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## Mössbauer spectra of tin in binary Si–Sn oxide glasses

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**Abstract.** The Mössbauer spectra of  $^{119}\text{Sn}$  in binary glasses of  $\text{SnO}$  and  $\text{SiO}_2$ , in varying proportions of between 16.8 and 71.5 mol%  $\text{SnO}$ , have been obtained at 77 K. From these spectra the tin was found to be predominantly in the  $2^+$  state. The isomer shift and the quadrupole splitting were both significantly greater than those in crystalline  $\text{SnO}$  and were found to decrease with increasing tin content, which also corresponds to decreasing molar volume. A second series of spectra of two of the samples was taken at temperatures between 10 and 300 K. These spectra show a decrease in shift with temperature which was the same for the two samples and which could only partly be accounted for by the second-order Doppler shift. The remainder was ascribed to the temperature dependence of the isomer shift. By using these data together with the measured expansivity and increase in density with tin content, it was possible to correct the isomer shift for the effects of the change in volume, and it was found that the volume-corrected isomer shift *increased* with increasing tin content. This showed that there was an increase in s-electron density at the tin nuclei, while the accompanying decrease in quadrupole splitting showed a decrease in the p-electron character, as expected for a decrease in covalency. From the decrease in absorption area with temperature the Debye temperature of tin was estimated to be  $\sim 190$  K, which is slightly less than that of crystalline  $\text{SnO}$ , and decreased with increasing tin content. All the data suggest that the Sn–O bonds become progressively less covalent as more tin is added to  $\text{SnO}$ – $\text{SiO}_2$  glasses, and possibly indicate a change from 4-fold to 6-fold co-ordination.

A third series of spectra was obtained for the glass containing 40.9 mol% of  $\text{SnO}$  after a series of heat treatments. The spectra show changes in the oxidation state of the tin which depended upon the different conditions applied.

### 1. Introduction

There is a need to understand the structural rôle of tin in silicate glasses since it is a major constituent in the surface of float glass and also in coatings applied to float. Particularly important are the changes which occur during heat treatment. To study this role we looked initially at the simplest compounds, namely the binary glasses. Tin can exist in either the divalent or quadrivalent state in glass but the two oxidation states behave very differently.  $\text{Sn}^{4+}$  has a very low solubility in pure  $\text{SiO}_2$  since its preference for octahedral co-ordination is difficult to accommodate in a tetrahedral network.  $\text{Sn}^{2+}$ , however can be incorporated into  $\text{SiO}_2$  to levels which suggest it must behave as an intermediate rather than a network modifier.

In this work binary  $\text{SnO}$ – $\text{SiO}_2$  glasses were prepared so as to maintain the tin in the  $2^+$  oxidation state. The paper examines the changes in the Mössbauer parameters of  $^{119}\text{Sn}$  when

the amount of stannous oxide and the temperature are varied. The Mössbauer isomer shifts and quadrupole splittings are sensitive to the chemical state of the tin, and the Mössbauer fraction ( $f$ -factor) gives the strength of the chemical binding.

This work has been the precursor of a study of float glass itself which will be reported in a later publication.

Previous Mössbauer work on amorphous tin oxides has been carried out by Collins *et al* [1] and on tin in silicate glasses by many others [2]. In general both  $\text{Sn}^{4+}$  and  $\text{Sn}^{2+}$  were present in the samples, and  $\text{Sn}^{4+}$  acted as a network former while  $\text{Sn}^{2+}$  could be either a network former or modifier according to the other atoms present. Some of the present results have been briefly reported in conference proceedings [3, 4].

## 2. Experimental details

### 2.1. Sample preparation and characterization

Samples were prepared from Wacomsil quartz and stannous oxalate. They were melted in alumina crucibles, with a lid, and the melt was allowed to cool in the crucible. A certain amount of disproportionation occurred as a result of which tin metal falls to the bottom of the melt and  $\text{SnO}_2$  floats to the top, leaving a stannous silicate glass in between.

The samples were chemically analysed and the composition, density, molar volume and coefficient of linear thermal expansion were measured. Differential thermal analysis (DTA) was carried out to determine temperatures of crystallization and decomposition. On the basis of this some samples were heat treated to study phase formation.

### 2.2. Mössbauer spectroscopy

Three series of Mössbauer spectra were measured. The first and third series were taken at 77 K in a liquid nitrogen cryostat; the second series was taken in a variable temperature cryostat which could be operated between 10 and 300 K. All measurements were in transmission geometry.

A constant acceleration Mössbauer drive was used with a 10 mCi  $^{119}\text{Sn}$  Mössbauer source in a matrix of calcium stannate,  $\text{CaSnO}_3$ . To calibrate the energy scale a  $^{57}\text{CoRh}$  source and iron foil absorber were used at room temperature. A least-squares fitting program was used to fit the spectra and the parameters obtained were chemical shift, quadrupole splitting and the area of each component. The chemical shifts are quoted relative to  $\text{CaSnO}_3$  at room temperature.

