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Some Physical Properties of Tin-Doped Float Glass

Beberapa Sifat Fizikal Kaca Apung Didop Timah

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Abstract

Tin-doped float glass samples were made by remelting the float glass with varying amounts of tin(II) oxalate (SnC_2O_4) under ordinary conditions. These samples mimic in terms of tin content, the tin oxide distribution found along the tin diffusion region of float glass. The effect of tin oxides (SnO and SnO_2) content on thermal expansion, density, refractive index and microhardness of tin-doped float glass samples were found to be related to SnO acting as modifier oxide and SnO_2 as intermediate oxide.

Keyword Tin-doped float glass, modifier oxide, intermediate oxide, physical properties of float glass

Abstrak

Beberapa sampel kaca apung yang didop dengan timah telah dihasilkan dengan melebur kaca apung bercampur dengan pelbagai amaun stanum(II) oksalat (SnC_2O_4) dalam keadaan biasa. Kandungan timah pada sampel-sampel ini menyamai dengan kandungan timah dalam kaca apung yang diresapi timah semasa proses pembuatan kaca. Kesan oksida timah (SnO and SnO_2) kepada sifat pengembangan terma, ketumpatan, indeks biasan dan kekerasan mikro kaca apung yang didop ini adalah bergantung kepada kandungan SnO yang bertindak sebagai oksida pengubahsuai dan SnO_2 pula bertindak sebagai oksida pertengahan dalam kaca.

Kata kunci Kaca apung didop timah, oksida pengubahsuai, oksida pertengahan, sifat-sifat fizikal kaca apung

Introduction

Tin is not a common constituent of glasses. But the most important use of tin in the glass industry is in the production of flat and parallel sheet glass by the float glass process. This glass is commercially known as float glass and chemically referred as soda-lime-silica glass. In the float process, the molten glass is floated on top of molten tin kept at 1050ºC in float chamber of slightly reducing atmosphere. High concentration of tin of different oxidation states diffuses into the lower surface of the glass through direct contact and a smaller amount diffuses into the upper surface from tin vapour in the float chamber (Sieger,

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(1975); Colombin et al. (1977); Lie & Chao (1990); Principi, Maddalena & Gupta (1993) and Pantano et al. (1993)). The float glass surfaces were therefore chemically different from the bulk. Previous study on the effect of tin concentration on properties of float glass Karim & Holland (1995) has shown that tin species of Sn^{2+} and Sn^{4+} found in the surfaces of float glass played different structural role. We now report results of thermal expansion, density, refractive index and microhardness measurements of tin-doped float glass samples which were made to mimic compositions which might occur within the tin diffused region of float glass.

Experimental

The glass preparation and analysis of tin contents of the glass samples has been reported elsewhere (Karim & Holland (1995); Holland et al. (1993) and Johnson et al. (1995). Thermal expansion measurement was carried out in a fused quartz dilatometer with heating rate of 2 ºC per minute. Density was obtained by Archimedes' method using pure degassed distilled water as immersion medium. Refractive index was measured using an Abbé refractometer with light source of sodium lamp (λ = 589.6 nm). Microhardness measurements were carried out using a Knoop diamond indenter with a load of 50g applied for 30 seconds.

Results and Discussion

The results of some physical properties measurements of tin-doped float glass are presented in Table 1.

Table 1

Sample	Tin oxide (mol.%)	TCE, α±1.5 ($\times 10^{-7} K^{-1}$) [25-600ºC]	T_g (±5 ºC)	M_g (±5 ºC)	Density (g/cm^3)	Refractive index, *n* (at 589.6 nm)	H_K ±27 (50g/30s)
PK0	0	89.7	535	590	2.494	1.5175	456
PK2.5S	1.19	89.1	555	600	2.540	1.5233	523
PK5S	1.39	86.2	575	610	2.554	1.5239	589
PK7.5S	3.64	83.2	580	620	2.623	1.5374	626
PK10S	5.26	79.3	595	645	2.707	1.5442	661
PK12.5S	6.00	78.6	590	635	2.705	1.5488	689
PK15S	6.97	77.2	570	625	2.704	1.5536	594

TCE - Thermal Coefficient of Expansion
T_g - Transition temperature
M_g - Dilatometric softening temperature
H_K - Knoop Hardness

Composition

The analysed compositions (mol.% above 100% float) are presented in Table 2 along with the ratio of the oxidation states Sn^{4+}/Sn^{2+}.

