Investigations on sodium tin phosphate and tin pyrophosphate glasses

K C SOBHA and K J RAO*

Materials Research Centre, Indian Institute of Science, Bangalore 560012, India

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Abstract. Glasses of the alkali tin phosphate system have been investigated. The infrared absorption and fluorescence spectra of the glasses have been examined. It is found that tin is present in both $+2$ and $+4$ oxidation states. Also tin ions occupy four- or six-coordinated sites in the glass.

Keywords. Tin glasses; tin pyrophosphate; NASICON; flame melting.

1. Introduction

Tin oxides are special constituents of commercial glasses, added mainly to improve the stability of the glasses (Tick 1984; Musić *et al* 1991). But reported studies on glasses with tin oxide (SnO or SnO_2) as the main constituent are rather few. From the Mössbauer study of the ^{119}Sn nucleus (Evtrop'ev *et al* 1970), it has been found that Sn is present mainly as Sn^{4+} ions in silicate and borate glasses whereas it is present only as Sn^{2+} ions in phosphate glasses. The compound sodium tin phosphate $NaSn_2(PO_4)$, which is a NASICON-type material (NASICON is the acronym for Na-Super ionic conductor, based on $NaZr_2(PO_4)_3$ (Goodenough *et al* 1976, Alamo and Roy 1986)) forms a glass when melted in a graphite crucible using an oxy-butane flame. In this paper we present the results of our investigations on some alkali tin phosphate glasses and tin pyrophosphate glass prepared using the above method.

2. Experimental

Crystalline $NaSn_2(PO_4)_3$ was prepared from Analar Grade Na_2CO_3, SnO_2 and diammonium hydrogen phosphate. The reactants were mixed thoroughly and heated to 573 K to decompose the diammonium hydrogen phosphate. The mixture was again ground and heated at 1073 and 1273 K for 12 h each with intermittent grinding. A similar procedure was adopted to make compositions of $LiSn_2(PO_4)_3$ and $KSn_2(PO_4)_3$. These compositions were melted in graphite crucibles by directly contacting an oxy-butane flame. Drops of the melt were quenched into glass between stainless steel plates. The batches melt incongruently with loss of material, but ultimately result in a good glass-forming melt. The NSP glass pieces (obtained from $NaSn_2(PO_4)_3$) were powdered and mixed with $NaPO_3$ glass powder (which had been initially made by melting $NaPO_3$ in an electric furnace at 1173 K) and the batches were again melted using the flame and quenched into glasses. For preparing the tin pyrophosphate, appropriate amounts of SnO and $(NH_4)_2H(PO_4)$ were mixed and

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*For correspondence

heated at 573 K (5 h), ground and heated at 1073 K (10 h). The batch was then melted using the flame and quenched. Compositions were analysed using an EDAX-AN-10000 X-ray analyser attached to an S-360 Cambridge scanning electron microscope. The glass transition temperature (T_g) and the heat capacities $(C_p$'s$)$ were determined using a Perkin–Elmer DSC-2 Differential Scanning Calorimeter. Dry nitrogen was used as purge gas. T_g was determined from a 20 K/min scan. For the specific heat determination, the NSP sample was first annealed at temperatures about 20 K below T_g and scans for the specific heat measurements were carried out at 10 K/min. Single crystalline sapphire was used as standard for C_p measurement. The infrared transmission spectra were recorded from 4000 to 200 cm^{-1} using a Perkin–Elmer 580 double beam IR spectrometer using pellets of the glass powder with KBr. The Fourier Transform IR (FTIR) spectra were recorded using a Bruker IFS 113 FTIR spectrometer. Pellets of the glass powder in polyethylene were used for recording the FTIR spectra. The fluorescence excitation and emission spectra were recorded using a Shimadzu spectrofluorophotometer Model RF-510 and a 150W xenon lamp. Band widths for both excitation and emission were 10 nm.

3. Results and discussion

The energy dispersive X-ray analysis (EDAX) patterns for $Sn_2(PO_4)_3$ compound and the glass obtained by melting it (NSP) and quenching are given in figure 1. EDAX was not accurate for analysing Na and hence it could not be determined. The EDAX for the glass gave a proportion of Sn:P = 52:48 which clearly shows enrichment of glass composition with respect to Sn. In fact it is almost the composition of pyrophosphate glass. Tin pyrophosphate glass showed Sn:P ratio of 53:47 suggesting very little loss of components from the glass during melting. Glasses have been prepared based on NSP glass itself as one of the constituents with $NaPO_3$ (NP) as the other constituent. Several binary NSP-NP glasses have been examined in this system. A glass containing some added SnO_2 (which readily dissolves in molten NSP) has also been studied. Various glass compositions are listed in table 1.