## 3. Results

### 3.1. Glass properties

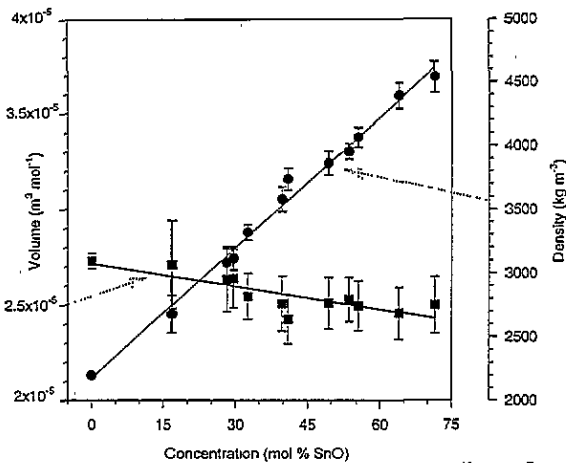
The analysed compositions and physical properties are summarized in table 1. The density and molar volume data are shown in figure 1, which shows that the molar volume  $V$  decreases with tin content  $c$  according to the relation

$$d(\ln V)/dc = -(0.16 \pm 0.11)\text{mol}^{-1}. \quad (1)$$

The Mössbauer spectra at 77 K of a series of samples with different concentrations of tin are shown in figure 2. It is seen that most of the tin exists in the  $2^+$  state, although a small amount of  $\text{Sn}^{4+}$  is present in each case. The spectra were fitted to two quadrupole doublets, one for each valence state. The lines were broad ( $\sim 1.15 \text{ mm s}^{-1}$ ) as expected

**Table 1.** The nominal and analysed composition, density, molar volume and linear expansivity ( $\alpha$ ) of SnO-SiO<sub>2</sub> glasses.

Nominal SnO content (mol%)	Analysed composition (mol%) $\pm 3\%$		Density ( $\rho$ ) $10^3 \text{ kg m}^{-3}$ $10^{-6} \text{ m}^3 \text{ mol}^{-1}$	Molar volume ( $V_m$ )	$\alpha \times 10^7 \text{ (K}^{-1}\text{)}$ [303-673 K]
	SnO	SiO <sub>2</sub>			
0.0	0.0	100.0	2.20	27.31	5.7
20.0	16.8	83.2	2.678	27.12	25.8
32.0	28.2	71.8	3.081	26.33	
33.3	29.6	70.4	3.116	26.37	44.1
40.0	32.6	67.4	3.318	25.44	42.5
47.2	39.7	60.3	3.579	25.06	
50.0	40.9	59.1	3.738	24.24	43.9
60.0	49.4	50.6	3.864	25.09	50.1
65.0	53.5	46.5	3.955	25.28	53.2
70.0	55.4	44.6	4.065	24.95	54.1
75.0	64.0	36.0	4.391	24.56	61.6
80.0	71.5	28.5	4.538	24.99	

**Figure 1.** The density and molar volume of binary SiO<sub>2</sub>-SnO glasses as a function of SnO content.

for a disordered system. Better fits could be obtained by fitting to two components with different quadrupole splittings and shifts for each site, and this reduced the linewidths to a more realistic value ( $\sim 0.9 \text{ mm s}^{-1}$ ), as shown in figure 3. However it was not possible with these data to get consistent values of the fitted parameters (shift, quadrupole splitting and relative area) over the whole range of composition and temperature. Hence, although the disorder is better modelled by considering two sites for the  $\text{Sn}^{2+}$ , the data did not allow an unambiguous fit to a more complicated model. So the spectra were fitted with two components and the values quoted are average values.

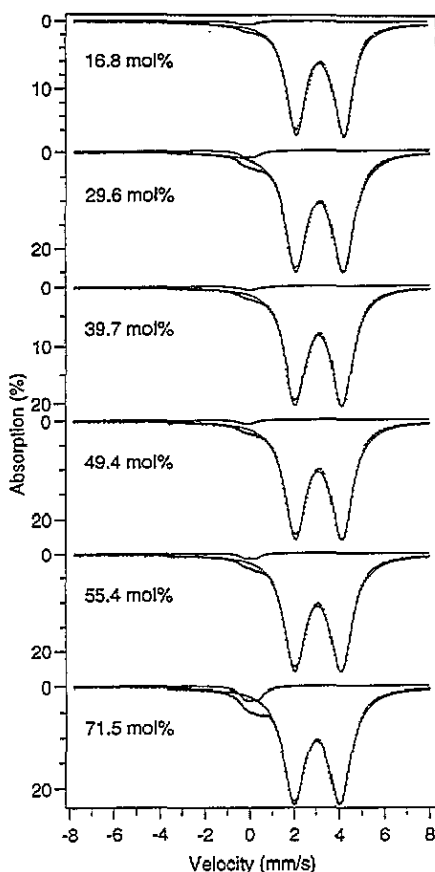


Figure 2. The Mössbauer spectra of  $^{119}\text{Sn}$  in binary  $\text{SiO}_2\text{-SnO}$  glasses at 77 K. The velocity scale is relative to  $\text{CaSnO}_3$  at room temperature.

