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The ^{121}Sb Mössbauer spectra of antimony-containing glasses

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The ^{121}Sb Mössbauer spectra of a series of $Na_2O-B_2O_3-Sb_2O_3$, $(Na_2O, 2P_2O_5) + Sb_2O_3$, and $(Na_2O, 2SiO_2) + Sb_2O_3$ glasses have been measured. The chemical isomer shifts, δ, and the quadrupole couplings, eQV_{zz}, for antimony (III) in different glasses have been estimated. From the changes of isomer shift is has been deduced that the ionicity of the Sb–O bond increases with decreasing Na_2O content in $Na_2O-B_2O_3-Sb_2O_3$ glasses; and when the network former is changed, with equivalent molar composition, the ionicity of the Sb–O bond increased in the order borate $\leqslant$ silicate $<$ phosphate.

1. Introduction

Sb_2O_3 is a glass former; molten Sb_2O_3 when cooled rapidly produces a clear transparent glass [1]. Although the use of Sb_2O_3 in conventional glasses is only limited in small (about 0.5 wt%) additions as refining agent [2], it has a potential as a major constituent in low-loss glass fibres for communication purposes. This is due to the fact that a substantial amount of Sb_2O_3 can be dissolved in other glass-forming oxides like SiO_2, B_2O_3, P_2O_5 etc; usually these binary mixtures are low melting, and various antimony (III) compounds having high vapour pressures are available with high purity. Unfortunately the structural role of Sb_2O_3 in glass-forming melts is not clearly known. Thus in this investigation we have studied the Mössbauer spectra of Sb_2O_3-containing glasses of controlled compositions to determine the changes in Sb–O bonding in various glasses.

2. Experimental

The chemical compositions of glasses are given in Table I, and shown in Fig. 1 in a three component diagram. Glass compositions were varied systematically in three ways:

(1) Series A (glasses 1 to 4): different amounts of Sb_2O_3 were mixed with a parent melt of Na_2O, $2B_2O_3$ composition. Thus in all these glasses the sodium oxide to boric oxide ratio was constant (1:2).

(2) Series B (glasses 2, 5 and 6): in this series a constant amount of Sb_2O_3 (about 5 mol%) was mixed with a series of sodium borate melts in which the sodium oxide to boric oxide ratio was varied from 0.11 to 0.50.

(3) Series C (glasses 2, 7 and 8): here a constant amount of Sb_2O_3 (about 5 mol%) was dissolved in a series of different glasses having the same network former to network modifier ratio (2:1); the nature of the network former was varied from B_2O_3 to SiO_2 to P_2O_5.

All the batch materials Na_2CO_3, H_3BO_3, NaH_2PO_4, $NH_4H_2PO_4$, Sb_2O_3 were of Analar quality. Acid-washed Indian quartz (iron content less than 0.002 wt% as Fe_2O_3) was used as source of silica. All the glasses were melted in fused silica crucibles at different temperatures in a controlled atmosphere furnace. The effective p_{O_2} in the furnace atmosphere was adjusted to $\sim 10^{-6}$ atmosphere so as to minimize the oxidation of Sb_2O_3 to Sb_2O_5. Melting history of all the glasses is also given in Table I. After 3 h melting the melts were air-quenched, and crushed to fine powder for chemical analysis and Mössbauer measurements.

