

Dielectric relaxation studies in some alkali doped vanadotellurite glasses

M. PRASHANT KUMAR, T. SANKARAPPA*

Department of Physics, Gulbarga University, Gulbarga 585 106, Karnataka, India

The dielectric properties in two series of single and mixed alkali doped vanadotellurite glasses have been investigated in the frequency range 50 Hz to 5 MHz and temperature range 300 K to 500 K. Hunt's model was invoked to analyze the data and the results indicated that the relaxation process has a local character which can be described by hopping between pairs of multivalent sites. Activation energies for dielectric loss process were found to be in close agreement with dc activation energies. The linear relationship between ac and dc conductivities has been confirmed in both systems.

(Received February 11, 2008; accepted April 2, 2008)

Keywords: Tellurite glasses, Transition metal ions, Alkali ions, Dielectric relaxation processes, Activation energies

1. Introduction

Among various types of glasses, the tellurite based glasses are well known for their high dielectric constant and electrical conductivity compared to other glass systems, which is speculated to be due to the unshared pair of electrons of the TeO_4 group that do not take part in the bonding [1]. Alkali ions doped glasses are mainly explored for applications in solid state devices, cathode materials for batteries, electrochemical and electro-optical devices [2-5]. The frequency and temperature dependent electrical conductivity in many binary and ternary alkali doped tellurite glasses has been reported [6-10].

The Mott's small polaron hopping model was used to interpret the dc and ac conductivities of different glasses doped with transition metal ions (TMI) and alkali ions [11-13]. The similarity in terms of the sizes of activation energies associated with the conductivity and dielectric relaxation processes has been one of the most important properties of TMI doped oxide glasses [14-17].

The carrier-diffusion process occurring in the glasses was identified by Barton [18], Nakijama [19] and Namikawa [20] (BNN) by correlating the dc conductivity with the dielectric relaxation peak. Hunt's model correlates the peak frequency in dielectric spectra to the electron transfer between multivalent TMI sites present in the glass network [21]. The Hunt's theory postulates a linear relationship between ac and dc conductivities within the pair approximation regime. This linear relation indicate the existence of a single mechanism for all the processes operated in the glass system, which is probably connected with the electron transfer between multivalent TMI sites [22].

The dielectric properties of phosphate glasses containing mixed TMIs (Fe and V) have been understood in terms of Hunt's model [14-15]. The internal frictions, conductivity and dielectric properties of Mg, Ca, Ba doped iron-metaphosphate glasses have been reported and noted almost the same value of activation energy for all the three processes which hinted at a single mechanism to be

responsible for all the three processes [16]. The dielectric properties and ac conductivity in $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3$ glasses were successfully explained in the light of Hunt's and BNN models and it was shown 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 glasses under present investigation have been reported for the frequency dependence conductivity and the data was analyzed in the framework of correlated barrier hopping model [24].

In the present communication, we report the dielectric studies in lithium and potassium oxides doped vanadotellurite glasses in the following mentioned compositions,

- i. $(\text{V}_2\text{O}_5)_{0.4}\text{-(Li}_2\text{O)}_x\text{-(TeO}_2)_{0.6-x}$, $x=0.10, 0.20$ and 0.40 labeled as SA1, SA2 and SA4.
- ii. $(\text{V}_2\text{O}_5)_{0.25}\text{-(Li}_2\text{O)}_{0.25}\text{-(K}_2\text{O)}_x\text{-(TeO}_2)_{0.5-x}$, $x=0.05, 0.10, 0.15$ and 0.20 , labeled as MA1, MA2, MA3 and MA4.

The present work is aimed at understanding the dielectric relaxation processes and activation energies associated with it and to check whether frequency dependent and independent conductivities can be correlated as envisaged by Hunt's and BNN models.

2. Experimental

The melt-quench technique was employed to synthesize the glass samples using analytical grade V_2O_5 , Li_2CO_3 , K_2CO_3 and TeO_2 (Sigma-Aldrich) as the starting materials. The relevant chemicals in appropriate weight ratios were taken in a porcelain crucible and melted in a muffle furnace at 1200 K. The melt was quickly quenched to room temperature by pouring on a stainless steel (SS) plate and covering it with another SS plate. The random pieces of the glass samples thus formed were collected. In order to relieve mechanical stresses, present in the glasses,

the samples were annealed at 500 K. The glassy nature of the samples was confirmed by XRD 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 50 Hz to 5 MHz and temperature from 300 K to 600 K. The dielectric constant (ϵ') and dielectric loss factor (ϵ'') were determined as per the following expressions [24],

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (1)$$

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

Where, ϵ_0 is the permittivity of free space, d is thickness of the glass sample and A is cross sectional area of the sample.

