

Conductivity studies in SnO–NaPO₃ glasses

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Abstract. Na⁺ ion conductivity has been studied in SnO–NaPO₃ glasses, which have been prepared over a wide range of compositions using a microwave melting technique. D.c. activation barriers seem to reflect the structural changes in system. A.c. conductivity analysis has revealed that while the power law exponent, s , seem to bear correlation to the structural changes, the exponent b of the stretched exponential function describing the dielectric relaxation is largely insensitive to the structure. Possible importance of the correlation of transport property to the variation of available non-bridging oxygen (NBO) atoms in the structure is discussed.

Keywords. Conductivity studies; SnO–NaPO₃.

1. Introduction

SnO and NaPO₃ form glasses over a wide range of compositions. The structure of these glasses and the oxidation state of tin in these phosphate glasses have been examined in detail (Harish Bhat *et al* 2001). Contrary to the earlier literature reports (Carbo Nover and Williamson 1967; Paul *et al* 1977; Silver *et al* 1977; Ishikawa and Akagi 1978; Shaw and Shelby 1988; Xu and Day 1990; Karim and Holland 1995; Sobha and Rao 1995; Mori and Sakata 1997; Sato *et al* 1997; Yung *et al* 1997; Bent *et al* 1998; Williams *et al* 1998; Yamashita *et al* 1998; Chiodini *et al* 1999; Courtney *et al* 1999), it has been established that tin is present in partially oxidized Sn⁴⁺ state. It has also been shown using ¹¹⁹Sn Mössbauer studies that [Sn⁴⁺]/[Sn²⁺] concentration ratio attains a constant value of 0.4/0.6. The oxidation of Sn²⁺ to Sn⁴⁺ occurs by incorporation of O₂ from the atmosphere and not by disproportionation (Carbo Nover and Williamson 1967). Also, the constancy of [Sn⁴⁺]/[Sn²⁺] ratio, irrespective of composition, is due to the unique consequences of pre-equilibrium kinetics. This is well supported by infrared, Raman and ³¹P HR MAS NMR studies, which together provide quantitative estimates of meta and pyrophosphate units present in the glasses. The structural model proposed earlier, which is consistent with the observations, suggests that the SnO in the glass behaves like a modifier till 26 mol% concentration, above which it behaves as a network former (Harish Bhat *et al* 2001). Sn⁴⁺ is always present as a network former, and the oxygen for its coordination is provided by both meta and pyrophosphate units in the glass. In the region between 26 and 33 mol% SnO (initial nominal composition), modification of metaphosphate units to

pyrophosphate units essentially stops, and above 33 mol% added SnO, Sn⁴⁺ is coordinated only to pyrophosphate units. Therefore, there are three composition regimes, 0–26 mol%, 26–33 mol%, and > 33 mol% SnO, in which structural features are significantly different. Indeed, molar volumes and glass transition temperatures do bear out the expected consequences of such structural features (Harish Bhat *et al* 2001).

Therefore, it is to be expected that the electrical transport behaviour of the Na⁺ ions in these glasses also reflect the structural changes. Further, Na⁺ ion transport studies in such glass matrices have not been reported in the literature. The covalent network forming tendencies of tin in both of its valence states, together with the covalently bonded metaphosphate chains can be expected to give rise to significant Na⁺ ion conductivity. Further, the glass transition temperatures in this system are both reasonably high but are spread over a narrow range of only ~ 30 K, which is an advantage for practical applications. In this background, we have investigated both the d.c. and a.c. responses of the glasses. In the following section, we present the experimental procedures and discuss them in the subsequent section.

2. Experimental

SnO–NaPO₃ glasses were prepared by melt-quenching technique as described elsewhere (Harish Bhat *et al* 2001). Glasses of composition A SnO : B NaPO₃ ($0 \leq A \leq 45$) series, were prepared by a simple microwave melting method using analytical reagent (AR) grade NaH₂PO₄·2H₂O and SnO (99+ %, Aldrich) as starting materials. Calculated quantities of starting materials were placed in a clean silica crucible and heated in a microwave oven (Batliboi, Eddy; 2.45 GHz; 980 W power,

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tunable in steps). Within 3 min of exposure to microwaves at 980 W, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ decomposes completely to NaPO_3 . A good homogenous melt was found to form in about 7 min and the melt was thereafter rapidly quenched between stainless steel plates.

