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Dielectric relaxation studies in single and mixed alkali doped cobalt-borate glasses

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The cobalt-borate glasses containing Li and Li-K ions in single and mixed proportions have been investigated for dielectric properties in the frequency range 50Hz to 5MHz and temperature range 300K to 600K. The dielectric constant and loss were found to decrease with increase in frequency in both the series of glasses. Activation energies for dielectric loss derived by employing Hunt's model indicated that the relaxation process has a local character and can be described by hops between pairs of sites. Activation energies for dielectric loss process were found to be in close agreement with dc activation energies. BNN's linear relation between ac and dc conductivities has been verified in both the glass systems. It is for the first time that Hunts and BNN's theories have been verified in cobalt-alkali doped borate glasses.

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1. Introduction

The conductivity in pure transition metal ions (TMI) doped glasses has always been observed to be semiconducting type and that was due to polaron hopping between low and high valency states of TMI. If ions are also present along with TMI then the conductivity will be of mixed type i.e., polaron and ionic [1-4]. Alkali doped borate glasses are mainly used for applications in solid state devices, cathode materials for batteries, gas sensors, and chemical sensors, electrochemical, electronic and electro-optical devices [5-9]. The dc and ac conductivity studies in various different types of glasses doped with transition metal ions (TMI) revealed the conduction mechanism in them was due to small polaron hopping [10-14]. One of the most important properties of TMI doped oxide glasses is that the activation energies associated with the conductivities are identical to that for the relaxation and dielectric processes [15-17].

A correlation between dc conductivity and the dielectric relaxation peak has been established by Barton [18], Nakijama [19] and Namikawa [20] (BNN). Hunt's model correlates the peak frequency in dielectric spectra to the electron transfer between multivalent TMI sites present in the glass network [21]. A linear relation between ac and dc conductivity has been predicted by Hunt's theory in the pair approximation regime. This kind of a linear relation suggests the existence of a single mechanism for all the processes operated in the glass system [22].

Dielectric properties of iron and vanadium phosphate glasses containing different glass modifiers have been studied and interpreted in the framework of Hunt's model [11,16]. Chomka et al [15] reported the conductivity, dielectric properties and internal frictions of doped iron-phosphate glasses doped with Mg, Ca and Ba and, observed almost the same value for activation energy for conductivity, dielectric relaxation and internal friction and it made to conclude that a single mechanism was responsible for all the three processes. The ac conductivity behavior in V_2O_5-B_2O_3 glasses was successfully explained using Hunt's and BNN models and showed that the relaxation process has a local character [17]. Dielectric relaxation processes have been studied using BNN's and Hunt's models for different rare earth ions doped vanado-tellurite glasses [23]. The ac conductivity of present glasses has been studied and the frequency response of conductivity was understood in the light of correlated barrier hopping model [13].

In the present communication, we report the dielectric studies in Li_2O and K_2O doped cobalt-borate glasses in the following mentioned compositions,

1. $(CoO)_{0.2}$-$(Li_2O)_x$-$(B_2O_3)_{0.8-x}$; x = 0.1, 0.2, 0.3 and 0.4 labeled as SA1, SA2, SA3 and SA4.

2. $(CoO)_{0.2}$-$(Li_2O)_{0.2}$-$(K_2O)_x$-$(B_2O_3)_{0.6-x}$; x = 0.05, 0.10, 0.15 and 0.20 labeled as MA1, MA2, MA3 and MA4.

The present work is aimed at understanding dielectric relaxation processes and activation energies associated with them and to verify the relation between frequency dependent and independent conductivities as envisaged by Hunt's and BNN models.

2. Experimental

The melt-quenching technique was adopted for synthesizing the glass samples using analytical grade Sigma Aldrich make chemicals Co_3O_4, Li_2CO_3, K_2CO_3 and H_3BO_3. The glassy nature of the samples was confirmed by XRD studies. The details of the preparation of glasses were reported elsewhere [10].