3. Results and discussion

3.1 Dielectric constant and loss

The dielectric constant, ϵ' , and dielectric loss, ϵ'' , were observed to be in the range 10^1 to 10^5 and 10^1 to 10^6 for SA glasses and 40 to 470 and 2 to 2470 for MA glasses. The typical plots of dielectric constant, ϵ' , versus frequency, F , for glasses SA1 and MA4 at various temperatures is 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 [23-26].

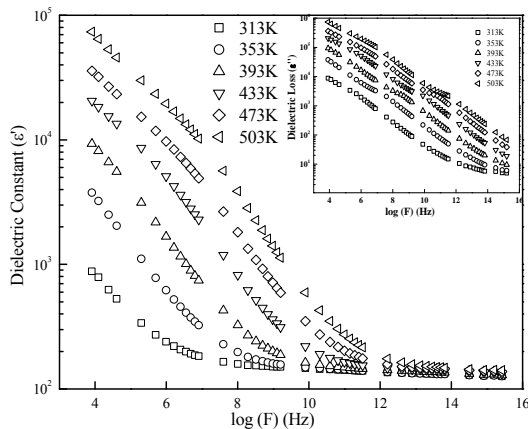


Fig. 1. Plot of $\log(\epsilon')$ versus $\log(F)$ for the glass SA1 at different temperatures. Inset shows the frequency dependency of ϵ'' for the same sample.

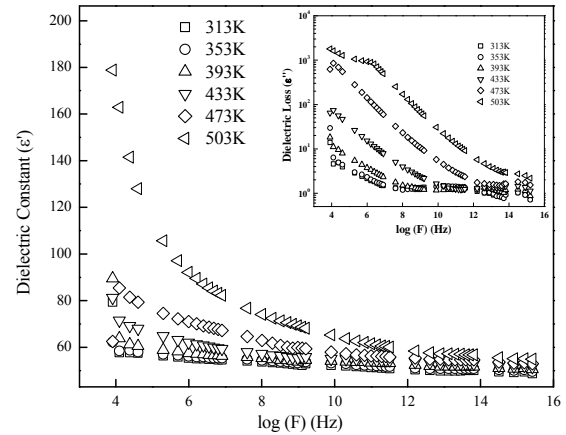


Fig. 2. Plot of $\log(\epsilon')$ versus $\log(F)$ for the glass MA4 at different temperatures. Inset shows the frequency dependency of ϵ'' for the same sample.

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 [27]. 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.

3.2 Dielectric relaxation process

For present glass systems the Hunt's model is used to study the dielectric relaxation processes, which has been used to the oxide glasses [14-17,21-22]. 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,

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

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

where, $r = 1 + d - d_f$, d being the dimensionality and $d_f = 2.66$ [15], A and $K(d)$ are the constants [17].

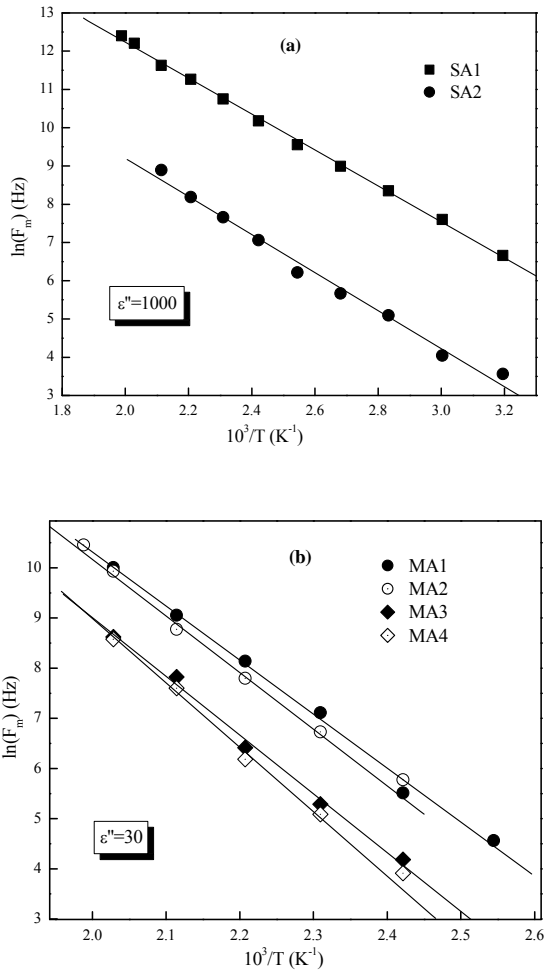


Fig. 3. Variation of characteristic frequency, F_m vs $(1/T)$ for (a) SA and (b) MA glasses. Solid lines are the least square linear fits to the data.