The glasses were annealed at $(T_g - 20)$ K, after which their electrical conductivities were measured using a Hewlett-Packard HP 4192A LF Impedance-Gain Phase Analyser (Hewlett-Packard, USA) from 10 Hz to 13 MHz in the temperature range of 298 K to 525 K. A home built cell assembly (a 2-terminal capacitor configuration and spring loaded electrodes of silver) was used for the measurements. The sample temperature was measured using a Pt-Rh thermocouple positioned very close to the sample. The temperature was controlled using a Heatcon (Bangalore, India) temperature controller and the temperature constancy of ± 1 K was achieved in the entire range of measurements. Annealed circular glass pieces, coated with silver paint on both sides and having thickness of about 0.1 cm and a diameter of 1 cm were used for measurements. The real (Z') and imaginary (Z'') parts of the complex impedance (Z^*) were obtained from the measured conductances and capacitances using the relations

$$Z' = G/(G^2 + w^2C^2),$$

$$Z'' = wC/(G^2 + w^2C^2),$$

where, G is the conductance, C the parallel capacitance, and w the angular frequency. The real (e') and imaginary (e'') parts of the complex dielectric constant were calculated from the relations

$$e' = Cd/(e_0A),$$

$$e'' = s/(we_0),$$

where d is the sample thickness, A the cross-sectional area, s the conductivity, and e_0 the permittivity of free space.

The data were also analysed using the electrical modulus formalism (Rao 2002). The real (M') and imaginary (M'')

parts of the complex electrical modulus ($M^* = 1/e^*$) were obtained from e' and e'' values using the relation,

$$M' = e'/((e')^2 + (e'')^2),$$

$$M'' = e''/((e')^2 + (e'')^2).$$

3. Results and discussion

The compositions of the glasses investigated in this study are given in table 1 along with their codes. In order to ensure that the conductivities arise only from ion transport, variation of the current as a function of time was studied by applying a constant d.c. voltage. It was observed that there was an almost instantaneous rise in current, which decayed very rapidly to zero indicating that there was no electronic contribution to conductivity. Therefore, it has been assumed that presence of Sn^{2+} and Sn^{4+} do not contribute to the measured electrical transport. The d.c. conductivities were determined from impedance plots of the type shown in figure 1(a). From the intercepts on the X axis corresponding to zero frequency, resistances and the corresponding conductivities were determined at various temperatures (Simmons and El-Bayoumi 1993). Variation of logarithmic conductivity as a function of mol% SnO are shown in figure 1(b). In general, the conductivity decreases with increase in SnO, although the decrease is somewhat lower at higher temperatures as evident from the variation of conductivities at 413 K and 513 K. Corresponding variation of the activation barriers as a function of composition are shown in figure 1(c). Activation barriers (see also table 1) are highest around 25 mol% SnO (25 : 75 glass). It decreases moderately up to about 35 mol% SnO, above which activation barrier registers a moderate increase (Note: The percentages of SnO in the glass composition indicate the initial quantity used to prepare the glass. Indeed, $x\text{SnO}$ is in reality $0.6 \times \text{Sn}^{\text{II}}\text{O} + 0.4 \times \text{Sn}^{\text{IV}}\text{O}_2$). The region corresponding to rise in activation barrier is the regime of composition where SnO acts as a modifier. It is also in this region that Sn^{4+} ties up to four metaphosphate units by coordination,

Table 1. Codes, compositions, densities, molar volumes, glass transition temperatures and d.c. activation barriers of $\text{SnO} \cdot \text{NaPO}_3$ glasses.