The samples of 3 mm in thickness and cross sectional areas ranging from 20 mm^2 to 40 mm^2 were cut for frequency dependent conductivity measurement and the silver electrodes were painted on two major surfaces of the samples. The frequency dependent measurements of capacitance, C, and dissipation factor, tanδ, were obtained using a computer controlled LCR HiTester (HIOKI, 3532-50) for different frequencies in the range 50 Hz to 5 MHz and temperature from 300K to 600K. The dielectric constant (ε') and dielectric loss factor (ε'') were determined as per the following expressions [13],

$$\varepsilon' = \frac{Cd}{\varepsilon_o A} \tag{1}$$

$$\varepsilon'' = \varepsilon' \tan\delta \tag{2}$$

Where, ε_o is the permittivity of free space, d is thickness of the glass sample and A is cross sectional area of the sample.

3. Results

The dielectric constant, ε', and dielectric loss, ε'', were observed to be in the range 37 to 14000 and 120 to 57000 for SA glasses and 95 to 647 and 2 to 6470 for MA glasses. The typical plots of dielectric constant, ε', versus frequency, f, for glasses SA1 and MA1 at various temperatures are shown in Figs.1 and 2, respectively. It can be noticed that in both the glasses, ε' decreases with frequency and increases with increase in temperature. Similar results were observed in the case of other TMI doped glasses [23-27].

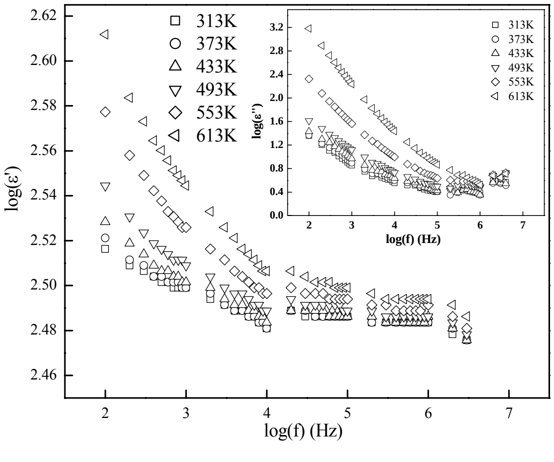

Fig.1 Plot of log (ε') versus log (f) for the glass SA1 at different temperatures. Inset shows the frequency dependence of ε'' for the same sample.

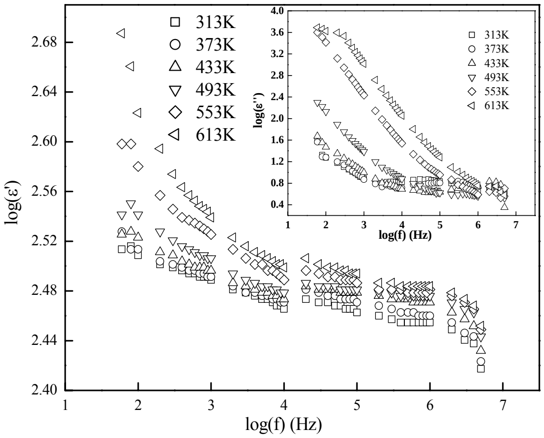

Fig. 2. Plot of log (ε') versus log (f) for the glass MA1 at different temperatures. Inset shows the frequency dependency of ε'' for the same sample.

4. Discussion

The increase of ε' with increase in temperature is usually associated with the decrease in bond energies, that is, as the temperature increases two effects on the dipolar polarization may occur; i) it weakens the intermolecular forces and hence enhances the orientational vibration, ii) it increases the thermal agitation and hence strongly disturbs the orientational vibrations. The dielectric constant becomes larger at lower frequencies and at higher temperatures, which is normally observed in oxide glasses [28]. This may be due to the fact that as the frequency increases the contribution to the total polarization from ionic and orientation sources decreases and finally disappears due to the inertia of the ions.