Table 2

Samples	PK0	PK2.5S	PK5S	PK7.5S	PK10S	PK12.5S	PK15S
Mol.%(SnO+ SnO_2)	0	1.19	1.39	3.64	5.26	6.00	6.97
Mo1.% SnO_2/Mol.%SnO	0	1.57	1.65	1.82	2.29	1.52	0.97

Error in the analysis is ±3%

During the melting of the glass, stannous oxalate decomposes to SnO and CO + CO_2 and these gases help to maintain a slightly reducing atmosphere. However some oxidation of SnO to SnO_2 does occur. Thus the compositions mimic points along the diffusion profile of tin in float, in terms of tin content, but the distribution of oxidation states may differ. Both oxides are soluble in float initially but traces of crystalline SnO_2 were observed in some regions of samples PK12.5S and PK15S, suggesting that saturation had been reached. These regions were rejected before any measurements were made.

Thermal Expansion

The thermal coefficients of expansion (TCE) for the glasses as a function of tin content are shown in Figure 1. Values of the glass transition temperature T_g and the dilatometric softening point M_g were also obtained from the thermal expansion curves and these values are depicted in Figure 2 as a function of tin content. The decrease in the thermal expansion coefficient and the increase in T_g with increasing tin content reflect the network/ intermediate characteristics of both tin oxidation states. Hence, the thermal properties of the glasses improved with added tin.

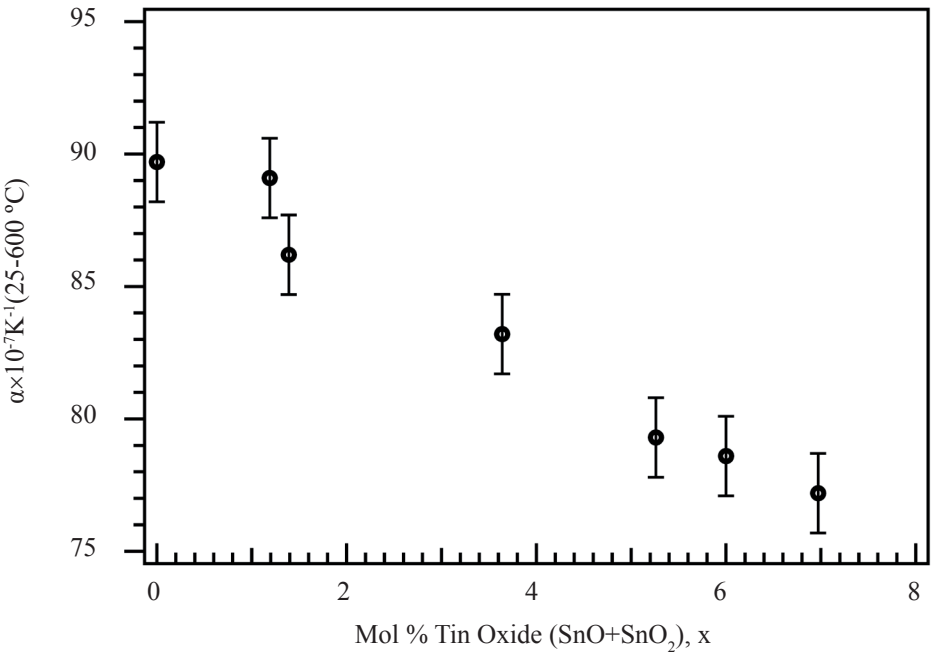

Figure 1 Thermal coefficient of expansion (TCE) versus tin content of tin-doped float glasses