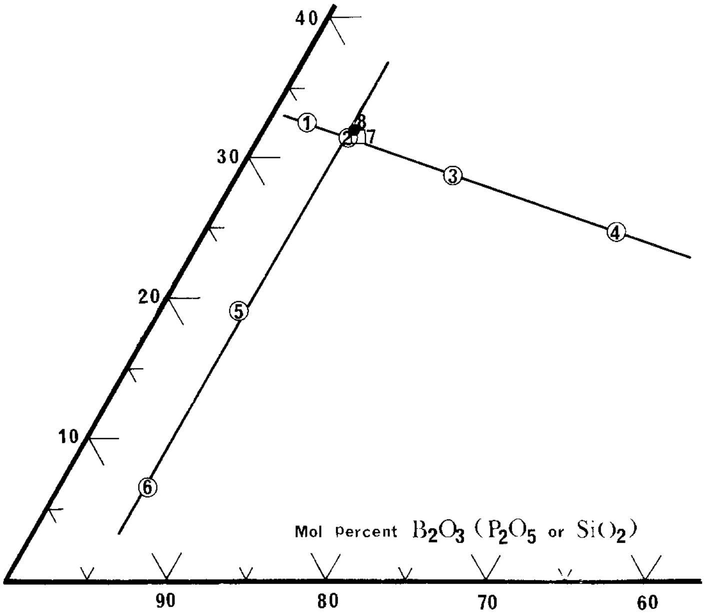

Figure 1 Chemical composition of glasses.

All the major components of glass (Na_2O, B_2O_3, P_2O_5 and SiO_2) were estimated with conventional analytical methods. Total antimony was estimated with potassium iodide [3], and antimony (III) with iodine monochloride [4]; antimony (V) was calculated from the difference of total and trivalent antimony.

For Mössbauer measurements the source used was a $Ba^{121}SnO_3$ (1 mCi) obtained from New England Nuclear Corporation. The 37.2 keV γ radiation was detected using a Xe/methane proportional counter, counting on the 6 keV escape peak. Absorbers were prepared by mixing a finely ground sample, containing about 10 mg antimony, with grease and spreading the mull over a thin aluminium foil 1 cm^2 in area. Both source and absorber were maintained at 4.2 K throughout the experiment. The spectrometer was calibrated initially using a Michelson interferometer and checked by means of an Fe_2O_3 absorber.

The Mössbauer spectra were computer-fitted by a least square procedure to the sum of eight Lorentzian peaks as previously reported [5].

3. Results and discussion

The ^{121}Sb Mössbauer parameters for the glasses described in this work are given in Table II. The data show that the antimony in all these glasses is predominantly in the 3+ oxidation state but that small amounts of antimony (V) are formed during their preparation; this is consistent with the results of chemical analysis as shown in Table I. The chemical shifts of the minor antimony (V) phases are similar to those in other compounds containing antimony (V) in oxide and antimonates [6].

The chemical isomer shift, δ, depends upon the s-electron density at the antimony nucleus, and a more negative value of δ corresponds to an increase in the s-electron density. All antimony (III) compounds have large negative shifts relative to a

TABLE I Chemical composition (after analysis) and melting history of different glasses.

Glass no.	Mol %						Melting (° C) temperature
	Na_2O	B_2O_3	P_2O_5	SiO_2	Sb_2O_3	Sb_2O_5	
1	32.50	65.00	–	–	2.48	0.02	1000
2	31.51	63.03	–	–	5.40	0.06	1000
3	28.88	57.77	–	–	13.34	0.01	1000
4	24.76	49.51	–	–	25.72	0.01	1000
5	19.16	76.43	–	–	4.38	0.02	1000
6	7.34	88.13	–	–	4.51	0.02	1000
7	31.50	–	63.00	–	5.49	0.02	850
8	31.69	–	–	63.37	4.89	0.05	1400

TABLE II Mössbauer parameters of different glasses

Glass no.	Major glass phase			Minor glass phase		
	δ^* ± 0.1 mm sec^{-1}	eQV_{zz} ± 1.0 mm sec^{-1}	Γ ± 1.0 mm sec^{-1}	δ ± 0.1 mm sec^{-1}	eQV_{zz} ± 1.0 mm sec^{-1}	Γ ± 1.9 mm sec^{-1}
1	−11.4	+16.5	3.6	0.7	0	2.9
2	−11.6	+18.7	3.4	0.6	0	3.2
3	−11.5	+18.8	3.3	–	–	–
4	−11.5	+17.4	3.2	–	–	–
5	−11.9	+17.9	3.2	0.6	0	2.6
6	−12.4	+19.8	4.1	0.9	0	2.8
7	−14.7	+15.2	4.0	1.3	0	2.8
8	−12.0	+16.9	3.8	0.9	0	2.9
Sb_2O_3	−11.3	+18.8				

δ^* Relative to the $Ba^{121}SnO_3$ source.
†eQV_{zz} Constrained to zero, since the peak was narrow and symmetrical.