4.1 Dielectric relaxation process

For present glass systems the Hunt's model is used to study the dielectric relaxation processes, which has been previously used by many authors for oxide glasses [15-16, 21-22]. Hunt's model considers two distinct charge migration processes depending on the frequency domains i.e., $\omega < \omega_m$ and $\omega > \omega_m$, where ω_m is the frequency corresponding to the peak in dielectric loss. In these two domains, the total conductivity is expressed as,

$$\sigma_t(\omega) = \sigma_{dc}\left(1 + A\left(\frac{\omega}{\omega_m}\right)^s\right) \quad \text{for } \omega > \omega_m \tag{3}$$

$$\sigma_t(\omega) = \sigma_{dc}\left(1 + K(d)\left(\frac{\omega}{\omega_m}\right)^r\right) \quad \text{for } \omega < \omega_m \tag{4}$$

where, $r = 1 + d - d_f$, d being the dimensionality and d_f =2.66 [16], A and $K(d)$ are constants [17].

The frequency dependence of dielectric loss, ε" for the systems SA1 and MA1 at different temperatures are shown as insets to Figs.1 and 2 respectively. From these figures, it can be observed that if there was a maximum in dielectric loss, it would have appeared below our starting frequency i.e., 50HZ. This kind of behavior has been observed in V_2O_5-P_2O_5, V_2O_5-B_2O_3 and V_2O_5-TeO_2 glasses [16-17,29]. Hence, the determination of characteristic frequency ω_m of the dielectric loss for present glasses is not possible. However, it has been demonstrated that the Arrhenius law holds not only for the peak frequency ω_m but also for frequencies lower or higher than ω_m [17, 20-23]. The relation between characteristic frequency, f_m, and temperature, T, is expressed as,

$$f_m = f_{m_o} \exp\left(-\frac{W_f}{k_B T}\right) \tag{5}$$

From insets of Figs.1 and 2 the characteristic frequency values corresponding to some ε" value at different temperatures have been determined. As per Eq.(5), the reciprocal temperature dependence of characteristic frequency, f_m, for SA and MA glasses are plotted and shown in Fig. 3. The data appeared to be perfectly linear in these glasses. The activation energies, W_f, associated with dielectric loss process were calculated from the slopes of the least square linear lines that were fit to the data. The W_f values are presented in Table 1 and are of the same size as that of dc activation energies [10]. Similar result has been reported for V_2O_5-B_2O_3 and La and Ce ions doped V_2O_5-TeO_2 glasses [17, 23].

Table 1 Variation of dc activation energy, W and activation energies W_f associated with dielectric loss processes for SA and MA glasses.

Glass	Composition in mole fractions				W (eV)	W_f (eV)
	B_2O_3	CoO	Li_2O	K_2O		
SA1	0.70	0.20	0.10	--	1.099	1.060
SA2	0.60	0.20	0.20	--	0.989	0.985
SA3	0.50	0.20	0.30	--	0.918	0.905
SA4	0.40	0.20	0.40	--	0.877	0.859
MA1	0.55	0.20	0.20	0.05	1.116	1.095
MA2	0.50	0.20	0.20	0.10	1.138	1.127
MA3	0.45	0.20	0.20	0.15	1.149	1.154
MA4	0.40	0.20	0.20	0.20	1.161	1.159

According to BNN theory, the dc conductivity is related to the frequency ω_m of the dielectric relaxation peak as [17-20],

$$\sigma_{dc} = 2\pi\omega_m \varepsilon_0 (\Delta\varepsilon) p \tag{6}$$

where p is a constant which is generally taken as unity for the glasses containing TMI and $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$. From Eqs.(5) and (6) we have,

$$\sigma(\omega) = A(\varepsilon_0 \Delta\varepsilon\omega)^s \sigma_{dc}^{1-s} \text{ or } \ln\sigma(\omega) = \ln k + (1-s)\ln(\sigma_{dc}) \tag{7}$$