### 3.2. Glass reactions during heat treatment

Carbo-Nover and Williamson [5] reported that a crystal phase, which they considered to be  $\text{SnSiO}_3$ , could be formed by devitrification of certain compositions of the binary  $\text{SnO-SiO}_2$  glass system in order to study phase formation in these materials. The binary glass containing 40.9 mol% of  $\text{SnO}$  underwent a series of heat treatments. A more detailed discussion of the behaviour of the other compositions will be given elsewhere. Because of the thermodynamic instability of  $\text{Sn}^{2+}$ , several changes can occur on heating under different conditions. This can be seen from the DTA trace in figure 4 for the 40.9 mol%  $\text{SnO}$  sample. This was obtained in air and, in addition to the glass transition  $T_g$ , three overlapping exotherms can be seen. These can be assigned to the following events: the broad feature centred on  $\sim 660^\circ\text{C}$  corresponds to crystallization; the second event centred on  $\sim 740^\circ\text{C}$  corresponds to decomposition; and the third event centred on  $\sim 780^\circ\text{C}$  to oxidation.

Using the DTA information, samples of the 40.9 mol%  $\text{SnO}$  glass were heat treated in air for (i) 3 h at  $670^\circ\text{C}$ , (ii) 4 h at  $730^\circ\text{C}$  and (iii) 5 h at  $770^\circ\text{C}$ . The temperatures chosen are slightly lower than the maxima to attempt to minimize the amount of concurrent reaction arising from the overlap with the neighbouring peak. Such overlap means that there is finite

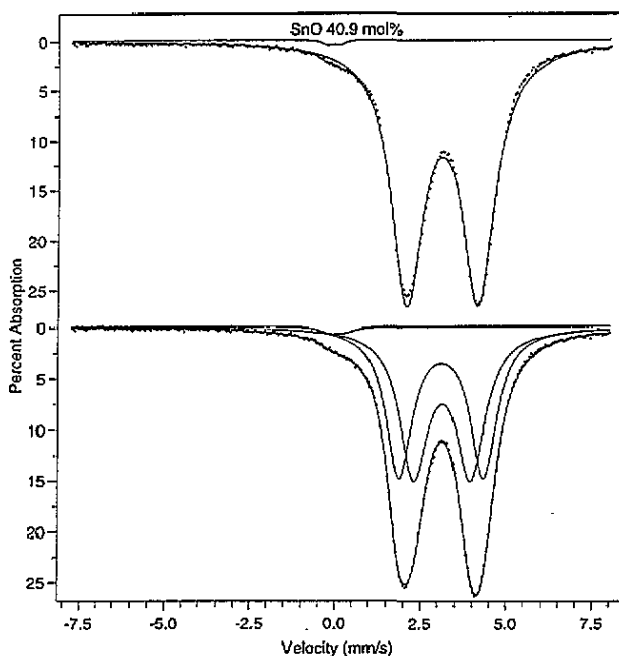


Figure 3. The Mössbauer spectra of the 40.9 mol% SnO glass at 77 K fitted to (a) a single  $\text{Sn}^{2+}$  doublet and (b) two  $\text{Sn}^{2+}$  doublets.

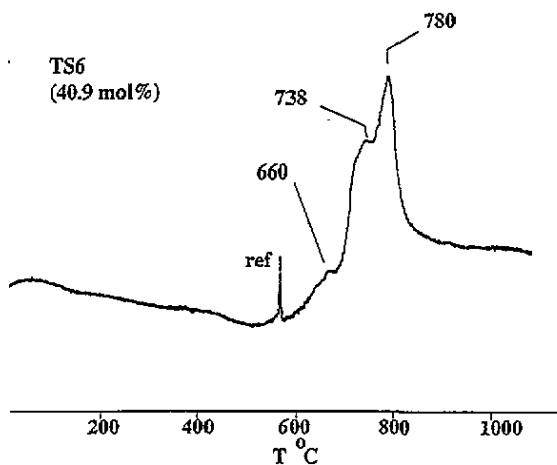


Figure 4. A DTA trace of the 40.9 mol% SnO glass heated in air.

reaction during the DTA experiment). In addition to the treatments in air, one sample was heat treated in argon at 600 °C for 4 h, in an attempt to avoid oxidative reactions. The resulting materials were examined by x-ray diffraction and Mössbauer spectroscopy.

The x-ray diffraction spectra are shown in figure 5 and show that some crystallization had occurred in all the heat-treated specimens. The main phases present were identified as  $\text{SiO}_2$ ,  $\text{SnO}_2$ , SnO and  $\text{SnSiO}_3$ .

