Effect of strontium on the AC conductivity and dielectric properties of vanadium borate glasses

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Abstract: In the present study, the strontium doped vanadium borate glasses were prepared by melt quenching technique. The non-crystalline nature of the samples has been established by the XRD studies. The ac electronic conduction in the temperature form 313 K to 473 K and in the frequency 100 Hz to 5.5 MHz have been studied. The dielectric constant and dielectric loss found to be increased and with increase in frequency they found to be decreased as temperature increases in these glass systems. The high temperature dependent of electronic conduction has been analyzed using Mott's small polaron hopping model and activation energies were determined. The ac conductivity was observed to quickly fall as soon as the SrO is brought into the glass matrix. Correspondingly, the activation energy is found to increase rapidly. This could be a sign for Sr+ ions may not at all donate to the total ac conductivity and the observed conductivity may be electronic alone which is due to the hopping of electrons between multivalent states of Vanadium ions.

***Key words* - AC conductivity; Dielectric properties; Electronic; Frequency dependent conductivity.**

I. INTRODUCTION

The presence of ions in multiple valence states due to the existence of transition metal ions and alkali ions in oxide glasses leads to semiconductor behavior and gained much importance over the last few years due to its technological applications in solid state devices, cathode materials for batteries, electronics and electro-optical devices. [1]. Electrically conducting and semiconducting transition metal oxide glasses have attracted by many researchers due to their possible applications in numerous scientific fields [2]. Vanadate glasses are very promising materials in this type of glass, V_2O_5 take part in the glass network with VO_5 pyramidal structural units containing $V4^+$ and $V5^+$ ions [3,4].

On the other hand, boron trioxide (B_2O_3), is recognized as a very decent glass network former, has outstanding glass-forming capability due to its good resistance in the direction of vibration, lower thermal expansion, high toughness, stress and chemical resistance as well as lower viscosity [5]. when strontium oxide was bringing together into borate glass, the further oxygen from alkali oxide cause alteration from trigonal boron atom BO_3 into four-fold BO_4 coordinated boron [6]. When alkali oxides are incorporated to borate glass, nonlinear behavior were observed in the structural and physical. For instance, the density and glass transition temperature, Tg are increased with low concentration of alkali oxide [7]. Kundu et al. [8] studied the structural and physical properties of xFe_2O_3-(40-x) B_2O_3-$60V_2O_5$ ($0 \le x \le 20$) glass system. They obtained electrical conductivity of up to $4.194 \times 10^{-2} Sm^{-1}$ when x=20. Nevertheless, their study was incomplete to the glass form of this system.

To the best of our knowledge, no earlier studies were done on this specific composition of glass-system. Consequently, the present study aims, for the first time, to study the ac electrical conductivity of the system B_2O_3-V_2O_5-SrO. Moreover, the SrO^+ ions were introduced into the glass network as the cost of V_2O_5 in order to understand the effect of incorporating the SrO^+ ions on ac electrical conduction and dielectric properties.

In this work, a series of (0.5) B_2O_3 - (0.5-x) V_2O_5 – x SrO (x = 10, 20, 30, 40, 50) coded as BVSr1, BVSr2, BVSr3, BVSr4 and BVSr5 glasses were studied to investigate the effect of SrO^+ ions content on the AC conductivity and dielectric properties with the help of impedance analyzer. These glasses were measured in the temperature range 313-473 K and in the frequency range 100 Hz -5.5 MHz.

II. EXPERIMENTAL

Glass series with general formula x(SrO)-(50-x) V_2O_5-0.5(B_2O_3) were prepared by melt-quenching method. AR grade chemicals with 99.99% purity, of $SrCO_3$, V_2O_5 and H_3BO_3 procured from HI-media were used for synthesis of the glass samples. The chemical quantities in required weight ratios were taken in silica crucibles and the composition was systematically mixed in order to get the uniformity. These silica crucibles are employed into the electrical muffle furnace and melted at the temperature 1373 K. When the uniform crystal clear melt was formed, the melt was poured on to a thick stainless steel plate and quickly quenched by pressing it with another stainless steel plate. The different sized glass samples were collected. The collected samples were then annealed at 473 K in order to remove thermal strains, if any, in them. As prepared samples were subjected to XRD to confirm their amorphous nature. For the ac conductivity measurements, the random size samples of 12 x 10 x 0.9 mm were cut into regular shape for ac measurement.