where, $k = A(\varepsilon_0 \Delta\varepsilon\omega)^s$

This expression shows that at a given frequency, the σ(ω) and σ_{dc} are linearly related to each other with a slope (1-*s*). Figs.(4a) and (4b) illustrates the linear relation between ln(σ_{ac}) and ln(σ_{dc}) in both the glass systems. Similar behavior was observed between ln(σ_{ac}) and ln(σ_{dc}) for the remaining SA and MA glasses. The parameter *s* evaluated from the slopes of the least square linear fits is of the order of 0.69 and 0.72 for SA and MA systems respectively. The frequency exponent, *s* values at 500 K, determined using the relation $\sigma = A\omega^s$ has been reported to be in the range 0.71 to 0.66 and 0.75 to 0.69 for SA and MA glasses respectively [13]. The fact that frequency exponent determined from different methods are almost same indicates that the Hunt's model is good enough to explain the frequency dependence of conductivity in the present glasses. The study is limited to frequency domain $\omega > \omega_m$ and in this frequency range the relaxation process occurs with a local character and can be described by electronic hops between multivalent vanadium ion sites. Similar conclusions were drawn in [15-17,23].

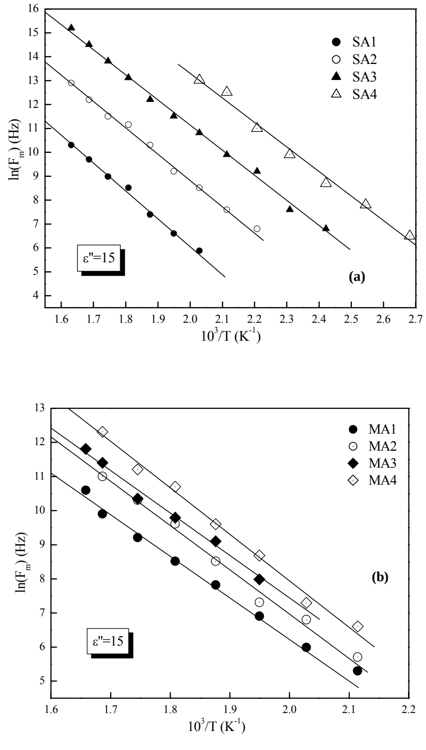

Fig. 3. Variation of characteristic frequency, F_m vs (1/T) for (a) SA and (b) MA glasses. Solid lines are the least square linear fits to the data.

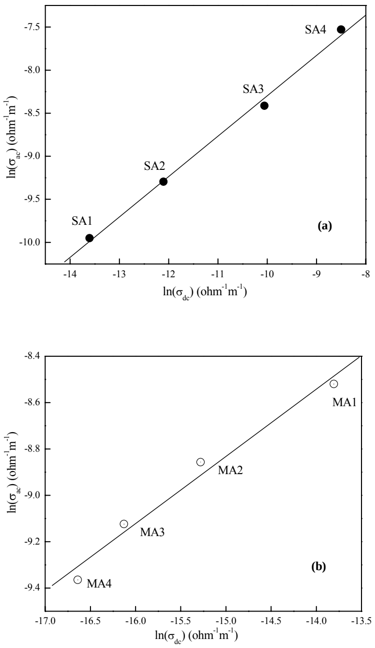

Fig. 4. The plots of $\ln(\sigma_{ac})$ vs $\ln(\sigma_{dc})$ for frequency of 1MHz and temperature of 400 K for (a) SA and (b) MA glasses. Solid lines are the least square linear fits to the data.

4. Conclusions

(i). The cobalt-borate glasses containing Li and K alkali ions in single and mixed proportions have been investigated for dielectric properties as a function of frequency and temperature. The dielectric constant and loss decrease with increase in frequency which are attributed to the decrease in electronic contribution and increase in dipolar contribution to the total polarizability with increase of frequency.

(ii). Hunt's model has been invoked to determine the activation energy for dielectric relaxation process and the activation energies were found to be in close agreement with dc activation energies and, therefore, it is concluded that in both single and mixed alkali glasses the relaxation process has a local character implying hops of polarons between multivalent TMI sites.

(iii). The BNN's linear relation between frequency dependent and independent conductivities has been verified in respect of both SA and MA systems, despite the absence of dielectric loss peaks. It is for the first time that the dielectric properties of Li and K alkali doped cobalt-borate glasses have been analyzed and understood in terms of Hunt's and BNN models and verified.