Code A : B (molar)	Composition	Density (g/cc)	Molar volume (cc)	T_g (K)	$E_{\text{d.c.}}$ (eV)
05 : 95	05SnO : 95NaPO ₃	2.57	40.25	534.0	0.75
10 : 90	10SnO : 90NaPO ₃	2.67	39.37	529.0	0.85
15 : 85	15SnO : 85NaPO ₃	2.77	38.51	528.0	0.99
20 : 80	20SnO : 80NaPO ₃	2.89	37.52	526.0	1.03
25 : 75	25SnO : 75NaPO ₃	3.00	36.65	524.0	1.14
30 : 70	30SnO : 70NaPO ₃	3.12	35.84	530.0	1.11
35 : 65	35SnO : 65NaPO ₃	3.24	34.96	547.0	1.02
40 : 60	40SnO : 60NaPO ₃	3.33	34.49	551.0	1.00
45 : 55	45SnO : 55NaPO ₃	3.46	33.76	554.0	1.07

which therefore tightens up the structure. The combination of gradual breakdown of metaphosphate chains and local tight reorganization around Sn⁴⁺ units (see molar volumes in table 1) may be responsible for the increased barriers for Na⁺ ion migration in this region.

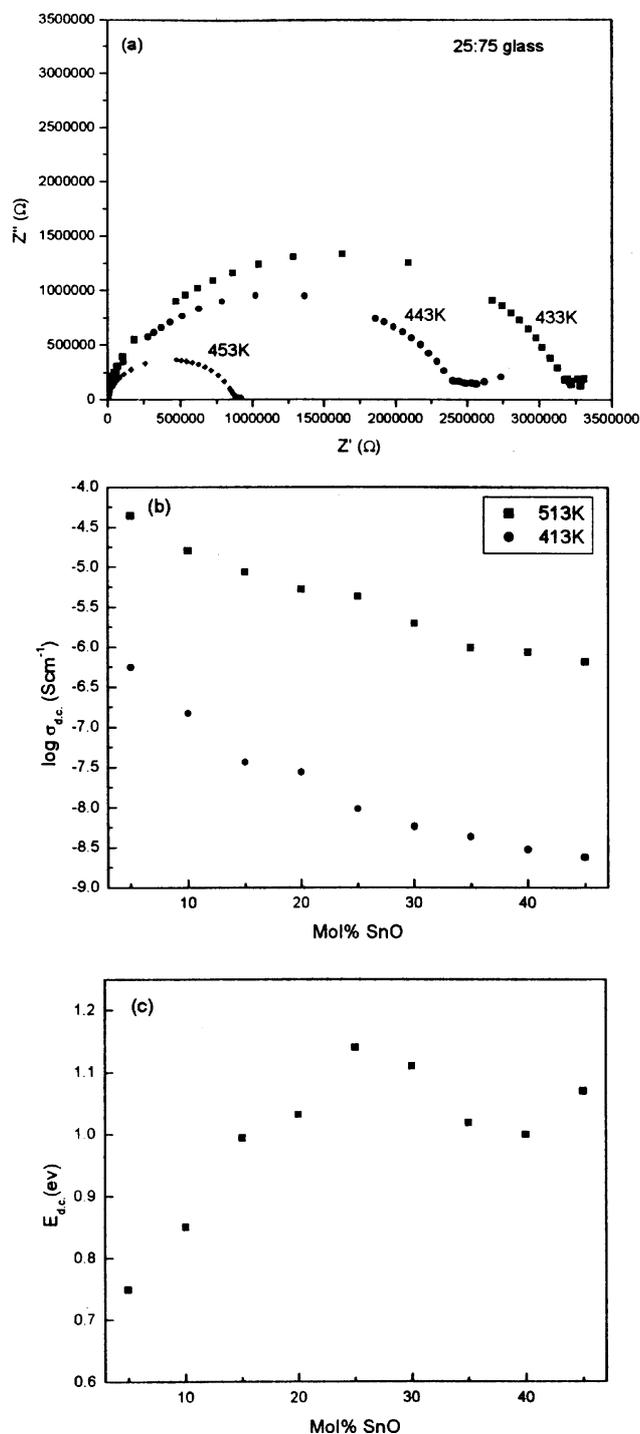


Figure 1. (a) Typical impedance plot for 25 : 75 glass, (b) variation of log of conductivity with composition at 413 K and 513 K for SnO–NaPO₃ glasses and (c) variation of d.c. activation barriers with composition for SnO–NaPO₃ glasses.