The frequency dependent measurements of capacitance, *C*, and dissipation factor, *tan δ*, were obtained using a computer controlled LCR meter (ZM2376, NF Corporation, Japan) for different frequencies in the range 1mHz to 5.5 MHz and temperature from 313 K to 473 K. The ε′, ε″ and ac conduction (σ_{ac}) were calculated as per the following equations [9],

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

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

$$\sigma_{ac} = \omega \varepsilon_o \varepsilon'' \quad (3)$$

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.

III. RESULT AND DISCUSSION

3.1. XRD

The Fig.1 shows the XRD pattern of BVSr4 and BVSr5 sample. No peak has been observed which confirms the non-crystalline nature of the glass samples. Same nature was observed for the remaining prepared glass samples.

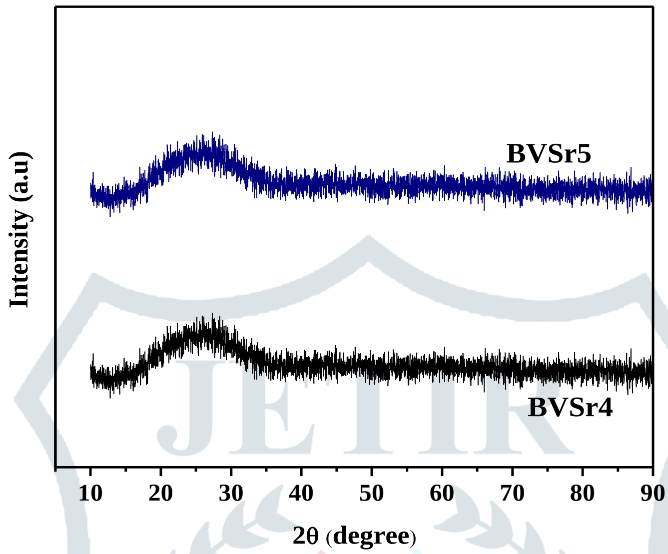

Fig.1- X-ray diffraction pattern of BVSr4 and BVSr5 samples

3.2. DIELECTRIC CONSTANT AND LOSS

The plot of dielectric constant, ε′ versus frequency for all glasses for different composition at 443 K is illustrated in Figs. 2 and Fig 3 represents the plot of dielectric constant versus frequency for all glasses for different temperatures. The measured ε′ and ε″ were found to lie in the range of 1×10^2 to 8×10^2 and 10^2 to 9×10^2 respectively. It can be observed from Fig. 2 that both ε′ and ε″ dropped with increase in frequencies and increases with increase in temperature [10]. This indicates that at higher frequency the alkali ions don't follow the field variation and also due to interfacial effects such as space charge polarization may lead to takes place [11].

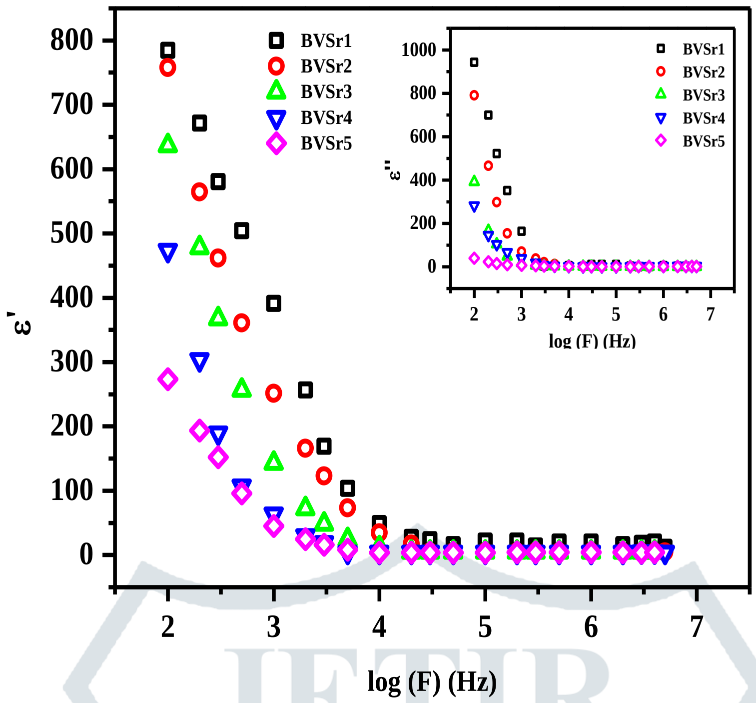

Fig. 2. Plot of log(F) versus (ε′) at T=443 K temperature for all glasses. Inset shows the frequency dependency of ε″ for all glass samples.