The T_g values for the Li, Na and K containing glasses (designated as LSP, NSP and KSP glasses respectively) estimated from the DSC were found to be very close (525, 529 and 530 K respectively). The specific heat variation of the NSP glass is shown in figure 2. Molar heat capacities have not been calculated in view of the compositional uncertainty and even possible contamination with carbon from the graphite crucible.

The infrared spectra of LSP, NSP and KSP glasses are shown in figure 3, along with that of crystalline $NaSn_2(PO_4)_3$. The change in composition is reflected in the spectra. The infrared spectrum of $Sn_2P_2O_7$ glass is shown in figure 4, along with that of $Pb_2P_2O_7$ glass (taken from Ananthraj 1991).

The T_g of $Sn_2P_2O_7$ glass is 525 K while the reported value of T_g of $Pb_2P_2O_7$ is 638 K (Ananthraj 1991). The similarity of the IR spectra of the two pyrophosphate glasses is striking. The IR spectra of $Sn_2P_2O_7$ and $Pb_2P_2O_7$ glasses are almost identical. The $Pb_2P_2O_7$ glass has been studied by Ananthraj *et al* (1991) and it is found that, in addition to the pyrophosphate units, rings of phosphate tetrahedra and isolated $[PO_4]^{3-}$ ions are also present in the glass, which are produced through the structural disproportionation given below
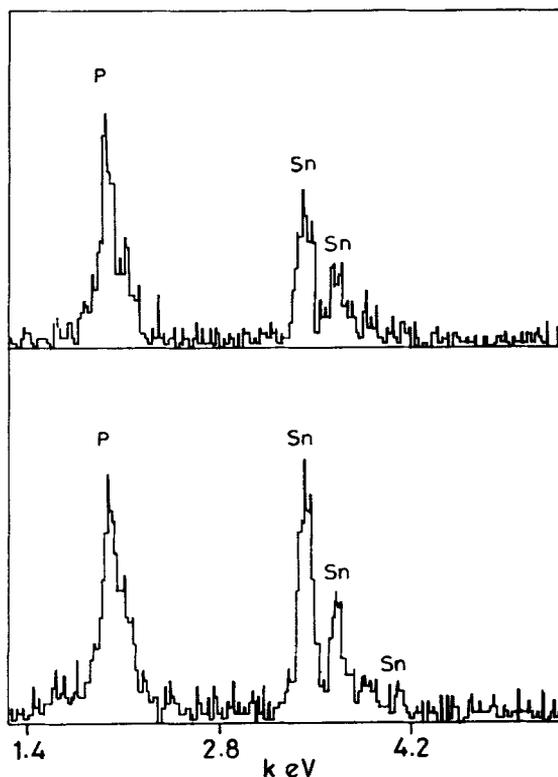
$$2P_2O_7^{4-} \rightleftharpoons PO_4^{3-} + P_3O_{10}^{5-} \qquad (1)$$
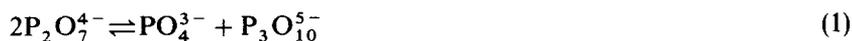
Figure 1. X-ray energy dispersive analysis (EDAX) patterns of crystalline $NaSn_2(PO_4)_3$ and the NSP glass.

Table 1. Glass composition and glass transition temperatures (T_g) of the glasses in the NSP–NP–SnO$_2$ system.