The frequency dependence of dielectric constant, ϵ' and dielectric loss, ϵ'' for the systems SA1 and MA4 at different temperatures are shown in Figs.1 and 2 respectively. From these figures it can be inferred that if there was a maximum in dielectric loss in both the glass systems, it would have appeared below the starting frequency i.e., 50HZ. This kind of behavior has been observed in V_2O_5 - TeO_2 , V_2O_5 - P_2O_5 and V_2O_5 - B_2O_3 glasses [10,15,17]. 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,

$$f_m = f_{m_0} \exp\left(-\frac{W_f}{k_B T}\right) \quad (5)$$

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. In Fig. 3, the characteristic frequency data for SA4 glass has not been shown as its dielectric loss values were found to be very smaller (>100), in the entire frequency range, compared to SA1 and SA2 glasses. The data, in Fig. 3, 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 [24]. Similar results have been reported for V_2O_5 - B_2O_3 and La and Ce ions doped V_2O_5 - TeO_2 glasses [17,23].

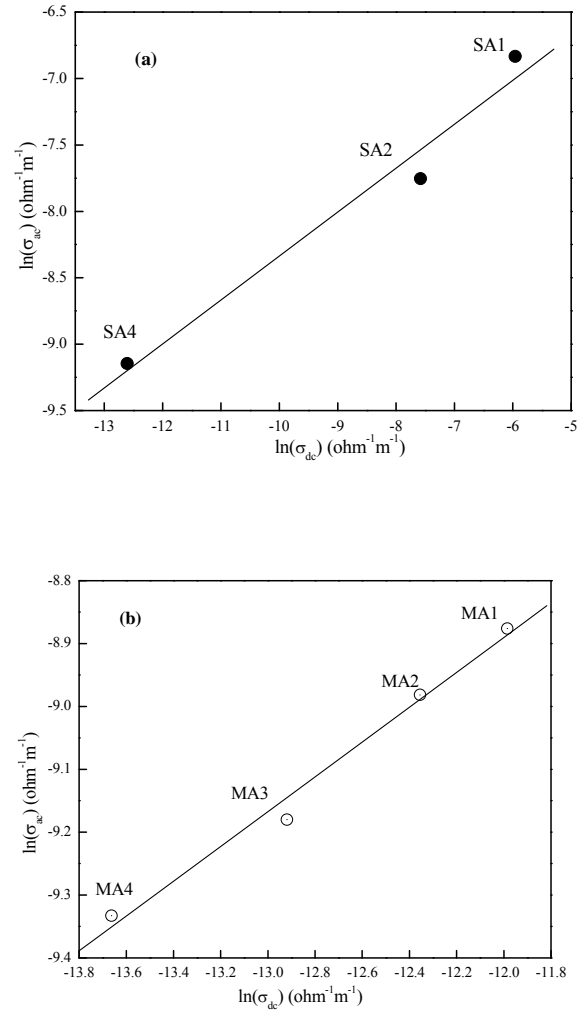


Fig. 4. The plots of $\ln(\sigma_{ac})$ vs $\ln(\sigma_{dc})$ for frequency of 1MHz and temperature of 450 K for (a) SA and (b) MA glasses. Solid lines are the least square linear fits.

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)
	TeO ₂	V ₂ O ₅	Li ₂ O	K ₂ O		
SA1	0.50	0.40	0.10	--	0.433	0.425
SA2	0.40	0.40	0.20	--	0.462	0.471
SA4	0.20	0.40	0.40	--	0.498	0.491
MA1	0.45	0.25	0.25	0.05	0.872	0.869
MA2	0.40	0.25	0.25	0.10	0.981	0.993
MA3	0.35	0.25	0.25	0.15	1.094	1.077
MA4	0.30	0.25	0.25	0.20	1.188	1.196

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

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

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

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

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

This expression shows that at a given frequency, the $\sigma(\omega)$ and σ_{dc} are linearly related to each other with a slope $(1-s)$. Figs. (4a) and (4b) illustrates the linear relation between $\ln(\sigma_{ac})$ and $\ln(\sigma_{dc})$ in both the glass systems. Similar behavior was observed between $\ln(\sigma_{ac})$ and $\ln(\sigma_{dc})$ 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 0.71 and 0.74 for SA and MA systems respectively. The frequency exponent, s values at 450 K, determined using the relation $\sigma = A\omega^s$ has been reported to be in the range 0.74 to 0.68 and 0.78 to 0.73 for SA and MA glasses respectively [24]. The fact that frequency exponents 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].