But it is more probable that the non-bridging oxygens (NBOs) in this region are increasingly immobilized being in the $[\text{POO}_{2/2}\text{O}]^-$ groups coordinating to Sn²⁺ ions. This is not fully compensated by the creation of additional NBOs by the addition of SnO. Migration of Na⁺ ions is impeded by the decreasing availability of NBOs, which manifests as increased barrier. In the region corresponding to > 33 mol% SnO, it has been shown earlier that the relative proportion of pyrophosphate (p) and metaphosphate (m) saturate. Increasing quantities of SnO and decreasing total phosphate again leads to depletion of available NBOs to which Na⁺ migration is tied up. In this region also, the activation barriers tend to exhibit an increasing trend. In the 27–33 mol% SnO region, we feel that the reorganization of m and p units in the structure leads to an increased availability of NBOs for transport. This manifests as a slight decrease in activation barriers.

The a.c. conductivities are shown in figure 2(a) as a function of temperature and frequency for the typical case of 25 : 75 glass. The variations are very well fitted to a.c. conductivity functions of the type, $s(\omega) = s(0) + A\omega^f$ (Almond *et al* 1982, 1983, 1984). The values of s obtained from curve fitting the data at various temperatures are shown in figures 2(b), (c) and (d) for all the glasses studied here, which fall into three composition regimes. In the regime 5–20 mol% SnO, the s values lie between 0.6 to 0.7 and are essentially temperature independent. In the 25–35 mol% SnO, s exhibits a decreasing trend but at lower temperatures, s values are quite high. But in the case of 40 : 60 and 45 : 55 glasses, s values are very high at low temperatures and decrease rapidly with temperature and reach values of about 0.6, although there appears to be some shallow minima in glasses like 30 : 70, which is indicative of differences in activation barriers determined from d.c. (diffusion-dependent) and a.c. (diffusion independent) studies (Rao *et al* 1984, 1993, 1998; Elliott 1987, 1988, 1989; Verhoef and den Hartog 1994). These aspects are not discussed any further in the following.

Glass compositions in figure 2(b) are those in which there is increasing modification as a result of increasing concentration of SnO. The a.c. conductivity in these compositions behaves as in typically ionic glasses and the s values fall in the so-called Jonscher regime (Jonscher 1977, 1983, 1996; Dyre and Schroeder 2000). In figure 2(c), the glasses are those in which a structural reorganization occurs and SnO begins to behave like a network former. It is not known if Sn(II) is coordinated to three or four oxygens. Since SnO is structurally equivalent to $[\text{SnO}_{2/2}]$, the additional coordination can only be realized from p units present in the structure. It may be recalled here that when SnO concentration increases, there is a corresponding decrease in the phosphate. Since Sn(IV) also requires to be coordinated to four NBOs, the p units also get depleted very fast. As a consequence, in the middle composition regime (25–35 mol% SnO), there is an effective rebuilding of network features in the glass.

These features, however, originate from coordination of Sn(II) and Sn(IV) to NBOs and are therefore unstable at high temperatures. The result is that at higher temperatures s decreases towards 0.6. Glasses in figure 2(d) are those in which network features have been restored to a great extent and they exhibit sharp decrease in s as a function of temperature and also very high values of s at lower temperatures.