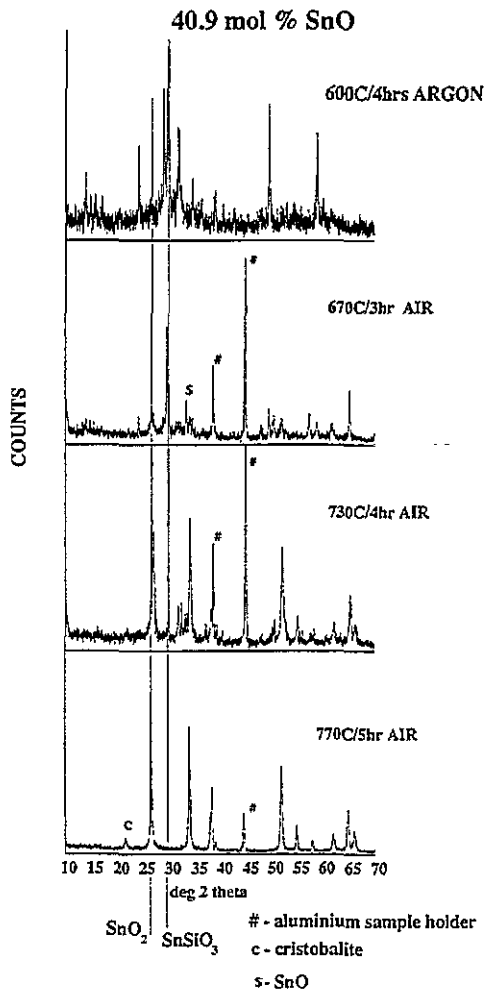


Figure 5. The x-ray powder diffraction patterns for the 40.9 mol% SnO glass heat-treated (a) in argon for 4 h at 600 °C, and in air (b) for 3 h at 670 °C (c) for 4 h at 730 °C and (d) for 5 h at 770 °C.

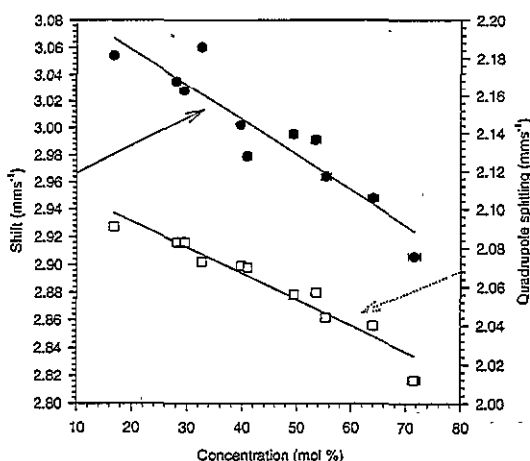
## 4. Discussion

### 4.1. The dependence of Mössbauer spectra on tin concentration

The isomer shifts of just over  $+3 \text{ mm s}^{-1}$  at room temperature are significantly greater than for crystalline and amorphous SnO ( $+2.68 \text{ mm s}^{-1}$  and  $+2.87 \text{ mm s}^{-1}$  respectively [1]) and the variation of the centre shift with tin concentration  $c$  is shown in figure 6. The isomer shift is a measure of the  $s$ -electron density at the Mössbauer nuclei and is given by

$$\delta^I = (2/5)\pi Ze^2 \Delta R^2 \Delta\rho(0) \quad (2)$$

where  $\Delta R^2$  is the change in the square of the nuclear radius in the Mössbauer transition,  $\Delta\rho(0)$  is the difference in electron densities at the Mössbauer nuclei in the source and absorber, and  $Ze$  is the nuclear charge. Since  $\Delta R^2$  is positive for  $^{119}\text{Sn}$ , a decrease in  $\delta^I$  corresponds to a decrease in the electron density  $\rho(0)$  at the nuclei.



**Figure 6.** The variation of the average centre shift  $\delta$  (●) and quadrupole splitting  $\Delta$  (□) at 77 K with SnO concentration.

The measured shift  $\delta$  is the sum of contributions from the second-order Doppler shift  $\delta^{SOD}$  and the isomer (chemical) shift  $\delta^I$ , i.e.

$$\delta = \delta^I + \delta^{SOD}. \quad (3)$$

Since  $\delta^{SOD}$  has only a weak dependence upon volume [6], the change in shift with tin concentration must arise principally from changes in the isomer shift. The slope of this curve was found to be

$$\partial\delta^I/\partial c = -(0.277 \pm 0.009) \text{ mm s}^{-1} \text{ mol}^{-1}. \quad (4)$$

As the tin content increases the density also increases and the change in volume will alter  $\delta^I$ . The effect of this may be of either sign and may be estimated from the change which accompanies thermal expansion, and will be discussed in section 4.3.

The quadrupole splittings of 2.00–2.05 mm s<sup>-1</sup> at room temperature are greater than those of crystalline SnO (1.36 mm s<sup>-1</sup> [1]) and amorphous SnO (1.71 mm s<sup>-1</sup> [1]), and decrease as the tin content is increased, i.e. as the molar volume decreases, as shown in figure 6. The slope was found to be

$$\partial\Delta/\partial c = -(0.135 \pm 0.009) \text{ mm s}^{-1} \text{ mol}^{-1}. \quad (5)$$

The quadrupole splitting is a measure of the distortion of the environment of the tin atom from cubic symmetry. The decrease in quadrupole splitting with increasing tin content shows that the environment is becoming more symmetrical, outweighing the effect of the decrease in molar volume which would increase it, and is consistent with a decrease in the number of p-electrons on the tin atoms [7].