No.	Composition NSP, NP, SnO$_2$ (weight %)	T_g (K)
1	0·8, 0, 0·2	560
2	1, 0, 0	529
3	0·8, 0·2, 0	522
4	0·6, 0·4, 0	527
5	0·4, 0·6, 0	531
6	0·2, 0·8, 0	539
7	0, 1, 0	566

or in general

$$2P_nO_{3n+1}^{(n+2)-} \rightleftharpoons P_{n-1}O_{3(n-1)+1}^{[(n-1)+2]} + P_{n+1}O_{3(n+1)+1}^{[(n+1)+2]-}. \tag{2}$$
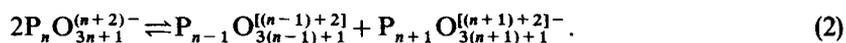
The $717\,cm^{-1}$ band has been attributed to P–O–P bending vibrations from ring structures and the shoulder at $1100\,cm^{-1}$ to orthophosphate ions. Similar assignments
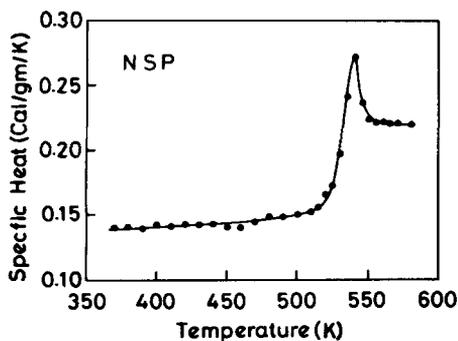
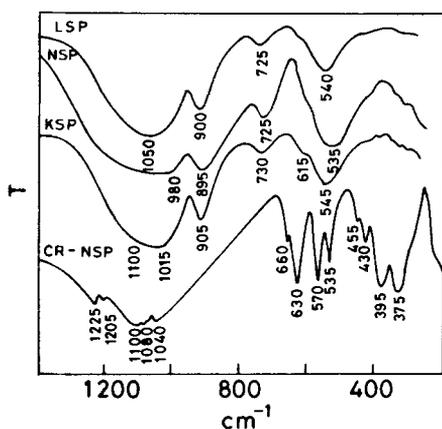**Figure 2.** Specific heat variation of the NSP glass with temperature.

Figure 3. Infrared spectra of LSP, NSP and KSP glasses and crystalline $NaSn_2(PO_4)_3$ (CR-NSP).

hold good for the tin pyrophosphate glass also, and we may conclude that the behaviour of tin is exactly similar to that of lead in glasses. Presence of lead in four- as well as six-coordinated positions has been established in many glasses (Damodaran *et al* 1988; Selvaraj and Rao 1988; Ananthraj 1991). The shoulder at $1150\,cm^{-1}$ and $910\,cm^{-1}$ indicate the presence of pyrophosphate units as found in our IR study on glasses with NASICON chemistry (Sobha and Rao 1995) as well as the crystalline pyrophosphates investigated by Ananthraj *et al* (1986) and Ananthraj (1991).

The T_g values obtained for the various NSP-NP glass compositions are tabulated in table 1. Highest T_g is exhibited by the $NaPO_3$ glass. However, the spread of T_g itself is very narrow. Addition of SnO_2 also increases the T_g of NSP glass. The T_g of NSP glass appears to be between that of $Sn_2P_2O_7$ and $NaPO_3$ glasses.

Given in figure 5 are the IR absorption spectra of the above glasses. The spectra suggest that as $NaPO_3$ content increases, peaks corresponding to the metaphosphate ($1270\,cm^{-1}$ of $P = O$ (Corbridge and Lowe 1954; Osaka *et al* 1984)) and $525\,cm^{-1}$ (–O– P–O bending mode in $[POO_{2/2}O]^-$ tetrahedra (Osaka *et al* 1984)) also increase. In the pure NSP glass the absorption band at $1270\,cm^{-1}$ band is merged into the shoulder. In the excess SnO_2 composition, the $985\,cm^{-1}$ band, barely identifiable in
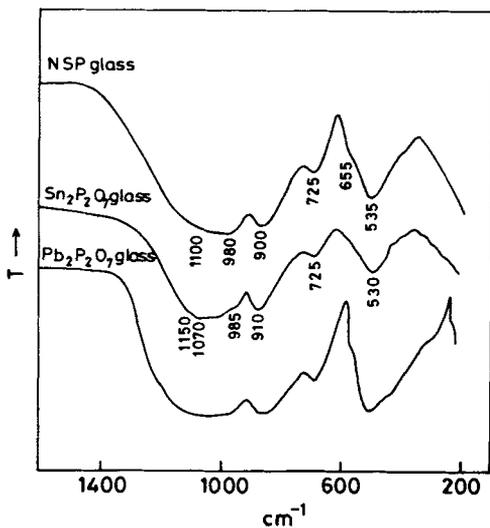
Figure 4. Infrared spectra of NSP glass and $Sn_2P_2O_7$ glass along with that of $Pb_2P_2O_7$ glass (taken from Ananthraj 1991).
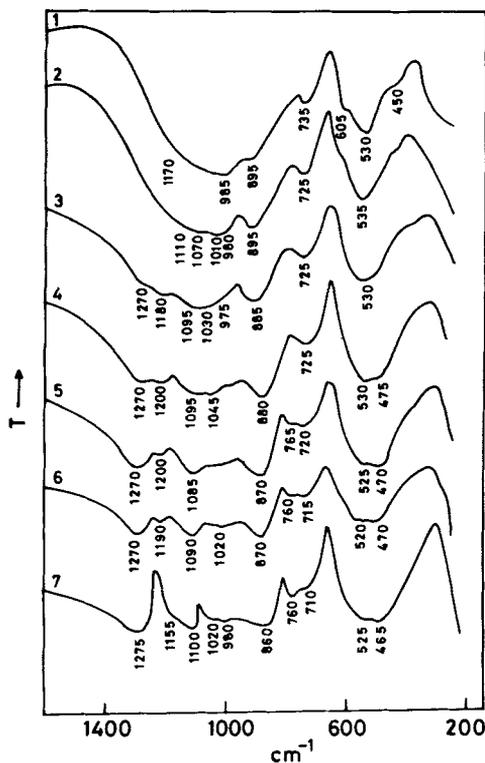

