INFLUENCE OF VANADIUM IONS ON DIELECTRIC PROPERTIES OF PbO-CaO-B_2O_3 GLASSES

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Abstract: Glasses of the composition 30PbO- (5-x) CaO-65B_2O_3: x V_2O_5 (x=0.2 to 1.0 in steps of 0.2) are prepared using melt quenching technique. The objective of this paper is to have a comprehensive understanding over the topology and valence states of vanadium ions in PbO-CaO-B_2O_3 glass network, by a systematic study of various dielectric properties (dielectric constant, loss tanδ, a.c conductivity $\sigma_{a.c}$, over a moderately wide range of frequency and temperature) coupled with spectroscopic investigations. The dielectric parameters viz., ε' tan δ and σ_{ac} are measured and are found to increase and the activation energy for ac conduction is found to decrease with the increase in the concentration of V_2O_5. The analysis of dielectric loss studies indicated that these glasses exhibit dipolar effects. There is a higher degree of disorder in the glasses mixed with higher concentration of vanadyl ions.

Keywords: Borate Glasses, Dielectric Properties, Vanadyl Ions.

1. Introduction: Semiconducting transition metal oxide glasses have gained importance in recent years due to their possible applications in various technological fields. Transition metal ions are very interesting ions to probe in the glass networks because of their broad radial distribution of outer d-orbital electron functions and their sensitive response to the surrounding actions. Among various semiconducting transition metal oxide glasses, the vanadate glasses find applications in memory, switching devices. The glasses containing vanadium ions have attracted much interest in solid-state chemistry and materials science. V_2O_5 is known to participate in the glass network with VO_5 pyramidal structural units. Several vanadate glasses show semiconducting behavior with the electrical conductivity of 10^{-3} to 10^{-5} $(\Omega\text{-cm})^{-1}$, which is known to be electron hopping between V^{4+} to V^{5+} ions, existing in the glass

network. The content of vanadium in different forms in different valence states exist in the glass depends upon the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the vanadium ion and the structure and physical properties of the glass is expected to be highly interesting. Such studies will pave the way for assessing the insulating character of the glasses. Further, the results of dielectric measurements together with spectroscopic properties may also throw some light on many aspects, such as the geometry of structural units of glass network, the character of chemical bonds and also the coordination of the polyhedra of vanadium ions.

2. Methodology: Within the glass forming region of PbO-CaO-B_2O_3 glass system, the following compositions with successive increase in the concentration of V_2O_5 are chosen for the present study:
V_x: 30PbO- (5-x)CaO-65B_2O_3: x V_2O_5. Dielctric properties are measured using standard procedures.

3. Results and Discussion: As the concentration of V_2O_5 is increased, the value of dielectric constant ε° is observed to increase for glasses, with considerable frequency dependence, exhibiting larger values at lower frequencies (Fig 1). The dielectric loss tanδ at room temperature with the concentration of V_2O_5 exhibited a similar behavior (Fig. 1). The temperature dependence of ε' for PbO-CaO-B_2O_3 glasses doped with different concentrations of V_2O_5 at 1 kHz is also studied. The values of ε′ is found to increase with temperatures slowly up to about 100 °C and beyond this temperature it increases at faster rates especially at lower frequencies. Fig. 2 shows that the rate of increase of ε′ with temperature is found to be the highest, for the glass containing the highest concentration of V_2O_5 (glass V_{10}).

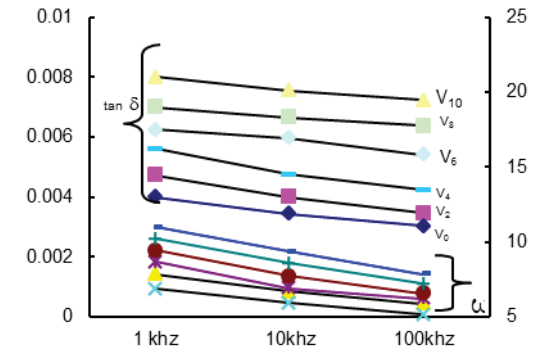

Fig. 1. Variation of dielectric constant and dielectric loss with frequency at room temperature for

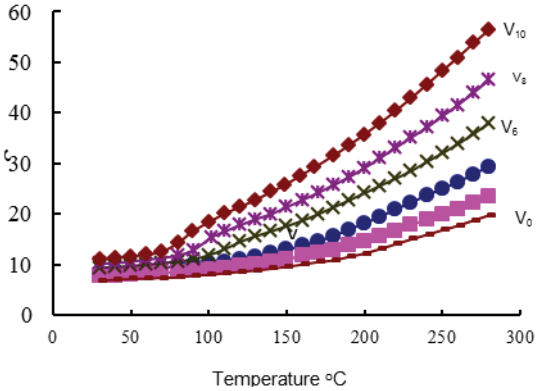

Fig. 2. Variation of dielectric constant with temperature for PbO-CaO-B_2O_3: V_2O_5 glasses at 1 KHz.