The linewidths were equal and were broad ( $\sim 1.05$  mm s<sup>-1</sup> for the glass containing least tin and 1.15 mm s<sup>-1</sup> for the remainder) compared with those observed for SnO (0.99 mm s<sup>-1</sup>). Some broadening arising from the random distribution of tin atoms in the glass would be expected, but the fact that the isomer shift and quadrupole splitting are correlated and decrease as the amount of tin is increased (figure 6) would lead to an unequal broadening of the lines with the higher energy line being broadened the most, i.e. it would have the smaller depth. This is in conflict with the observation that this line is slightly deeper for all the samples (see e.g. figures 2 and 3). Since texturing of disordered samples is



unlikely, we conclude that the Mössbauer  $f$ -factor is anisotropic (the Gol'danskii-Karyagin effect [8]).

#### 4.2. The dependence of Mössbauer spectra on temperature

The Mössbauer spectra of the 53.5 mol% glass are shown for different temperatures in figure 7. The width of the  $\text{Sn}^{2+}$  lines remained constant but the asymmetry of the intensities of the two lines increased as the temperature increased confirming that it arose from the Gol'danskii-Karyagin effect.

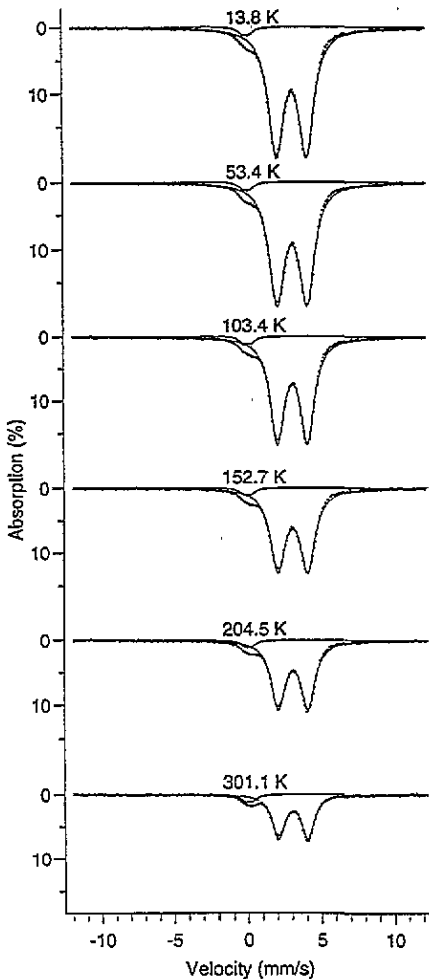


Figure 7. The Mössbauer spectra of the 53.5 mol% SnO glass at temperatures between room temperature and 13.8 K.

The area  $A$  of the  $\text{Sn}^{2+}$  component of the Mössbauer spectrum increased with decreasing temperature as expected, and was used to deduce the  $f$ -factor and the Debye temperature  $\Theta_D$  for the tin atoms. The Debye model is of course not strictly applicable to these glasses, but it is useful in parametrizing the data to make a comparison between different samples.

According to the Debye model

$$f = \exp \left\{ -\frac{3}{2} \frac{E_R}{k\Theta_D} \left[ 1 + 4 \left( \frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{xdx}{e^x - 1} \right] \right\}. \quad (6)$$

In the high temperature ( $T > \Theta_D/2$ ) limit

$$\ln f = -\frac{6E_R T}{k\Theta_D^2} \quad (7)$$

where  $E_R$  is the recoil energy of the  $\gamma$ -ray ( $2.572 \times 10^{-3}$  eV for  $^{119}\text{Sn}$ ). If the fraction of the 23.8 keV  $\gamma$ -rays is constant,  $f$  is proportional to  $A$ . Hence a graph of  $\ln A$  versus  $T$  is a straight line with slope  $-6E_R/k\Theta_D^2$  and may be used to determine  $\Theta_D$ . The data gave

$$\partial \ln f / \partial T = -(4.93 \pm 0.03) \times 10^{-3} \text{ K}^{-1} \quad (8)$$

for the 32.6% Sn glass, and slightly more for the 53.5% Sn sample. Hence for the  $\text{Sn}^{2+}$  ions  $\Theta_D = 191$  K and 181 K, respectively, for the two glasses. These values are somewhat lower than that (204 K) found for crystalline SnO but higher than amorphous SnO (181 K) [1]. (We were unable to obtain the corresponding information for the  $\text{Sn}^{4+}$  component due to the small amount which was present.) By adjusting the plot of  $\ln A$  versus  $T$  so that the high temperature linear portion kept the same slope but passed through the origin when extrapolated, the plots of  $\ln f$  versus  $T$  given in figure 8 were generated. The curves in the figure are fits to the Debye formula (6).