References

[1] G. B. Devidas, T. Sankarappa, B. K. Cougule, G. Prasad, J. Non-Cryst. Solids **353,** 426 (2007).
[2] R. J. Barczynski, L. Murawski, Mat. Sci. Poland **24,** 1 (2006).
[3] P. Jozwiak, J. E. Garbrczyk, Solid State Ionics **176**, 2163 (2005).
[4] G. D. L. K. Jayasinghe, M. A. K. L. Dissanayake, P. W. S. K. Bandaranayake, J. L. Souquet, D. Foscallo, Solid State Ionics **121**, 19 (1999).
[5] D. Xun, J. Yang, S. Xu, N. Dai, L. Wen, L. Hu, Z. Jiang, Chin. Phys. Lett. **20**(1), 130 (2003).
[6] M. F. Churbanov, G. E. Snopatin, E. V. Zorin, S. V. Smetanin, E. M. Dianov, V. G. Plotnichenko, V. V. Koltashev, E. B. Kryukova, I. A. Grishin, G. G. Butsin, J. Optoelectron. Adv. Mater. **7**(4), 1765(2005).
[7] J. Pisarski, W. A. Pisarski, J. Optoelectron. Adv. Mater. **7**(5), 2667 (2005).
[8] Xiang Peng, Feng Song, Shibin Jiang, N. Peyghambarian, Makoto K. Gonokami, Lei Xu, Appl. Phys. Lett. **82,** 10 (2003).
[9] H. Kenmotsu, T. Hattori, S. Nishiyama, K. Fukushima, J. Phys. Chem. Solids **60**, 1461 (1999).
[10] N. Nagaraja, T. Sankarappa, M. Prashant Kumar, J. Non-Cryst.Solids (2007), in press.
[11] L. Murawski, R. J. Barczynski, J. Non-Cryst. Solids **185**, 84 (1995).
[12] S. Chakraborty, H. Satou, H. Sakata, J. Appl. Phys. **82**, 5520 (1997).
[13] N. Nagaraja, T. Sankarappa communicated to J.Non-Cryst.Solids.
[14] H. Sakata, K. Sega, B. K. Chaudhari, Phy.Rev.B **60**, 3230 (1999).
[15] W. Chomka, D. Samatowicz, J. Non-Cryst. Solids, **57**, 327 (1983).
[16] L. Murawski, R. J. Barczynski, J. Non-Cryst. Solids, **196**, 275 (1996).
[17] H. El Mkami, B. Deroide, R. Backov, J. V. Zanchetta, J. Phys. Chem. Solids **61**, 819 (2000).
[18] J. L. Barton, Verres Refract. **20**, 328 (1966).
[19] T. Nakajima, Annual Report, Conference on Electric Insulation and Dielectric Phenomenon, National Academy of Sciences, Washington DC, 1972, p.168.
[20] H. Namikawa, J. Non-Cryst. Solids **18**, 173 (1975).
[21] A. Hunt, J. Non-Cryst Solids **144**, 21 (1992).
[22] A. Hunt, J. Non-Cryst Solids **160**, 183 (1993).
[23] M. Prashant Kumar, T. Sankarappa, Mat. Sci.- Ind.J., (2007), in press.
[24] M. Prashant Kumar, T. Sankarappa, Santosh Kumar, J. All. Comp. (2007) In Press.
[25] R. El-Mallawany, A. El-Sayed, M. El-Gawad, Mater.Chem.Phys. **41**, 87 (1995).
[26] M. M. Elkholy, Phys.Chem.Glasses **42**, 49 (2001).
[27] M. H. Shaaban, A. A. Ali, L. K. El-Nimr, Mater. Chem. Phys. **96**, 423 (2006).
[28] A. A. Bahgat, Y. M. Abou-Zeid, Phys. Chem. Glasses **42**, 01 (2001).
[29] A. Mansingh, V. K. Dhawan, J. Phys. C: Solid State Phys **16**, 1675 (1983).

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