a stannosil glass (Maddock, 1939). This has a low thermal expansion and transmits long ultraviolet (3000 – 4000 Å) but absorbs the harmful short wave ultraviolet (2537 Å).

The divalent state (Sn^{2+}) is fairly readily oxidized to the tetravalent but binary glasses with high SnO content can be formed as silicates, borates and germanates. Silver *et al.* (1977) studied the SnO- GeO_2 glass system, and found that glass can form with $x > 2$ ($\text{Sn}_x\text{GeO}_{2+x}$) which is beyond the orthogermanate composition. The refractive indices for the glasses are very high and are of the order of those found for PbO- GeO_2 glasses and higher than those found for all other two component oxide glasses (Philips & Scroger 1965). In the SnO- B_2O_3 glass system studied by Paul *et al.* (1977) glass can form with up to 58 mol% SnO which is beyond the metaborate composition. The ^{119}Sn Mössbauer spectroscopy of these glasses shows that, for glasses with high SnO content, the non-bridging oxygen ions are coordinated to Sn^{2+} ions. In the SnO- SiO_2 glass system, glass can be formed beyond the metasilicate composition. Two important past studies carried out on

this system are by Carbo Nover & Williamson (1967) and Ishikawa & Akagi (1978). Carbo & Williamson (1967) studied the crystallization and decomposition of glasses ranging in composition from 27 to 58 mol% SnO. Ishikawa *et al.* (1978) studied the structures of glasses ranging from 32 to 57 mol% by radial distribution studies from x-ray diffraction data. Thus we see that glass can form with a high SnO content in stannous germanate, stannous borate and stannous silicate system. But, why can high SnO content glasses form in these system? Past studies have not answered this question well. By analogy with PbO (Pb^{2+}), we might expect SnO to act in a rather complex manner. In PbO-SiO₂ glass, PbO acts as a modifier at low PbO content (< 30 mol%) (Dupree *et al.*, 1987). In this system glasses will form with PbO contents up to 90 mol%, implying that a lead-oxygen network must exist with considerable Pb-O covalency, whereas with corresponding ionic modifiers such as Sr-SiO₂ or Na₂O-SiO₂ it is very difficult to prepare glasses beyond the metasilicate compositions. Does Sn²⁺ behave like Pb²⁺ or as a modifier?

Based on the fact that divalent tin is a major component while tetravalent tin is minor in any glass system, the two valence states of tin must play a different role in the structure of the glass. The difference must be due to the structural difference between SnO and SnO₂ as explained below.

The Structure of The Oxides of Tin

Tin, as a *p*-element with atomic number 50, belongs to group IVA of periodic table. This group comprises C, Si, Ge, Sn and Pb. An atom of any of these elements has four electrons in its valence level. The oxides of Si and Ge are glass formers, while lead(II) oxide in silicate, germanate and borate glasses behaves as modifier or intermediate depending on its concentration in the respective glasses. The ground state electronic configuration of tin is shown in Table 1.

Table 1 The ground state electronic configuration of tin

Shell	K	L	M	N	O
Sn	1s ²	2s ² 2p ²	3s ² 3p ⁶ 3d ¹⁰	4s ² 3p ⁶ 4d ¹⁰	5s ² 5p ²

The oxidation states of tin are +2 and +4. The tetravalent state is the most stable and the formation of lower oxidation state of +2 is referred to as the inert pair effect, since the 5s² electron pair shows a reluctance or inability to ionize or to act as bonding electron (Puddenphatt & Monaghan, 1986). Table 2 gives the ionic radius, coordination number with respect to oxygen, field strength, ionic potential and ionic refraction of tin as well as silicon, lead, and sodium (Volf, 1984) for comparison purposes. According to Volf (1984), the field strength (bond strength) of network former elements is high, exceeding 1.3 and the modifiers have low field strength below 0.36 and the intermediate elements field strength values are between these two. Volf (1984) also states that network formers have high ionic potentials, exceeding 10, modifiers have low values up to 2 and intermediate ionic potential values are between these two. Based on these criteria tin can be classified empirically as an intermediate element along with lead. The values of ionic refraction give a measure of deformation (polarizability) of an ion (Fanderlik, 1983). The ionic refraction

of Sn^{2+} is much higher than Si^{4+} and Na^+ and comparable to Pb^{2+} . This indicates that Sn^{2+} is strongly deformable or polarizable.