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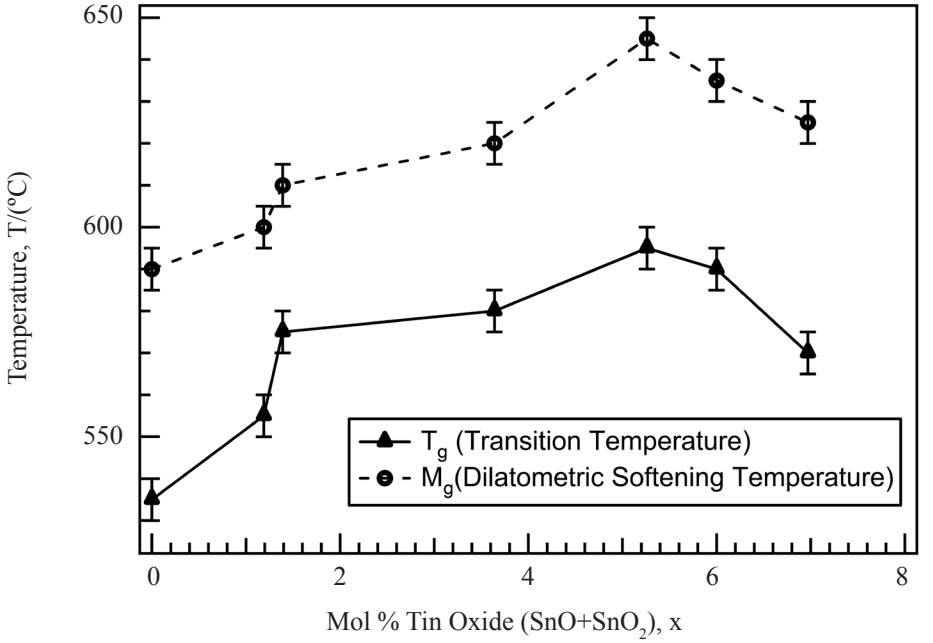

Figure 2 Transition temperature and dilatometric softening temperature versus tin content of tin-doped float glasses

