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Original Article

Electronic and ionic conductivity studies on microwave synthesized glasses containing transition metal ions

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ABSTRACT

Glasses in the system $xV_2O_5{\cdot}20Li_2O{\cdot}(80-x)$ [$0.6B_2O_3{:}0.4ZnO$] (where $10 \leq x \leq 50$) have been prepared by a simple microwave method. Microwave synthesis of materials offers advantages of efficient transformation of energy throughout the volume in an effectively short time. Conductivity in these glasses was controlled by the concentration of transition metal ion (TMI). The dc conductivity follows Arrhenius law and the activation energies determined by regression analysis varies with the content of V_2O_5 in a non-linear passion. This non-linearity is due to different conduction mechanisms operating in the investigated glasses. Impedance and electron paramagnetic resonance (EPR) spectroscopic studies were performed to elucidate the nature of conduction mechanism. Cole–cole plots of the investigated glasses consist of (i) single semicircle with a low frequency spur, (ii) two depressed semicircles and (iii) single semicircle without spur, which suggests the operation of two conduction mechanisms. EPR spectra reveal the existence of electronic conduction between aliovalent vanadium sites. Further, in highly modified ($10V_2O_5$ mol%) glasses Li^+ ion migration dominates.

1. Introduction

The conductivity in glasses has been of interest for long time because of their potential technological applications. Use of glasses as electrolyte and electrode materials has given a boost to the study of ion transport in glasses and search for new glassy materials [1–5]. The mechanism of electrical conductivity in ion-electron conducting glasses is a challenging problem [5–8].

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In recent years many glassy materials have been synthesized as binary or ternary systems using network forming oxides such as B_2O_3, P_2O_5, TeO_2 etc and alkali or silver oxides as modifiers by melt quenching method [1]. Microwave synthesis of materials is a new technology undergoing rapid developments due to potential advantages it offers such as reduced processing time, energy efficiency and products with enhanced properties. The only requirement of this method is that at least one of the components used for synthesizing materials should be a microwave susceptor [1,2].

Alkali borate glasses have been extensively studied over the past two decades to elucidate the nature and relative concentration of various borate units constituting the glass network [9]. B^{3+} atoms in these glasses are both in trigonal and tetrahedral state. The concentration of these borate species in the glass structure is however determined by the nature and the content of the modifier oxide. In glasses containing B_2O_3 and V_2O_5 the coordination number and connectivities of both borate and vanadate species vary in a complex manner as a consequence of modification [9]. Further, modification is understood to be the reaction of oxide ion (O^{2-}), which results in structural changes, by creating non-bridging oxygens (NBOs). These NBOs constitutes anionic sites with different binding energies in comparison to those oxygens localized in boron tetrahedra [1]. Horopanitis et al. [10] pointed out that, the Li^+ transport in lithiated boron oxide glasses increases with Li_2O concentration, not only due to Li^+ ion concentration but also due to structural modification. Ion conducting glasses with high $Li^+/Na^+/Ag^+/Cu^+$ concentration are called fast ion conductors (FIC) and they are promising glassy electrolyte for the solid state batteries [5,11,12].

Glasses containing transition metal oxide (TMO) such as V_2O_5, Fe_2O_3, CuO, MoO_3, WO_3, CoO, etc. are known to exhibit semiconducting property and hence these glasses have been studied extensively from the cathode point of view of batteries [1,13]. The existence of relative proportions of low and high valence states of transition metal ions (TMIs) is responsible for the electronic conduction in these glasses [6,14]. It is expected that TMO added to alkali modified glass, results in mixed conduction [6,15,16].

EPR spectra of V_2O_5 containing glasses originate from V^{4+} paramagnetic centers whose outer electronic structure $3p^6$, $3d^1$ enables unpaired magnetic moments of $3d^1$ electrons to interact with the electromagnetic field in the microwave range. Whereas, the electronic structure of V^{5+} is $3p^6$, which has total electron spin zero. Since the V^{4+} ion has electronic spin s = 1/2 and nuclear spin of ^{51}V is I = 7/2, one should expect interactions between corresponding magnetic moments resulting in the hyperfine structure [17]. Gupta et al. [18] pointed out that, long range electron spin–spin interactions between V^{4+} ions and the spin–orbit coupling cause an anisotropy of the g-factor and the broadening of the individual lines. In glasses, only orientation averaged spectra can be observed, which can lead to additional reduction of hyperfine structure lines. It was seen in V_2O_5–TeO_2 glasses that the disappearance of hyperfine structure lines at higher contents of V_2O_5 is due to super-exchange interaction of V^{4+}—O—V^{5+} chains [18]. In this study we used impedance and EPR spectroscopic studies to analyze conduction mechanisms in microwave synthesized $xV_2O_5{\cdot}20Li_2O{\cdot}(80-x)$ [$0.6B_2O_3$:0.4ZnO] glasses.

2. Experimental

Glasses were prepared by microwave heating technique using $xV_2O_5{\cdot}20Li_2O{\cdot}(80-x)$ [$0.6B_2O_3$:0.4ZnO] (where $10 < x < 50$) glass system. Analar grade vanadium pentoxide (V_2O_5) lithium carbonate (Li_2CO_3), orthoboric acid (H_3BO_3) and zinc oxide (ZnO) were used as starting materials. An appropriate quantity of weighed chemicals were mixed and thoroughly ground to homogenize the mixture and kept in a silica crucible inside a domestic microwave oven operating at 2.45 GHz and at a tunable power level up to a maximum of 850 W. When microwaves were switched on, complete decomposition of H_3BO_3 to B_2O_3, water and Li_2CO_3 to Li_2O, carbon dioxide was achieved in 2–3 min. Within 6–8 min of microwave exposure a good homogeneous melt was obtained, which was immediately quenched between brass blocks. The silica crucible was found to remain clean and unaffected during the short duration of melting. The glass was annealed in a muffle furnace for 1 h at 150 °C to remove thermal strains that could have developed during quenching. The samples were preserved in a sealed desiccator containing $CaCl_2$.

Glass transition temperature (T_g) of the samples was extracted from the thermograms recorded using Differential Scanning Colorimeter (Perkin Elmer DSC-2). For the electrical measurements, the annealed samples were thoroughly polished and coated with silver paste on both sides, which serve as electrodes having a thickness of about 0.1 cm and diameter of about 0.8 cm were used. The resistance of the sample was calculated by applying a dc field of 2 V and measuring the current through it using a digital electrometer (ECIL EA-5600). The conductivity of the sample was calculated using the relation:

$$\sigma_{dc} = \frac{d}{RA} \tag{1}$$

where d is the thickness of the sample and A is the area of the sample. Temperatures of the samples were measured using a chromel–alumel thermocouple placed very close to the sample holder. The measurements were repeated with changed polarity of the applied voltages.

Capacitance (C_p) and conductance (G) of the samples were measured as a function of frequency using a Hewlett-Packard HP 4192A impedance-gain phase analyzer from 100 Hz to 10 MHz in the temperature range 323–405 K. A home built cell assembly (having two terminal capacitor configuration and spring loaded silver electrodes) was used for the measurements. The temperature was controlled using Heatcon (Bangalore 560090, India) temperature controller with an accuracy of ±1 K in the entire range of measurements. The temperature of the sample was measured using Pt-Rh thermocouple positioned very close to the sample.

3. Results and discussion

The X-ray diffraction spectra of the annealed glasses did not show any sharp peaks (Fig. 1), indicating that the samples are

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