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Dielectric properties and conductivity in CuO and MoO_3 doped borophosphate glasses

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ABSTRACT

A novel set of glasses of the type $(B_2O_3)_{0.10}$–$(P_2O_5)_{0.40}$–$(CuO)_{0.50-x}$–$(MoO_3)_x$, $0.05 \leq x \geq 0.50$, have been investigated for dielectric properties in the frequency range 100 Hz–100 kHz and temperature range 300–575 K. From the total conductivity derived from the dielectric spectrum the frequency exponent, *s*, and dc and ac components of the conductivity were determined. The temperature dependence of dc and ac conductivities at different frequencies was analyzed using Mott's small polaron hopping model, and the high temperature activation energies have been estimated and discussed. The observed initial decrease in conductivity (ac and dc) and increase in activation energy with the addition of MoO_3 have been understood to be due to the hindrance offered by the Mo^+ ions to the electronic motions. The observed peak-like behavior in conductivity (dip-like behavior in activation energy) in the composition range 0.20–0.50 mol fractions of MoO_3 may be due to mixed transition effect occurring in the present glasses. The temperature dependence of frequency exponent, *s*, has been analyzed using different theoretical models. It is for the first time that the mixed transition metal ion (TMI) doped borophosphate glasses have been investigated for dielectric properties and conductivity over wide temperature and frequency ranges and the data have been subjected to a thorough analysis.

1. Introduction

Transition metal ion (TMI) doped glasses have always been studied to better understand the transport mechanisms in these electronic semiconductors [1–4]. In these glasses, the tendency for the formation of small polarons is quite high and the electrical conduction occurs by the hopping of small polarons between the ions of low and high valence states of the TMI [5]. The dc and ac conductivity investigations in different types of glasses doped with various TMI revealed that the conduction mechanism in them can be explained by Mott's small polaron hopping model [3,4]. Impedance spectroscopy over a wide frequency scale has been traditionally applied to understand the frequency dependence of complex conductivity in various glassy materials [6–9]. At low frequencies, a random diffusion of the ionic charge carriers via activated hopping has been observed to be resulting in a frequency-independent conductivity in different ion conducting materials [10,11]. However, conductivity exhibits dispersion at higher frequencies, which increases roughly in a power-law trend and eventually becoming almost linear at even higher frequencies. Interestingly, polaronic conductors also exhibit a behavior similar to the ionic ones. Nevertheless, the dispersion clearly reflects a correlated kind of motion of the ions occurring on relatively short time scales [12–14].

Among different types of glasses, the phosphate based glasses are interesting materials as they possess low melting and glass transition temperatures and their applications can be found in optoelectronics, solid state batteries, high power lasers, etc. [15–17]. The poor chemical durability and low thermal stability of phosphate based glasses have been major constraints for the practical utility of these glasses [18]. However, the addition of boron atoms (less than 15 mol%) into phosphate glass network has been shown to increase the chemical durability [6]. The electrical conductivity studies exclusively in phosphate and borate glasses doped with different single and mixed TMI have been studied by some authors [1–4,19]. There are not many reports in the literature on electrical conductivity studies in borophosphate glasses containing mixed TMIs. The borophosphate glasses are interesting and important materials. Zinc–calcium doped borophosphate glasses are considered to be potential candidates for applications in low-melting glass solders or glass seals [20]. Borophosphate glasses containing alkaline metals exhibited a high

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solubility [21] and zinc doped borophosphate glasses have been reported to possess aqueous durability comparable to that of silicate glasses [22,23].

Keeping in view of the fact that borophosphate glasses have attractive applications, chemically more durable compared to pure phosphate and borate glasses and, no many electrical studies have been reported previously on them, it was planned to investigate dielectric properties and ac conductivity as a function of temperature and frequency in copper–molybdenum doped borophosphate glasses in the composition, $(B_2O_3)_{0.10}$–$(P_2O_5)_{0.40}$–$(CuO)_{0.50-x}$–$(MoO_3)_x$, $x = 0.05$, 0.10, 0.15, 0.25, 0.30, 0.35, 0.45, 0.50, labeled as BPCM1, BPCM2, BPCM3, BPCM5, BPCM6, BPCM7, BPCM9, BPCM10.

It is for the first time that mixed TMI doped borophosphate glasses have been explored for such studies. These studies help in understanding the effect of doping of second TMI at the cost of first TMI while keeping the glass former content to be constant.

2. Experimental

Melt-quenching technique has been employed to synthesize the glass samples using analytical grade MoO_3, CuO, H_3BO_3 and $NH_4H_2PO_4$. The well ground mixture of chemicals in appropriate weight ratios were taken in porcelain crucible and melted in a muffle furnace at a constant temperature in the range 1200–1300 K for an hour. The melt was then quickly quenched by pouring on to a stainless steel plate and covering it with another stainless steel plate. The random pieces of samples formed were collected. It is possible that porcelain crucibles can get attacked by corrosive melts at high temperature. Due to unavailability of the facilities and expertise no chemical analysis has been performed on the present glasses and the set compositions are taken granted. Moreover, the integrity of our crucibles after quenching the melt was observed to be intact [24]. Samples were annealed at 550 K to remove mechanical stresses present, if any, in as quenched samples. The non-crystallinity of the samples was confirmed by X-ray diffraction studies.