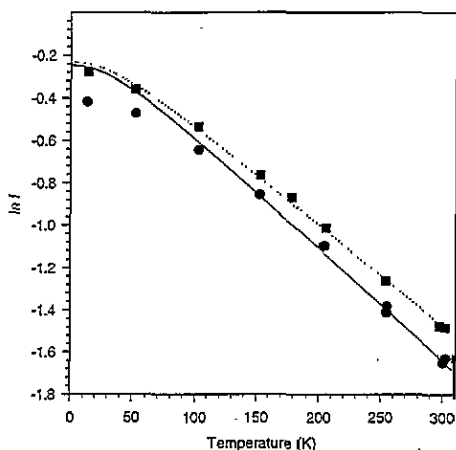


Figure 8. The temperature variation of the Mössbauer  $f$ -factor for the 32.6 (■) and 53.5 mol% SnO (●) glasses. The curves correspond to  $\Theta_D = 191$  K (.....) and  $\Theta_D = 181$  K (—).

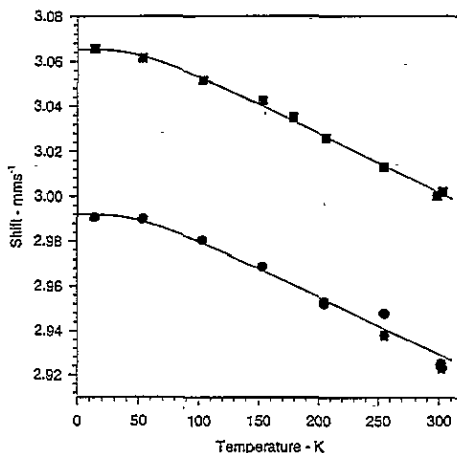


Figure 9. The variation of the centre shift  $\delta$  with temperature for the 32.6 (■) and 53.5 mol% SnO (●) glasses. The curves are fits to the Debye model with  $\Theta_D = 190$  K.

The centre shifts  $\delta$  of  $\text{Sn}^{2+}$  for the samples containing 32.6 and 53.5 mol% tin oxide are shown as a function of temperature in figure 9. Above 100 K the shift decreased linearly with temperature with a slope which was the same within experimental error for both samples and was

$$\partial \delta / \partial T = -(2.80 \pm 0.10) \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1} \quad (9)$$

The contribution to this from the second-order Doppler shift is given [11] by

$$\delta^{SOD} = -U/2MNC \quad (10)$$

where  $U$  is the internal energy, and  $M$  is the mass of the Mössbauer nuclei and  $N$  is the number of atoms. According to the Debye model  $U$  is given by

$$U = \frac{9Nk\Theta_D}{8} \left[ 1 + 8 \left( \frac{T}{\Theta_D} \right)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} \right]. \tag{11}$$

At high temperatures ( $T > \Theta_D$ )  $\delta^{SOD}$  is independent of  $\Theta_D$  and is linear with temperature according to

$$\delta^{SOD} = -3kT/2Mc \tag{12}$$

and for  $^{119}\text{Sn}$  this gives a slope of

$$\partial\delta^{SOD}/\partial T = -(3.5 \times 10^{-4}) \text{ mm s}^{-1}\text{K}^{-1}. \tag{13}$$

The temperature dependence of the isomer shift is the difference between (9) and (13) and is

$$\partial\delta^I/\partial T = +(0.70 \pm 0.10) \times 10^{-4} \text{ mm s}^{-1}\text{K}^{-1}. \tag{14}$$

The variation of the quadrupole splitting with temperature for the same two glasses is shown in figure 10. At temperatures above 100 K this showed a linear dependence upon temperature according to

$$\partial\Delta/\partial T = -(2.50 \pm 0.10) \times 10^{-4} \text{ mm s}^{-1}\text{K}^{-1} \tag{15}$$

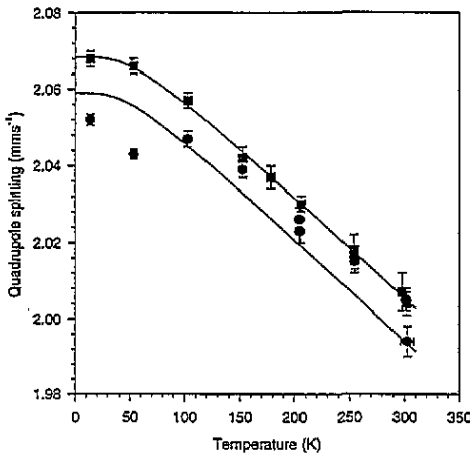


Figure 10. The variation of the quadrupole splitting  $\Delta$  with temperature for the 32.6 (■) and 53.5 mol% SnO (●) glass.

### 4.3. The dependence of Mössbauer spectra on volume

The change in isomer shift arising from the volume change when the tin content is varied may be related to the effects of pressure [6, 9] and thermal expansion [10].