Table 2 The ground state electronic configuration of tin

Ion	Ionic radius, r (Å)	Coordination number with respect to oxygen	Dietzel's field strength $= z/a^2$ (Å ⁻²) z = valency, a = interionic distance	Ionic potential = z/r (Å ⁻¹)	Ionic refraction, R_i
Si^{4+}	0.39	4	1.56	10.26	7.52
Sn^{2+}	-	4	0.46*	-	17.2
Sn^{2+}	0.93	6	0.41*	2.15	-
Sn^{4+}	-	4	1.13*	-	-
Sn^{4+}	0.69	6	1.01*	5.80	-
Pb^{2+}	1.18	6	0.31	1.69	27.4
Na^+	1.02	6	0.18	0.98	4.75

*Taken from Danheim *et al.* (1976)

Now let us look at the structure of SnO and SnO_2 . The nature of the bonding of SnO and SnO_2 is classified as ionic-covalent, the same as PbO and unlike the polymeric, more covalent bonding of SiO_2 and GeO_2 (Puddenphatt & Monaghan, 1986). According to Pye *et al.* (1972), the fraction of ionic character of the $\text{Sn}-\text{O}$ bond is ~ 0.6 and thus classified into intermediate group.

The Structure of SnO_2

Tin (IV) oxide (SnO_2) crystallizes with rutile structure and can be regarded as essentially an ionic crystal (Wells, 1962). The rutile crystal structure is a body-centered tetragonal with Sn^{4+} ions at the corners and centre of the cell and oxygen ions located at nonregular interstitial sites, causing distortion of the cell from cubic to tetragonal. The unit cell of SnO_2 crystal is depicted in Figure 4, where the environment of tin is an octahedron of oxygen ions, and the electron density distribution close to the tin nucleus can be regarded as approximately spherical (Cossement *et al.*, 1992)

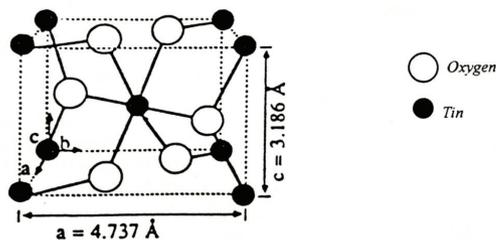


Figure 4 Rutile crystal structure of SnO_2 , showing the unit cel (Cossement *et al.*, 1992).

The poor solubility of SnO_2 in silicate melts can be explained by its bond strength (field strength) and structure. Oxides with bond strength values that exceed 0.8 and coordination number exceeding 4 have been classified by Volf (1984) as oxides that show poor solubility in glass. In this case the bond (field) strength of Sn^{4+} is 1.01 and its coordination number is 6. Owing to these factors, Sn^{4+} poses strong competition for silicon in polymerization. Sn^{4+} ion can form its own strong six coordinated oxygen polyhedra differing from the SiO_4 group and, as a consequence of its high bond strength and different geometry, it is more difficult to link to the polyionic network of silicon tetrahedra. This results in poor solubility in silicate glasses.

The Structure of SnO

Tin (II) oxide (SnO) is amphoteric. Cole (1947) classified an amphoteric oxide as generally belonging to the intermediate group, acidic oxides such as SiO_2 and B_2O_3 are network formers and basic oxides such as Na_2O and K_2O are modifiers. SnO has a complex tetragonal crystal structure, similar to PbO . The SnO crystal, unlike CaO or MgO , contains