The a.c. response of the glasses have also been examined by making measurements of dielectric properties (see experimental section). The variation of real (M') and imaginary (M'') part of the dielectric moduli as a function of temperature and frequency for a typical case are shown in figures 3(a) and (b). The asymmetric M'' is immediately suggestive of stretched exponential relaxation behaviour. Making use of the well known relation between full-width-at-half-maximum (FWHM) and the value of the stretching exponent b (Moynihan *et al* 1973), values of b have been determined over a wide range of

temperatures for all the compositions. These values of b are shown in figures 4(a), (b) and (c) for the three composition regimes. Surprisingly, the b values in all the three composition regimes not only have values between 0.6 and 0.7 but are also quite temperature insensitive. In the composition regime where SnO acts as a modifier, there is a slight spread in the b values. We, therefore, infer that there is no constraining relation between s and b , both of which are > 0.5 . The time-temperature superposition (Ganguli and Rao 1999) of the M'' plots have also been examined and shown for typical glasses in the three composition regimes in figures 5(a), (b) and (c). The collapse of the $M''/M''(\max)$ vs $\log(f/f(\max))$ plots for various temperatures is very good indicating that the ion transport mechanism remains unaffected at all temperatures of measurement.

Therefore, the electrical transport studies in these glasses reveal a general consistency with the structural model proposed earlier (Harish Bhat *et al* 2001). It has