The variation with temperature given by (14) shows that the electron density at the tin nuclei increases with temperature, i.e. there is an intrinsic dependence on molar volume. If it is assumed that this may be described by the thermal expansion, it may be related to the change of isomer shift with tin concentration by

$$\frac{\partial\delta^I}{\partial T} = \beta \frac{\partial\delta^I}{\partial c} \bigg/ \frac{\partial \ln V}{\partial c} \tag{16}$$

where  $\beta$  is the volume expansivity.

The values of  $\partial \ln V/\partial c$  (1) and  $\beta = 3\alpha$  (table 1) together with the deduced value of  $\partial \delta^I/\partial T$  (14) lead to a predicted contribution of  $-(0.74 \pm 0.51) \text{ mm s}^{-1} \text{ mol}^{-1}$  to  $\partial \delta^I/\partial c$ . This figure has large errors because of the uncertainty in the value of  $\partial \ln V/\partial c$  but it is considerably lower than the observed value of  $-0.277 \text{ mm s}^{-1} \text{ mol}^{-1}$  (2). It therefore appears that the volume-corrected isomer shift *increases* with concentration approximately according to

$$\partial \delta^I/\partial c_{\text{vol corr}} = +(0.46 \pm 0.51) \text{ mm s}^{-1} \text{ mol}^{-1}. \quad (17)$$

An expression for  $\delta^I$  which extends over the whole temperature range may be obtained by integrating (16) and using Grüneisen's law that the expansivity decreases at low temperatures and is proportional to the heat capacity at constant volume. Hence  $\int \beta dT$  is proportional to the internal energy  $U$  and

$$\delta^I = \delta_0 + \frac{\beta_\infty}{3} \frac{U}{Nk} \frac{\partial \delta^I}{\partial c} \bigg/ \frac{\partial \ln V}{\partial c} \quad (18)$$

where  $\beta_\infty$  is the high-temperature expansivity. Thus both  $\delta^I$  and  $\delta^{SOD}$  are proportional to  $U$ . The solid curves in figure 9 are fits to  $\delta$  using (13) and (18) with the values of  $\Theta_D$  which were obtained from the  $f$ -value data.

The decrease in quadrupole splitting as the temperature is increased is small but larger than would be expected from thermal expansion. The curves in figure 10 were calculated assuming that the changes are due to expansion according to Grüneisen's law ( $\beta \propto C_v$ ) and give an unrealistically high value for  $\beta$ . Hence the effect of increasing the temperature must be to change the structure (e.g. the O-Sn-O angles) in a way which increases the local symmetry around the tin atoms.

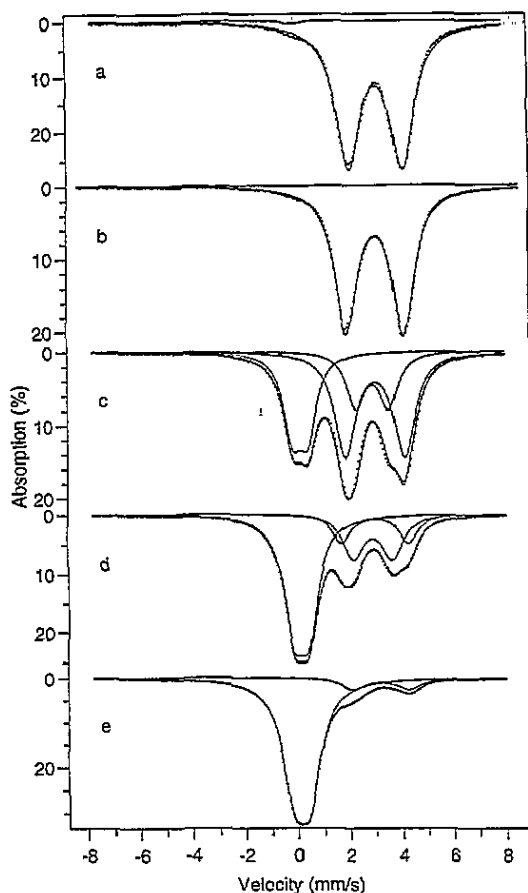
#### 4.4. The effect of heat treatment

The Mössbauer spectra of the heat-treated 40.9% samples are shown in figure 11 and the results are given in table 2. The spectra of the sample before and after heat treatment in argon are shown in figures 11(a) and (b) respectively. They were each fitted to a single quadrupole doublet with isomer shift  $\delta_1$  and quadrupole splitting  $\Delta_1$ . The sample heat treated in argon showed no detectable increase in  $\text{Sn}^{4+}$  over the small amount present in the initial glass, but there were small changes in  $\delta_1$  and  $\Delta_1$  which are presumably associated with the crystallization which is evident in the x-ray diffraction pattern (figure 5(a)).

Table 2. Shifts and quadrupole splittings of the 40.9 mol% SnO glass after heat treatment.