Vanadium ions are expected to exist mainly in V^{5+} states in the PbO-CaO-B_2O_3 glass matrix. However, during the melting of the glasses at higher temperatures there is every possibility for redox equilibrium to take place; the V^{5+} ions take part network forming positions with VO_5 trigonal bipyramidal structural units where as the V^{4+} ions form VO^{2+} complexes, may act as modifiers and distort the glass network.

The dielectric constant of a material is due to electronic, ionic, dipolar and space charge polarizations. Out of these, the space charge contribution depends upon the purity and the perfection of the glasses. Its influence is in general negligible at very low temperatures and noticeable in the low frequency region. The dipolar effects can some times be seen in the glasses even up to 10^6 Hz. The considerably higher values of dielectric constant and loss of PbO-CaO-B_2O_3: V_2O_5 glasses at room temperature observed at low frequencies may be ascribed to the bonding defects produced in the glass network which contribute to the space charge polarization.

Recollecting the data, on dielectric properties of the chosen glasses, a gradual hike in the values of the dielectric parameters has been observed with increase in the concentrations of V_2O_5; such an increase is obviously due to the increasing presence of VO^{2+} ions; these ions act as modifier ions, and generate bonding defects by breaking the B-O-B bonds. The defects thus produced create easy pathways for the migration of charges that would build up space charge polarization and lead to an increase in the dielectric parameters.

Tan δ versus temperature curves for PbO-CaO-B_2O_3: V_2O_5 glasses show dipolar relaxation effects, with increasing relaxation character with increasing concentration of V_2O_5. Increase in $(\tan \delta)_{max}$ and broadening of relaxation curves with increase in V_2O_5 concentration indicate an increase in the lattice distortion that facilitates the orientation of dipoles in the field direction more freely. The way tan δ varies with temperature suggests the spreading of relaxation times; such spreading indicate additionally VO^{2+} complexes, also act as electric dipoles and participate in relaxation effects [1]-[2]. The low temperature part of the conductivity (a near temperature independent part, as in the case of present glasses up to nearly 373 K) can be explained on the basis of quantum mechanical tunneling model. In general, the a.c. conductivity of the amorphous material where charge carriers experience an approximately random potential energy on diffusing, obeys the equation: $\sigma(\omega) = A\omega^s$, (1)
with the exponent $\sigma < 1$ (up to the frequency of 1 MHz), is considered to signify the coupling of an ion's movement with its environment [3]. The equation for a.c. conductivity due to quantum mechanical tunneling is given by [4]: $\sigma(\omega) = \eta e^2 KT\,[N(E_F)]^2\,\alpha^{-5}\omega\,[\ln(\nu_{ph}/\omega)]^4$, (2)
where $N(E_F)$ is the density of the energy states near the Fermi level, α is the electronic wave function decay constant, ν_{ph} is the phonon frequency and η is a constant and its value is given by $\eta = \pi/3$ (Austin & Mott [4], = $3.66\,\pi^2/6$ (Butcher & Hyden [5]), = $\pi^4/96$ (Pollak [6]).

Thus, the quantum mechanical tunneling of a carrier through the potential barrier between the sites separated by a distance R demands that s should be temperature independent but dependent on frequency. The plot of log $\sigma(\omega)$ *vs* log ω for all the glass at low temperatures yielded a straight line.

Perhaps, the more accurate model for a.c. conduction in which 's' is less dependent on frequency (as observed) for a.c. conduction in PbO-CaO-B_2O_3: V_2O_5 glasses is the correlated barrier hopping (CBH) model (as per this model a pair of electrons are assumed to hop

together from a D^- centre to D^+ centre) proposed by Elliott [7] in which the height of the potential barrier is correlated with inter site separation.

Among various mechanisms of conduction in the amorphous materials (such as band conduction, conduction in extended states, conduction in localized states near the band edge and conduction in the localized states near the Fermi level), the conduction in the localized states near Fermi level occurs when a.c. conductivity is nearly temperature independent and varies linearly with frequency. The conduction in the present PbO-CaO-B_2O_3: V_2O_5 glasses in the low temperature region (up to 373K) can safely be attributed to take place by this mechanism.

Conclusion: The dielectric parameters viz., ε' tan δ and σ_{ac} are found to increase and the activation energy for ac conduction is found to decrease with the increase in the concentration of V_2O_5. This result point out that there is a gradual increase in the concentration of V^{4+} ions that act as modifiers in the glass network. The analysis of dielectric loss studies indicated that these glasses exhibit dipolar effects. The ac conduction could be explained both due to classical activation energy and due to the tunneling phenomena. The comparison of data of these properties for all the glasses under investigation indicates that there is a higher degree of disorder in the glasses mixed with higher concentration of vanadyl ions.

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