Figure 5. IR absorption spectra of the glasses in the $NSP-NP-SnO_2$ system. The numbering of the glasses is the same as in table 1.
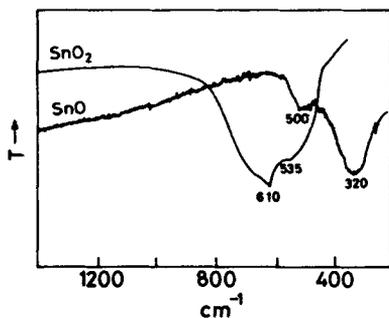
Figure 6. IR absorption spectra of SnO_2 and SnO.

pure NSP glass, becomes clearly identifiable. The enhanced intensity of the $985\,cm^{-1}$ compared to the low NP glasses suggests that this peak may be assigned to Sn–O–P linkages associated with tin in Sn^{4+} state. Similarly, the shoulder at $605\,cm^{-1}$ in the NSP glass spectrum appears as a more prominent peak at $605\,cm^{-1}$ in the $(NSP + SnO_2)$ glass spectrum. This can be assigned to Sn^{4+} in six-coordination (Wyckoff 1971) on comparison with the spectrum of pure SnO_2 itself given in figure 6. Thus, both Sn^{4+} and Sn^{2+} appear to be present in pure NSP glass.

The features in the IR spectra of NSP glass look more like a combination of the spectra of $Sn_2P_2O_7$ and NP glasses (figures 4 and 5). In fact, the preparation of NSP

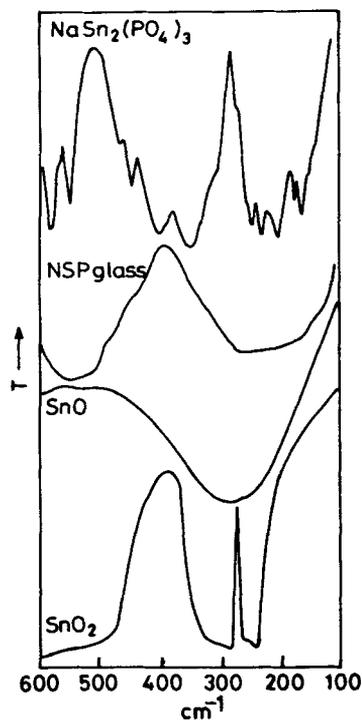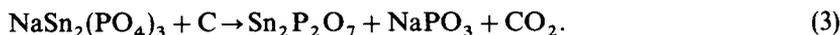**Figure 7.** FTIR spectra of $NaSn_2(PO_4)_3$ and NSP glass together with those of crystalline SnO and SnO_2.

glass suggests that the glass may contain $NaPO_3$ resulting from the reaction

$$NaSn_2(PO_4)_3 + C \rightarrow Sn_2P_2O_7 + NaPO_3 + CO_2. \tag{3}$$

The FTIR spectra of the NSP glass and $NaSn_2(PO_4)_3$ together with those of the crystalline SnO and SnO_2 are shown in figure 7. Presence of features arising from both Sn^{4+} and Sn^{2+} can be seen in the spectra of NSP glass. Na^+ ion cage vibration band is also expected in this region (Exarhos and Risen 1972; Nelson and Exarhos 1979) but it is mixed with the bands arising from both SnO and SnO_2 in this region. The shoulder near $330\,cm^{-1}$ in the spectra of NSP glass which is found in SnO also suggests the presence of 4-coordinated Sn^{2+} in the NSP glass.