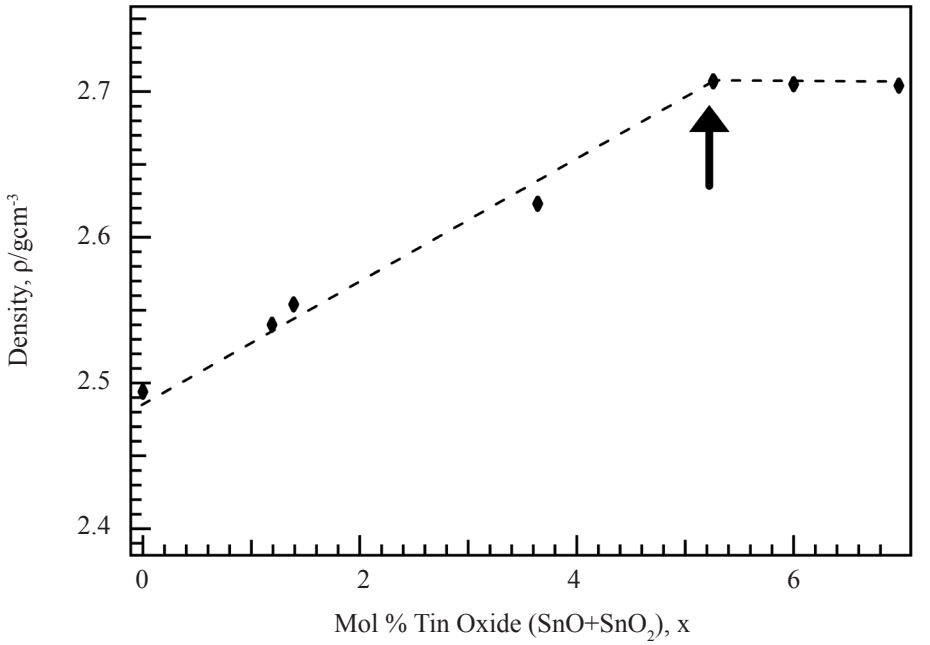

Figure 3 Density variation with tin content of tin-doped float glass. The arrow shows the approximate limit point where the density has achieved its maximum and remained constant

Density

Figure 3 shows the variation in the density of the glasses with increasing tin content. This seems to increase in a near linear fashion until the tin content exceeds ~5 mol.%, after which, the density appears to remain constant. Since this is the point beyond which Sn^{4+} remains constant and Sn^{2+} increases, it indicates that the structural roles of each ion are very different.

Refractive index

Figure 4 shows that the refractive index, n increases linearly with tin content, x, by given relation $n = (1.5173 \pm 0.000418)x + 0.052 \pm 9.75 \times 10^{-5}$ irrespective of the relative amounts of tin oxidation states. This suggests that Sn^{2+} and Sn^{4+} have similar molar volumes and polarisabilities or those differences in one are compensated by changes in the opposite sense of the other as the relative amounts of the oxidation states vary. Generally the effect of tin is to improve the glass optical property.

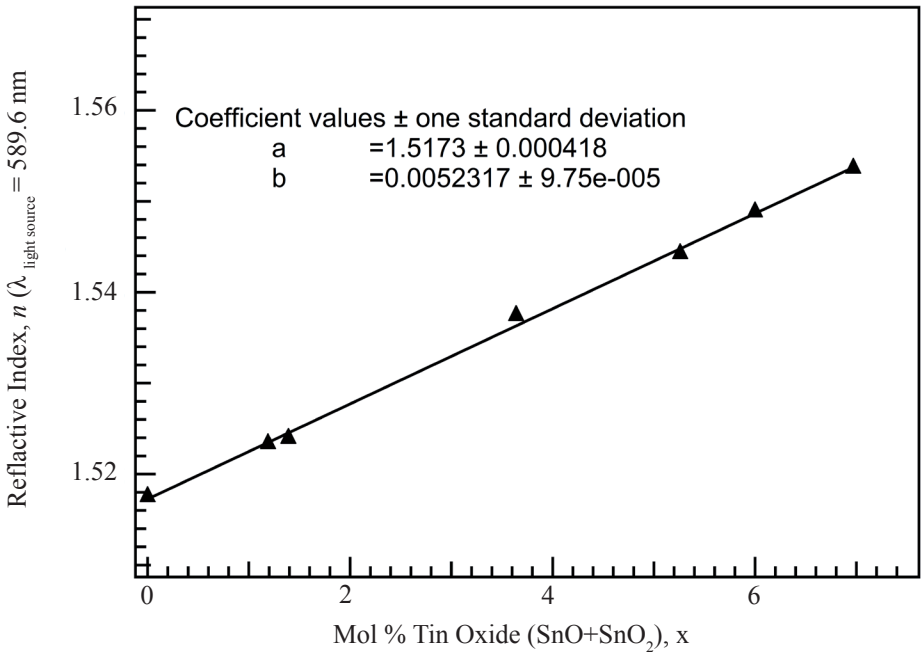

Figure 4 Refractive index as a function of tin content of tin-doped float glasses

Knoop Hardness

Figure 5 shows the variation of Knoop Hardness as a function of tin content. The microhardness of the glass increases with increase of tin content, reaching a maximum value at 6 mol % tin oxide. Beyond 6 mol.%, when the Sn^{4+} species began to saturate and Sn^{2+} species increases to about the same amount of Sn^{4+}, the hardness decreases a little but its value is still very much greater than the float glass with 0 mol.% tin oxide. This suggests that the effect of Sn^{2+} on the hardness of the glass is to soften the glass whereas the effect of Sn^{4+} species harden the glass.