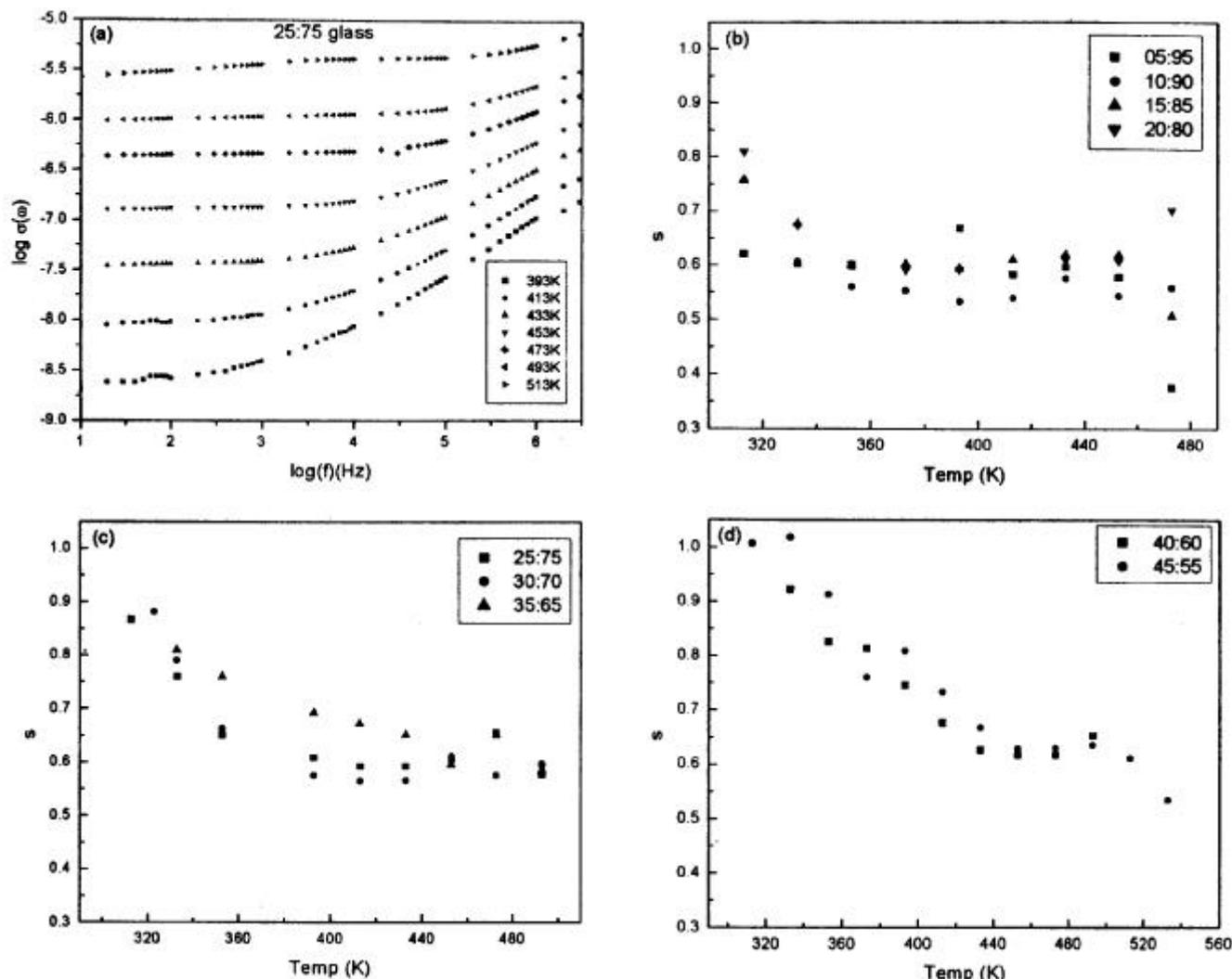


Figure 2. (a) Typical variation of $\log s_{d.c.}$ as a function of $\log f$ for the case of 25 : 75 glass. Variation of s with temperature for (b) 5–20 mol% SnO glasses, (c) 25–35 mol% SnO glasses and (d) 40–45 mol% SnO glasses.

also been remarked (Harish Bhat *et al* 2001) that in SnO–NaPO₃ binary glasses, the molar volume decreases with increasing SnO (table 1) because of the decrease in the total number of oxygens in the system which contribute to the molar volume. Since NBO concentrations increased monotonically, this amounts to rapid rise of NBO to BO ratio. In the composition regime up to 20 mol% SnO, the breakdown of the metaphosphate chains by $m \rightarrow p$ conversion therefore makes the glasses more ionic and this is well reflected in the rapid decrease of glass transition temperature (table 1). In the region between 26 and 33 mol% SnO, the nature of coordination of Sn^{IV} may undergo change in the sense that fewer number of p units will replace larger number of m units in coordination. This involves structural reorganizations which also bring about concomitant changes in the environment of Na⁺ ions which, we believe, slightly decreases the activation barrier, although it does not manifest in any

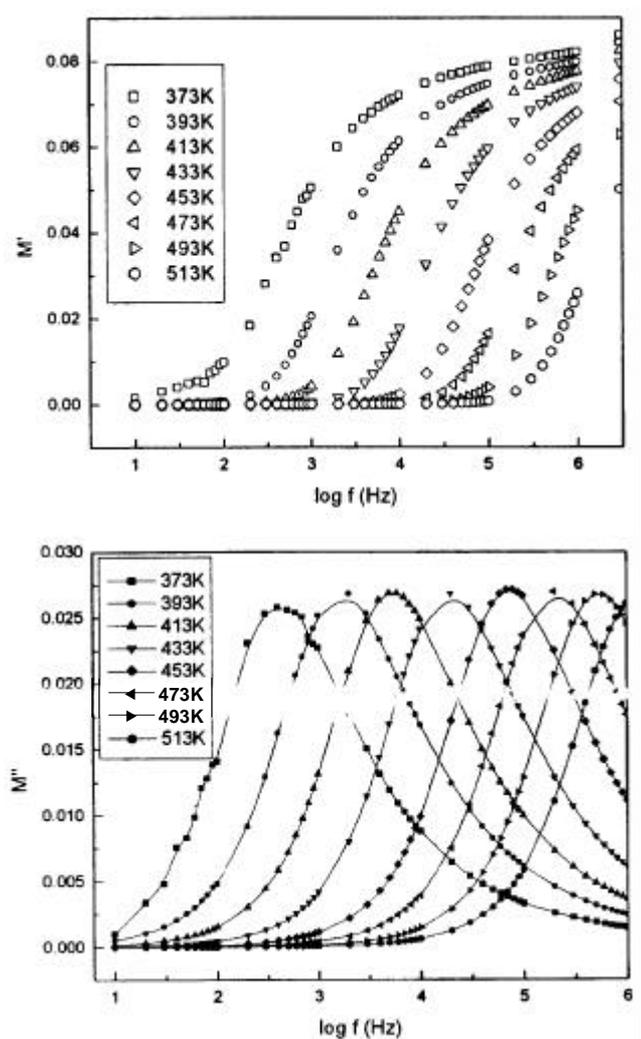


Figure 3. Variation of real (M') and imaginary (M'') part of dielectric moduli with frequency at different temperatures for 15 : 85 glass.