Fluorescence of Sn^{2+} in glasses is well-known (Parke and Webb 1971; Reisfeld *et al* 1975). The excitation as well as the emission wavelengths of Sn^{2+} are greatly affected by the nature of the crystalline or glassy matrix (Mooney 1959, 1960; Parke and Webb 1971; Reisfeld *et al* 1975; Mărculescu *et al* 1980; Donker *et al* 1989). The NSP glass is found to fluoresce with a somewhat weak green emission. The excitation and emission spectra of NSP glass are shown in figure 8. The emission spectrum is a broad one with maximum intensity near 515 nm. The excitation spectrum has a strong band centred near 345 nm and a weak one near 280 nm. It is seen that the shape as well as the position of the emission and excitation bands are considerably different from those reported for other Sn^{2+} containing glasses at doping concentrations of 1 wt% (Parke and Webb 1971; Reisfeld *et al* 1975). The excitation bands may be assigned to transitions from the $^1S_0$ ground state to the crystal field split levels of the $^3P_1$ excited state of the Sn^{2+} ion which is an s^2 (Mooney 1959, 1960; Donker *et al* 1989). The position of the excitation maximum indicates the presence of Sn^{2+} in octahedral coordination (Mooney 1959, 1960; Donker *et al* 1989).

The spectroscopic results (IR, FTIR and fluorescence) indicate that in the NSP glass, tin is present in both Sn^{2+} and Sn^{4+} oxidation states and in both 4- and 6-coordinations. Tin has been found to exist only in 2 + oxidation state in several phosphate glasses from Mössbauer studies (Evtrop'ev *et al* 1970). The stabilization of Sn^{4+} in NSP glasses which was prepared starting from $NaSn_2(PO_4)_3$ could arise from the fact that only a particular ratio of Sn^{4+} to Sn^{2+} can exist in the melts (which is also temperature-dependent). The melting conditions reduce Sn^{4+} to Sn^{2+} till such a ratio is attained. In fact such equilibrations have been shown to exist in tin containing silicate and borate glasses (Bartenev *et al* 1976; Dannheim *et al* 1976; Lechtenböhmer and
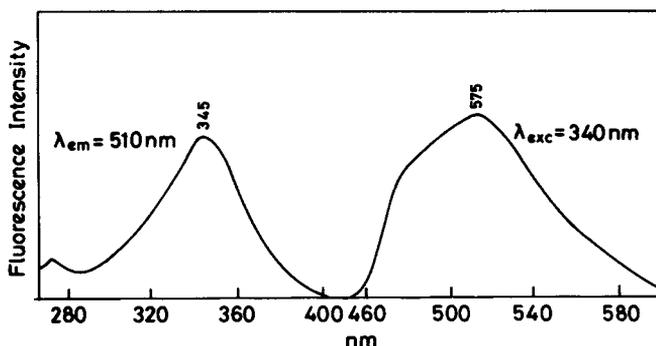

Figure 8. Fluorescence excitation and emission spectra of NSP glass.

Müller-Warmuth 1982). Attempts at quantitative estimation of Sn^{4+} and Sn^{2+} did not prove successful. Chemical routes for the estimation could not be employed because the glasses are insoluble in water. X-ray photoemission spectroscopy (XPS) also was not successful due to the closeness of the core electron binding energies of Sn^{4+} and Sn^{2+}. $NSP + SnO_2$ glasses suggest that glass can be made with up to 16% of tin in the Sn^{4+} state.

4. Conclusion

Tin in pyrophosphate glasses has a tendency to be present largely in Sn^{2+} state but a substantial proportion of tin can be stabilized as Sn^{4+} in phosphate glass. Tin ions may be present in both four- and six-coordinated sites.

Acknowledgement

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