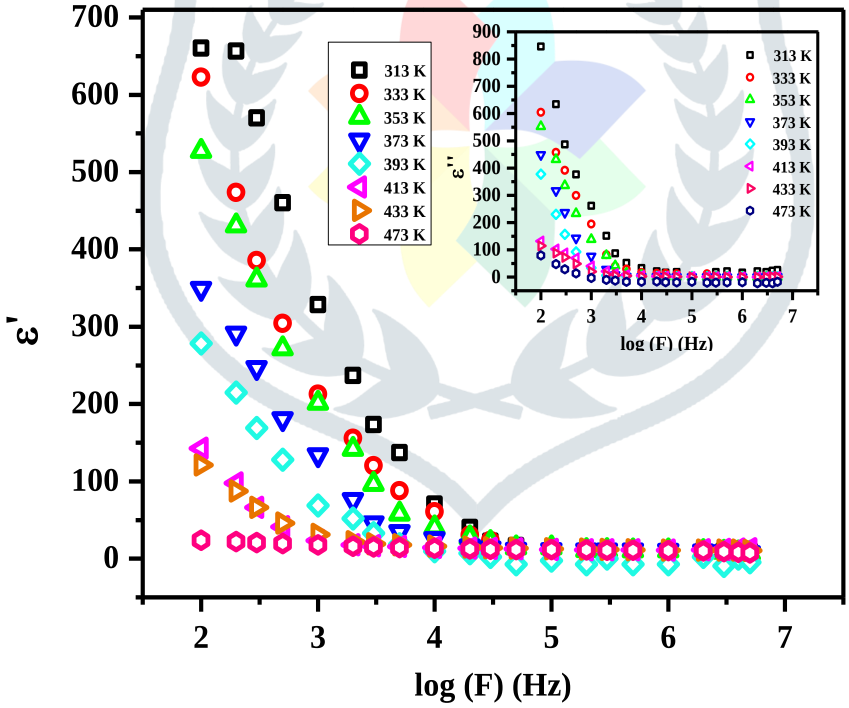

Fig. 3. Plot of log(F) versus (ε') for the glass BVSr3 at different temperatures. Inset shows the frequency dependency of ε″ at different temperatures.

3.3. AC CONDUCTIVITY

The ac conductivity variation was found to be in the present glass system due to thermally stimulated process and is due to the hopping of polarons among the multivalent states of V^{+} ions in the glass matrix [12]. Mott's SPH model was well-thought-out to be applicable for investigating the high temperature dependent ac conductivity. The plots of $\ln(\sigma_{ac}T)$ versus (1/T) at different frequencies for BVSr3 glasses are presented in Fig. 4. The ac conductivity values varied in the range from 10^{-5} $\Omega^{-1}m^{-1}$ to 10^{-7} $\Omega^{-1}m^{-1}$. These conductivity ranges are in agreement with the reported ac conductivities on similar and other glass systems [13,14].

Due to the semiconductor nature in all the present glass systems the high temperature dependence of ac conductivity follows Arrhenius law. As per the Arrhenius law, the electrical conductivity in non-adiabatic regime is expressed as [15],

$$\sigma = \frac{\sigma_o}{T}\exp\left(-\frac{W}{k_B T}\right) \qquad (4)$$

where, W is the activation energy and σ_o is the pre-exponential factor.

The profiles of ln(σ_{ac}T) versus (1/T) at a different frequency for BVSr3 glasses are made as per Eq. (4) and they are illustrated in Fig. 4. The plotted curves are linear at high temperature and non-linear at low temperature. The linear lines were fit to the data at high temperature. From the slopes of linear lines, the activation energy, W_{ac}, were determined. The determined activation energy, W_{ac} values are in the range 0.70-1.21 eV (Table 1). Fig 4 and Fig. 5 it is observed that the variation of ac conductivity at 443 K for all studied composition of BVSr series glasses were found decreased with increase in the SrO concertation. This type of variation in ac conductivity and activation energy indicates that Sr^+ ions may not at all contribute the total conductivity and the observed conductivity may be due to hopping of electrons alone between multivalent states of vanadium ions.