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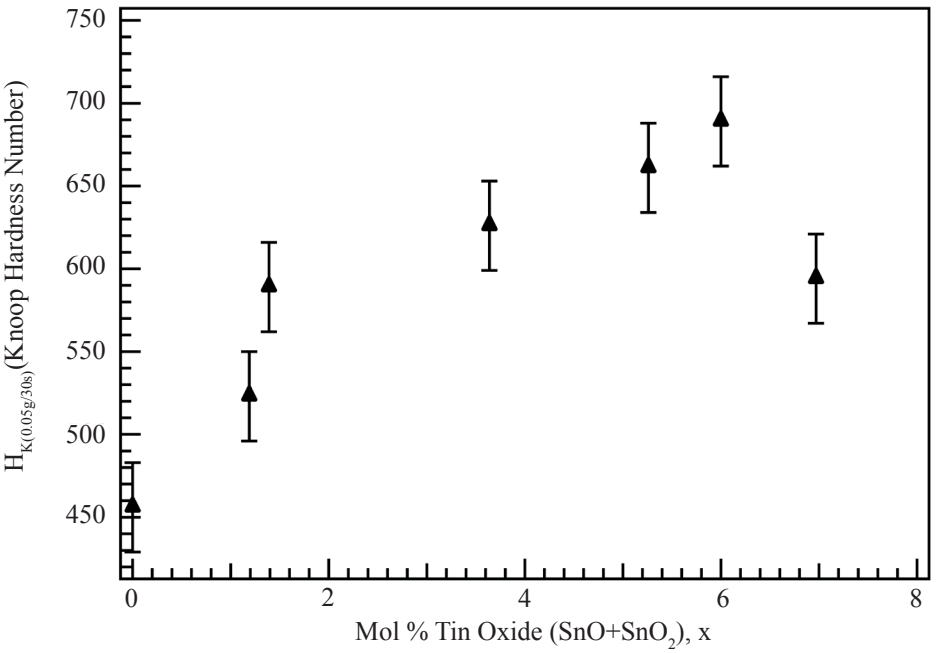

Figure 5 Knoop Hardness number as a function of tin content of tin-doped float glasses

Conclusions

Float glass is a complex material in terms of composition; and the small amount of tin that diffuses into the surface through the process of production can be detrimental to the quality of the glass. By remelting the float glass with tin(II) oxalate under ordinary conditions; we can mimic, in terms of tin content, the tin oxide distribution found along the tin diffusion region of float glass. Synthesis of the glass has shown that both Sn^{2+} and Sn^{4+} can be assimilated simultaneously in the glass but there is a solubility limit for Sn^{4+} (Karim & Holland(1995); Holland et al. (1993). The thermal expansion and refractive index vary approximately linearly with total tin content while the density and microhardness shows a discontinuity at tin contents above ~ 5 mol.%. This is the point at which Sn^{4+} content remains constant (saturation has probably occurred) and Sn^{2+} increases rapidly.

These observations reflect the following factors:

1. Properties which reflect only the strength of the bonding are unaffected by the oxidation state, suggesting that the Sn-O bond strengths are about similar for both oxidation states.
2. Properties which depend also on the rigidity of bonding are affected by oxidation state suggesting that the local symmetries of Sn^{2+} and Sn^{4+} are different.

This is not unexpected because Mössbauer studies on this glass by Holland et al. (1993) and Johnson et al. (1995) have shown that Sn^{2+} (SnO) is less rigidly bound to the network modifier sites while Sn^{4+} is rigidly bound at network former sites in the glass. Thus the two oxidation states will have different effects on the properties of the glass with SnO playing the role of modifier oxide while SnO_2 acting as intermediate oxide.

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