4. Conclusions

The decrease in dielectric constant and dielectric loss with increase in frequency in the studied glasses is attributed to the decrease in electronic contribution and

increase in dipolar contribution to the total polarizability with increase of frequency.

Hunt's model has been invoked to determine the activation energies for dielectric relaxation process in both sets of single and mixed alkali doped vanadotellurite glasses and the activation energies were found to be in close agreement with dc activation energies. Hence, 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. Despite the absence of dielectric loss peaks, the BNN's linear relation between frequency dependent and independent conductivities has been demonstrated in the studied systems. It is for the first time that the dielectric relaxation studies have been made on Li and K alkali doped vanadotellurite glasses and the results have been discussed in the light of Hunt's and BNN models.

Reference

- [1] A. Latia, C. Vancea, J. Optoelectron. Adv. Mater. **5**(1), 185 (2003).
- [2] D. Xun, J. Yang, S. Xu, N. Dai, L. Wen, L. Hu, Z. Jiang, Chin. Phys. Lett. **20**(1), 130 (2003).
- [3] M. F. Churbanov, G. E. Snopatin, E. V. Zorin, S. V. Smetanin, E. M. Dianova, V. G. Plotnichenkoa, V. V. Koltasheva, E. B. Kryukovaa, I. A. Grishinb, G. G. Butsinb, J. Optoelectron. Adv. Mater. **7**(4), 1765 (2005).
- [4] A. Petris, C. Popa, D. Popa, V. I. Vlad, J. Optoelectron. Adv. Mater. **6**(1), 57 (2004).
- [5] D. L. Sidebottom, M. A. Hruschka, B. G. Potter, R. K. Brow, Appl. Phys. Lett. **71**(14), 06 (1997).
- [6] C. Karlsson, A. Mandanici, A. Matic, J. Swenson, L. Borjesson, Phys. Rev. B. **68**, 064202 (2003).
- [7] P. Jozwiak, R. J. Barczynski, Mat. Sci. Pol. **24**(1), 221 (2006).
- [8] G. B. Devidas, T. Sankarappa, B. K. Chougule, G. Prasad, J. Non-Cryst. Solids **353**, 426 (2007).
- [9] R. El-Mallawany, A. El-Sayed, M. El-Gawad, Mater. Chem. Phys. **41**, 87 (1995).
- [10] A. Mansingh, V. K. Dhawan, J. Phys. C: Solid State Phys. **16**, 1675 (1983).
- [11] N. Nagaraja, T. Sankarappa, M. Prashant Kumar, J. Non-Cryst. Solids (2007) in press.

- [12] S. Chakraborty, H. Satou, H. Sakata, *J. Appl. Phys.* **82**(11), 5520 (1997).
- [13] N. Nagaraja, T. Sankarappa communicated to *J. Non-Cryst. Solids*.
- [14] L. Murawski, R. J. Barczynski, *J. Non-Cryst. Solids* **185**, 84 (1995).
- [15] L. Murawski, R. J. Barczynski, *J. Non-Cryst. Solids* **196**, 275 (1996).
- [16] W. Chomka, D. Samatowicz, *J. Non-Cryst. Solids* **57**, 327 (1983).
- [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 Solid.* **160**, 183 (1993).
- [23] M. Prashant Kumar, T. Sankarappa, *Mat. Sci.- Ind. J.*, (in press).
- [24] T. Sankarappa, M. Prashant Kumar, Santhosh Kumar (communicated to *J. Non-Cryst. Solids*).
- [25] M. Prashant Kumar, T. Sankarappa, Santosh Kumar, *J. All. Comp.* (In Press).
- [26] M. M. Elkholy, *Phys. Chem. Glasses* **42**(1), 49 (2001).
- [27] A. A. Bahgat, Y. M. Abou-Zeid, *Phys. Chem. Glasses* **42**, 01 (2001).

*Corresponding author: sankarappa@rediffmail.com