$Ba^{121}SnO_3$ source and the negative value increases with increasing ionic character towards the antimony (III) ion with $5s^2$ configuration. All antimony (V) compounds have small negative, or positive shifts from $Ba^{121}SnO_3$. Increase in the positive value of the shift shows an increase in ionic character of antimony (V) towards the $4d^{10}$ $5s^{\circ}$ configuration; a schematic diagram is shown in Fig. 2.

The quadrupole splitting (coupling constant, eqV_{zz}) of a Mössbauer resonance line arises from the presence of an electric field gradient at the antimony nucleus. This field gradient will result from any imbalance in the distribution of the antimony p- or d-electron density.

The Mössbauer parameters for glasses 1 to 4 show no change in the value of the chemical shift as compared with that of Sb_2O_3 as the concentration of Sb_2O_3 in the glasses is increased from 2.5 to 25.7 mol%. This suggests that there is no strong interaction between Sb_2O_3 and sodium diborate glass, or in other words molten Sb_2O_3 and Na_2O, $2B_2O_3$ produce almost a regular solution. However, the quadrupole coupling constant for glass 1 is significantly smaller than that for Sb_2O_3. This means that there is a smaller electric field gradient at the antimony nucleas than in Sb_2O_3, that is, the electron distribution around the antimony centre in this glass is more symmetrical than that around Sb_2O_3. Glass 1 has the lowest concentration of Sb_2O_3 and the smaller coupling constant can be explained if the Sb_2O_3 is distributed uniformly throughout the glass in such a way that there is very little interaction between neighbouring Sb–O polyhedra.

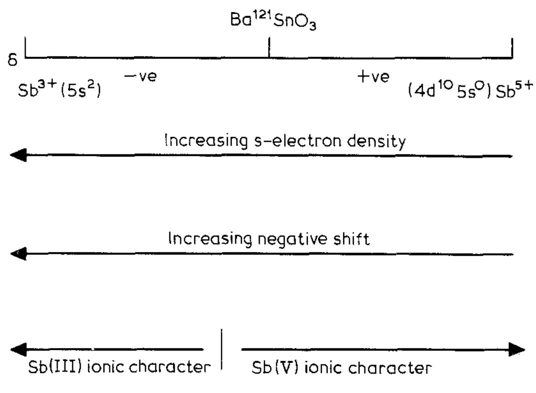

Figure 2 Schematic diagram for the isomer shift of antimony (III) and antimony (V).

In the second series of glasses (series B) the concentration of Na_2O in the glass is varied. There is a significant trend of increasing negative shift as the concentration of Na_2O is decreased. The change in shift is consistent with an increase in ionicity of the Sb–O bond as the amount of Na_2O is decreased; this is indeed a general observation with many other probe ions in binary alkali borate systems [7]. There is, however, no evidence of discontinuity around 20 mol% soda as has been reported for other sodium borate glasses [8].

The results for the third series of glasses (series C) show a significant trend of increasing negative shift as the glass former changes from B_2O_3 to SiO_2 and finally to P_2O_5. Although the chemical shifts in glasses 2 and 8 are not very different it should be pointed out that the atomic ratio of network former to network modifier in glass 2 is 2 whereas that in glass 8 it is 1. Thus it appears that borate and silicate groups do not exert the same influence on Sb–O bonding in glass. However, the chemical shift for the phosphate glass is much more negative than any other of the glasses. This shows that the Sb–O bond in phosphate glass is much more ionic than that in Sb_2O_3. The quadrupole coupling constant for this glass is also much smaller than any of the other glasses of the present investigation. This could be due to stronger interaction of Sb_2O_3 with P_2O_5 so much so that the electric field gradient around the antimony (III) centre has become more symmetrical.

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