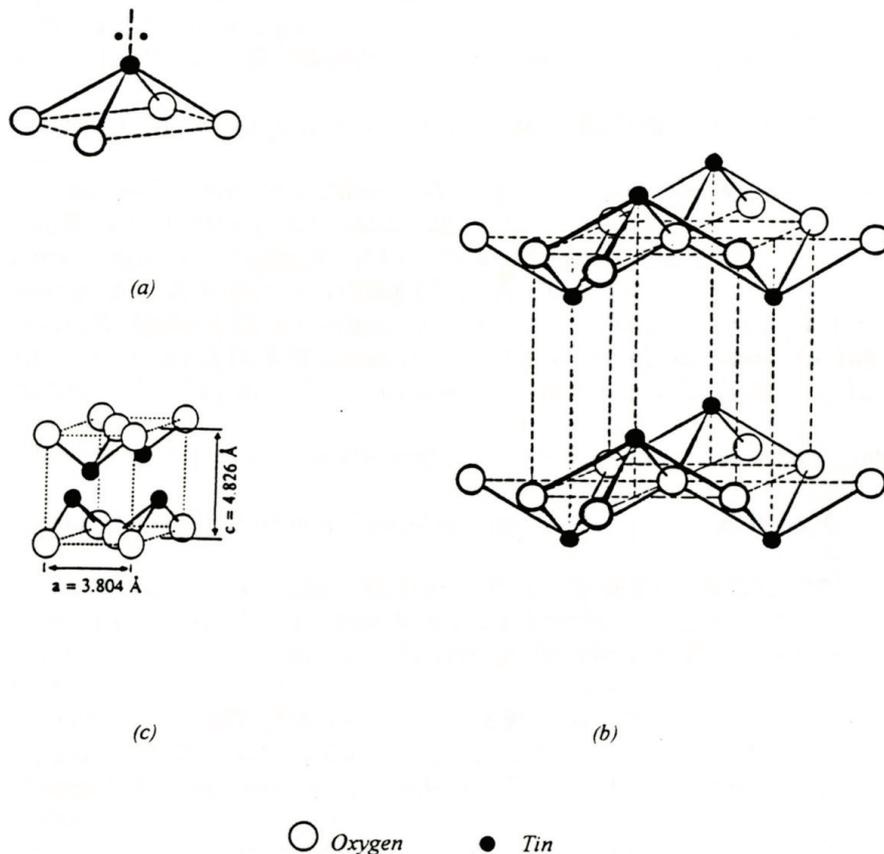


Figure 5 The crystal structure of SnO (Wells, 1962; Cossement *et al.*, 1992). (a) The arrangement of bonds from a tin atom to oxygen atoms, where the two dots represent the 'inert pair' of electrons. (b) The tetragonal layered structure. (c) Unit cell of SnO

asymmetrical units. In CaO and MgO each cation is symmetrically surrounded by six oxygen ions, therefore the valence force of each ion extends equally into space. In the SnO crystal, however, the valence forces extend more to one direction, so that the asymmetrical building units consists of a Sn atom located at the top of a square pyramid bonded with its four oxygen neighbours placed at the corners of the base of the pyramid as shown in Figure 5(a). The inert pair of 5s electrons that do not take part in the bonding is situated at the apex of the tetragonal pyramid and occupies a mixed ($s-p_z$) orbital (Wells, 1962). These asymmetrical building units of $(\text{SnO}_4)^{6-}$ are arranged forming a layered structure, where each tin atom has four oxygen near neighbours, all lying to one side, and all of the oxygen atoms lie between every other pair of tin layers as shown in Figure 5(b). The layered structure allows an electronic through-space interaction between tin atoms. Figure 5(c) shows a unit cell of SnO crystal.

Therefore the resulting tetragonal structure of SnO consists of a prism with O^{2-} ions in each of the eight corners and Sn^{2+} placed inside not at the centre but much closer to four of the corners than to the other four. The simplest interpretation of this structure is that the four near O^{2-} ions repel the easily polarisable shell of the Sn^{2+} , especially its two outermost (inert $5s^2$) electrons. The electronic structure of Sn^{2+} ion consists of an inner core of 18 electrons in the N-shell, and two 5s electrons in the O-shell. The two 5s electrons are easily repelled in the field of the negative ion O^{2-} . As a result the Sn^{2+} loses its spherical symmetry, and its electron distribution is such that towards the four near O^{2-} ions it extends only its 18 electrons of N-shell. Therefore towards the four near O^{2-} ions, the Sn^{2+} ion assumes the electron distribution of a much smaller and highly charged Sn^{4+} ion while the opposite side of Sn^{2+} is characterized by a higher electron density, much resembling the Sn atom. In this way according to Weyl (1967) Sn^{2+} ion possesses, what he term as 'metallophilic' character.

From the fact that the SnO crystal structure is complex and it can be a major component in many glass system, one can see that its structural role in glass must be complex and dependent on composition.

Conclusion

Tin in the divalent state can be a major component in many glass system. Divalent tin in the form of SnO has been shown to fulfill various structural roles as either modifier or intermediate, depending on the type of glass system and composition. SnO contents of more than 50 mol% can form glasses in binary SnO- B_2O_3 , SnO- P_2O_5 , and SnO- SiO_2 glasses. For example in binary SnO- B_2O_3 glasses the SnO role changed from modifier to intermediate at 20 mol% SnO. In the form of SnF_2 , divalent tin can be incorporated in the SnF_2 - P_2O_5 glass system up to 80 mol% SnF_2 . While glass in this system is not chemically durable, a major addition of SnO to form the ternary SnO- SnF_2 - P_2O_5 glass system, has dramatically improves the chemical durability of the glass. With the presence of SnO, it is evident that some fraction of Sn^{2+} are acting as network forming cations in the ternary SnO- SnF_2 - P_2O_5 glass system. Contrary to divalent tin, tetravalent tin in the form of SnO_2 is only a minor component in any glass system. This is because of its low solubility rate especially in alkali free glass. Only 0.1 mol% dissolved in stannous borate and 0.8 mol% dissolved in stannic silicate glass (stannosil glasses). The solubility of SnO_2 can be increased by the presence

of alkali oxide in the glass melt but the amount that can be dissolved does not exceed the alkali content of the glass. Studies of tin in float glass have shown that SnO (Sn²⁺) is the predominating species compared to SnO₂ (Sn⁴⁺).

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