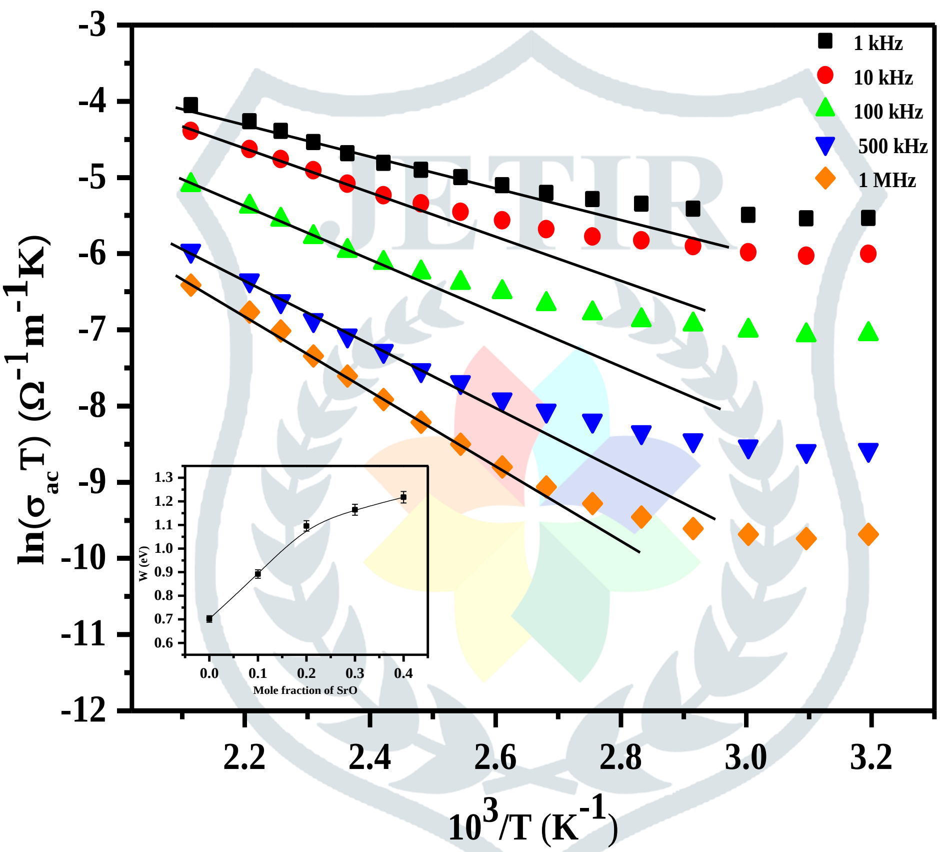

Fig. 4. Temperature dependence of ac conductivity at different frequencies for the glass sample BVSr3. Solid lines are the linear fits to the high temperature data. Inset shows the variation of activation energy with composition.

Table 1*:* Variation of ac conductivity and ac activation energy at different frequencies.

Glass Code	Glass Composition	Frequency (Hz)	σ_{ac} ($\Omega^{-1}m^{-1}$)	W_{ac} (eV)
BVS1	0	1kHz	1.23 x10^{-5}	0.70
BVS2	0.1	10kHz	7.55 x10^{-6}	0.89
BVS3	0.2	100kHz	2.70 x10^{-6}	1.09
BVS4	0.3	500kHz	5.92 x10^{-7}	1.16
BVS4	0.4	1MHz	1.86 x10^{-7}	1.21