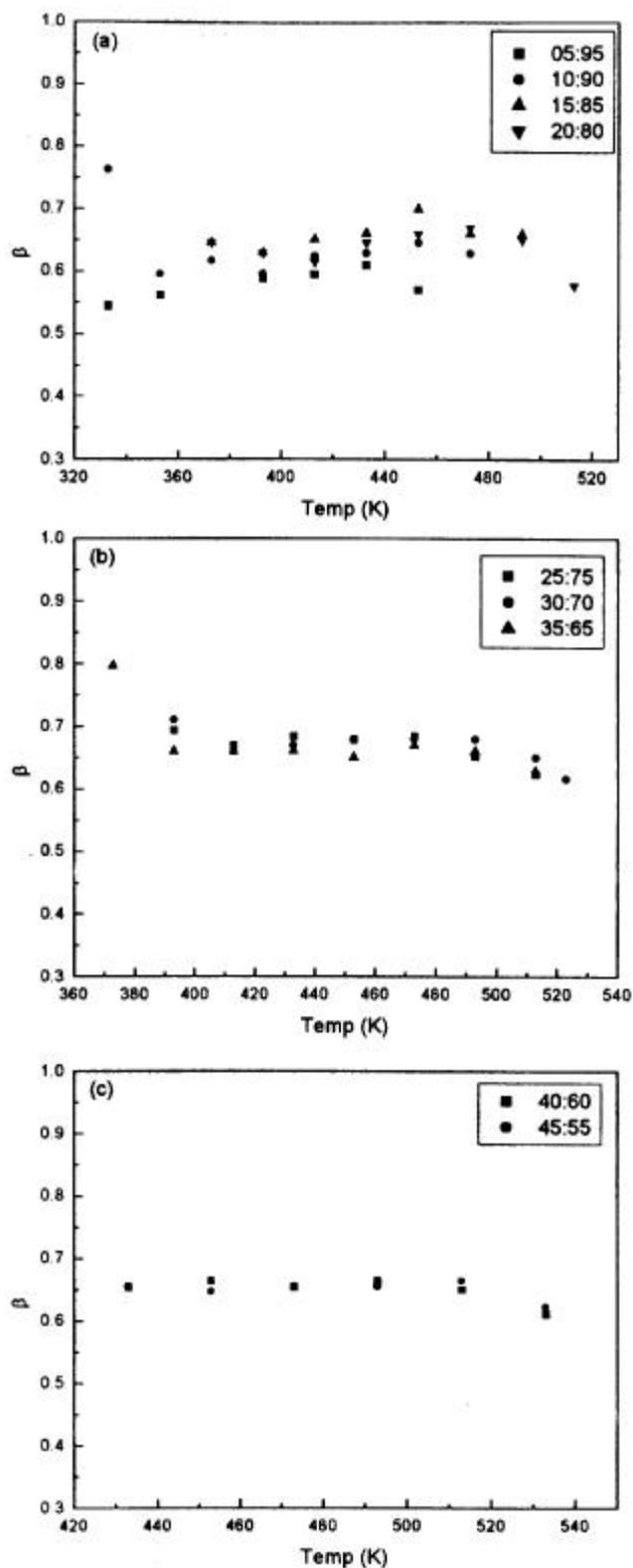


Figure 4. Variation of stretched exponent b as a function of temperature for (a) 5–20 mol% SnO glasses, (b) 25–35 mol% SnO glasses and (c) 40–45 mol% SnO glasses.

increase in ionic conductivity as the effect itself is small. Therefore, a careful analysis shows that the transport behaviour is related to the availability of NBOs for transport (Karthikeyan *et al* 1999) rather than the concentration itself. The structural locking up of m units which are

coordinated to Sn^{IV} may not be able to switch positions, which has to happen either prior to or after Na^+ ions move out of their positions during transport. There is thus a dual population of NBOs in this glass system. This aspect is being investigated in greater detail.