The frequency dependent measurements of capacitance, C, and dissipation factor, $\tan\delta$, were obtained using a computer controlled LCR HiTester (HIOKI, 3532-50) for different frequencies in the range 100 Hz–100 kHz and temperature from 300 to 575 K. The dielectric constant (ε'), dielectric loss factor (ε'') and conductivity (σ) were determined as per the following expressions;

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

$$\varepsilon'' = \varepsilon' \tan\delta \quad (2)$$

$$\sigma = \omega\varepsilon_0\varepsilon'' \quad (3)$$

where ε_0 is the permittivity of free space, ω is the frequency of the input signal, d is thickness and A is cross sectional area of the sample.

3. Results

For the present glasses, in the experimental frequency range, the dielectric constant ε' varied in the range 50–72 and the dielectric loss ε'' varied in the range 2–81. The typical plots for the variation of ε' and ε'' with frequency at different temperatures for BPCM10 glass are shown in Figs. 1 and 2, respectively. It can be noted that both ε' and ε'' decrease with increase in frequency and increase with increase in temperature. Similar results were observed in the case of remaining BPCM glasses. These results

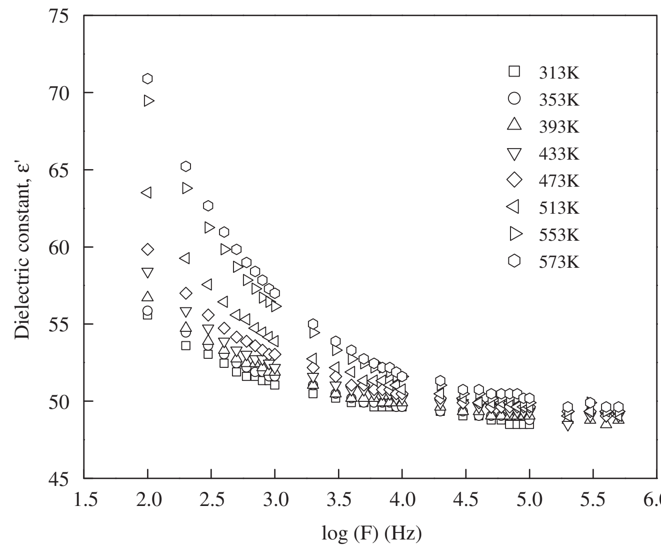

Fig. 1. Plots of log(ε') versus log(F) for the glass BPCM10 at different temperatures.

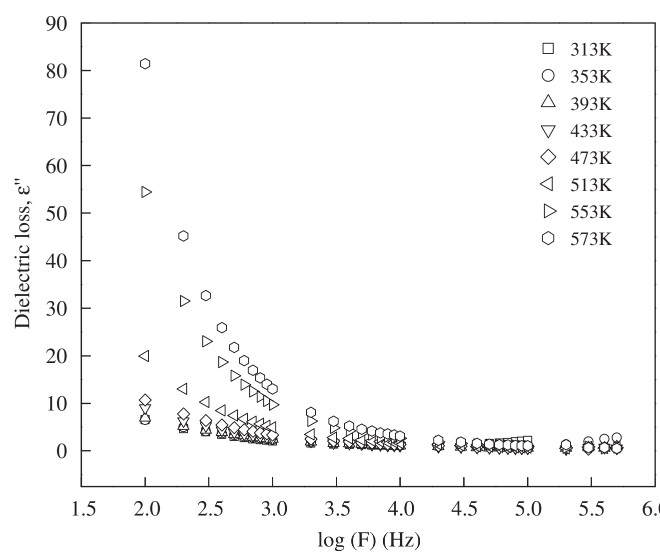

Fig. 2. Plots of log(ε'') versus log(F) for the glass BPCM10 at different temperatures.

are consistent with the reported literature for similar glass systems [25,26]. It can also be seen that both ε' and ε'' decrease abruptly with increase in frequency approximately up to 10 kHz. It may be due to electrode polarizations which include space charge polarization, etc. In order to understand the bulk dielectric properties of the present glasses, only the data for frequency above 10 kHz have been considered.

A close look at the total conductivity data of the present glasses revealed that it increases with increase in frequency and temperature.

4. Discussion

4.1. Dielectric properties

The increase in dielectric constant of the sample with increase in temperature is usually associated with the decrease in bond energies [27]. That is, as the temperature increases two effects on the dipolar polarization may occur: (i) it weakens the inter-