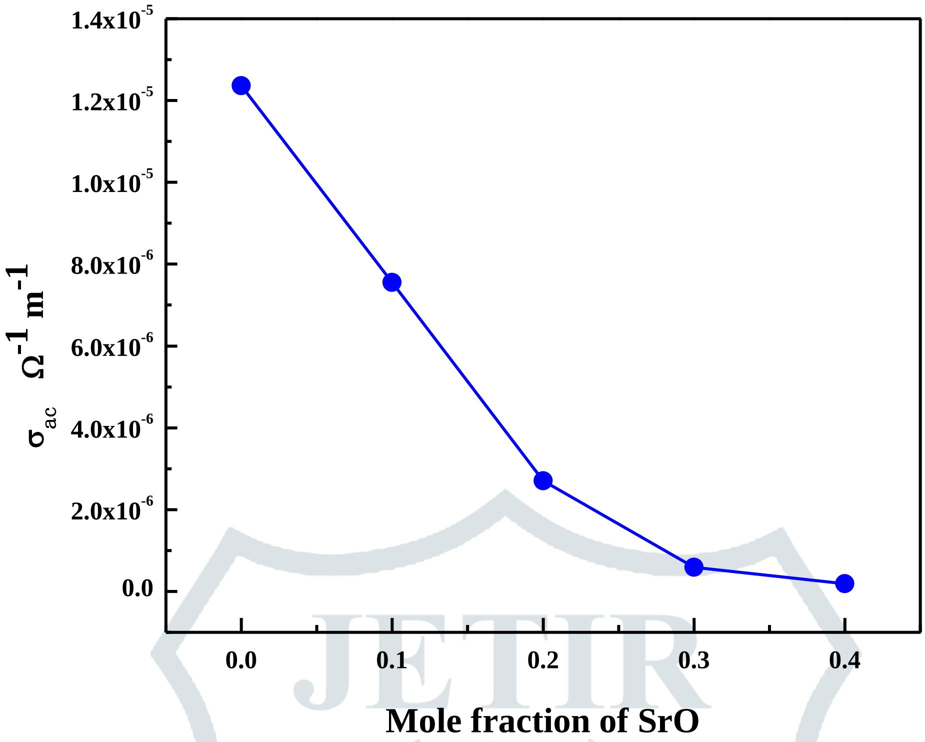

Fig.5. Variation of ac conductivity versus mole fraction of Sro.

CONCLUSION

A series of borate glasses doped with V2O5 and SrO were prepared by melt quenching technique with molar fraction x=0, 0.1, 0.2, 0.3 and 0.4. The amorphous nature of the sample was confirmed by XRD studies. The high temperature dependence of ac electrical conductivity of frequency dependent and dielectric properties as a function of temperature over a wide range have been studied. The ε′ and ε″ reduced with increase in frequency. This is attributed to the reduction in electronic contribution.

With the increase in SrO concentrations, the ac electrical conductivity decreased and activation energy increased. The conductivity is found to be highest for 0 mol% of SrO and it decreased continuously for further increase in SrO mol%. The activation energy for the glass containing 0 to 0.1% mole fraction of SrO are lower than that of other glasses in the present series. This type of variation in conductivity and activation energy indicates that Sr+ ions may not at all contribute the total conductivity and the observed ac conductivity may be due to hopping of electrons alone. The high temperature conductivity data has been analyzed in terms of Mott's Small Polaron Hopping (SPH) model.

REFERENCES

[1] J. Livage, J.P. Jolivet, E. Tronc, J. Non-Cryst. Solids 121 (1990) 35.
[2] R. Lakshmikantha, N.H. Ayachit, R.V. Anavekar, J. Phys.Chem. Solids 75 (2014) 168.
[3] A. Sheoran, S. Sanghai, S. Rani, A. Agarwal, V.P. Seth, J. Alloys Compd., 475 (2009) 804.
[4] T. Suzuki, M. Hirano, H. Hosono, J. Appl. Phys. 91 (2002) 41.
[5] G. Kaur, OP. Pandey and K. Singh, J. Non. Cryst. Solids 358 (2012) 2589.
[6] A. H. Khafagy, A. A. E-Adawy, A. A. Higazy, S. El-Rabaie and A. S. Eid, J. Non Cryst. Solids 354 (2008) 3152.
[7] Y.B. Saddeek, Physica B: Condense Matter 344 (2004)163.
[8] V. Kundu, R. Dhiman, A. Maan, D. Goyal, Adv. Condens. Matter Phys. 2008 (2008) 1.
[9] D. Dutta, A. Ghosh Phys. Rev. B 72 (2), (1993).: 024201-6.
[10] M.M. Elkholy, Phys. Chem. Glasses 42 (2001) 49.
[11] M. Prashant Kumar, T. Sankarappa, S. Kumar, J. Alloys Compd. 464 (2008) 393.
[12] J. Kawamura, M. Shimoji, J. Non. Cryst. Solids 79 (3) (1986)367.
[13] M.M. EI-Desoky, J. Non-Cryst. Solids, 351 (37-39) (2005) 3139-3146.
[14] J. Zhong, P.J. Bray, J. Non-Cryst. Solids 111 (1989) 67.
[15] N.F. Mott, J. Non-Cryst. Solids 1 (1968) 1.