4. Conclusions

In SnO-NaPO_3 glasses, electrical transport is due to ionic motion (Na^+ ions). The variation of d.c. conductivity activation barriers closely reflect the structural changes, which occur as a function of composition. In a.c. conductivities, the variation of s as a function of temperature seems to exhibit weak correlation with the structure. However, the stretching exponent, b , estimated from the behaviour of the imaginary part of dielectric moduli does not reflect any structural correlation. The concentration of NBOs available for transport is the determining factor in ionic conductivity of SnO-NaPO_3 glasses.

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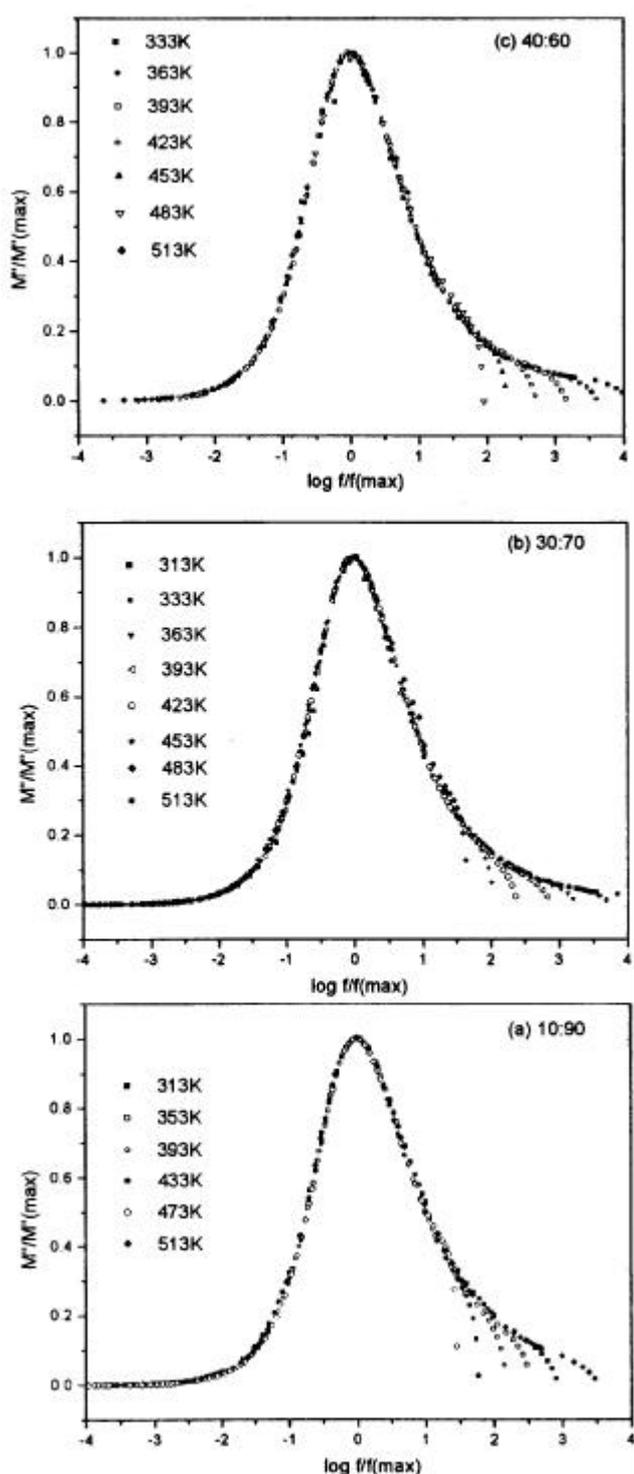


Figure 5. $M''/M''(\text{max})$ vs $\log(f/f(\text{max}))$ reduced plots for (a) 10 : 90, (b) 30 : 70 and (c) 40 : 60 glasses.

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