	$\delta_1$	$\Delta_1$	$\delta_2$	$\Delta_2$	$\delta_3$	$\Delta_3$
unheated	2.98	2.07	—	—		
argon/4h/600°C	2.93	2.20	—	—		
air/3h/670°C	2.89	2.28	2.79	1.25	0.13	0.59
air/4h/730°C	2.87	2.58	2.80	1.50	0.14	0.56
air/5h/770°C	3.06	2.15	—	—	0.14	0.60

Figures 11(c), (d) and (e) show the spectra for the samples heat treated in air. It is immediately seen that there was considerable oxidation to  $\text{Sn}^{4+}$  with isomer shift  $\delta_3$  and quadrupole splitting  $\Delta_3$ , the amount of which increased as the temperature of heating increased. It can be seen that the  $\text{Sn}^{2+}$  spectrum splits into two doublets, one of which



**Figure 11.** The Mössbauer spectra at 77 K of the 40.9 mol% SnO glass (a) before heat treatment (b) when heat treated in argon for 4 h at 600 °C and when heat treated in air for (c) 3 h at 670 °C (d) 4 h at 730 °C and (e) 5 h at 770 °C.

has almost the same parameters ( $\delta_1$  and  $\Delta_1$ ) as that of the untreated sample while the other has a similar shift ( $\delta_2$ ) and a smaller quadrupole splitting ( $\Delta_2$ ). The possible  $\text{Sn}^{2+}$  species present are  $\text{Sn}^{2+}$  in glass,  $\text{Sn}^{2+}$  in  $\text{SnSiO}_3$  and  $\text{Sn}^{2+}$  in  $\text{SnO}$ . The doublet with the smaller quadrupole splitting (1.2–1.4  $\text{mm s}^{-1}$ ) seems to correspond to crystalline  $\text{SnO}$  (which has a value of 1.36  $\text{mm s}^{-1}$ ). Therefore, the doublet with the larger quadrupole splitting must incorporate  $\text{Sn}^{2+}$  in  $\text{SnSiO}_3$  and any  $\text{Sn}^{2+}$  remaining in the glass phase.

## 5. Conclusions

When the isomer shift is corrected for the change in volume, it is found to increase slightly as the tin content increases. This corresponds to an increase in s-electron density at the nuclei and is consistent with the decrease in quadrupole splitting which suggests that there is a decrease in the number of p-electrons [7]. These facts suggest that the tin becomes slightly less covalent (or possibly that its co-ordination number increases) with increasing concentration of tin.

The Debye temperature decreases as the amount of tin increases and the reduction in

the strength of the chemical binding supports the decrease in covalency (or increase in ionic binding) suggested by the isomer shift data.

A possibility is that small amounts of  $\text{Sn}^{2+}$  enter the  $\text{SiO}_2$  glass network with 4-fold co-ordination substituting for silicon as a network former, but that as the amount of tin increases there is an increasing tendency towards 6-fold co-ordination (i.e. to ionic bonding in interstitial sites as a network modifier).

## References

- [1] Collins G S, Kacknowski T, Benczer-Koller N and Pasternak M 1979 *Phys. Rev. B* **19** 1369
- [2] Mitrofanov K P and Sidorov T A 1967 *Sov. Phys.—Solid State* **9** 693  
Bartenev G M, Magomedev G M, Tsyganov A D and Zelenev Yu V 1976 *Sov. J. Glass Phys. Chem.* **2** 114  
Dannheim H, Oel H J and Tomandl G 1976 *Glastechn. Ber.* **49** 170  
Nishida T 1995 *Hyper. Int.* **95** 23
- [3] Holland D, Karim M M, Johnson C E, Williams K F E and Johnson J A 1993 *Fundamentals of Glass Science and Technology (Supp. to Revista della Stazione Sperimentale del Vetro)* vol XXIII p 223
- [4] Johnson J A, Johnson C E, Williams K F E, Holland D and Karim M M 1995 *Hyper. Int.* **95** 41
- [5] Carbo-Nover J and Williamson J 1967 *Phys. Chem. Glasses* **8** 164
- [6] Williamson D L 1978 *Mössbauer Isomer Shifts* ed G K Shenoy and F E Wagner (Amsterdam: North-Holland) p 317
- [7] Flinn P A 1978 *Mössbauer Isomer Shifts* ed G K Shenoy and F E Wagner (Amsterdam: North-Holland) p 593
- [8] Gol'danskii V I, Gorodinskii G M, Karyagin S V, Korytko L A, Kryzhanskii L M, Markorov E F, Suzdalev I P and Khrapov V V 1962 *Dokl. Acad. Nauk.* **147** 127; 1963 *Sov. Phys. Dokl.* **147** 766
- [9] Pound R V, Benedek G B and Drever R 1961 *Phys. Rev. Lett.* **7** 405
- [10] Rothberg G M, Guimard S and Benczer-Koller N 1970 *Phys. Rev. B* **1** 136
- [11] Josephson B D 1960 *Phys. Rev. Lett.* **4** 341