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Dielectric dispersion and ac conduction phenomena of $Li_2O-Sb_2O_3-PbO-GeO_2:Cr_2O_3$ glass system

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ABSTRACT

Lithium antimony lead germanate glasses doped with different concentrations of Cr_2O_3 (ranging from 0 to 0.5 mol %) were synthesized. The optical absorption and ESR spectral studies have indicated that there is a gradual increase in presence of octahedral chromium ions with increase of Cr_2O_3 concentration in the glass network. These studies have also revealed that a fraction of chromium ions get oxidized into Cr^{5+} and Cr^{6+} states. IR and Raman spectroscopic studies have pointed out that there is an increasing degree of depolymerization of the titled glass network with increase of Cr_2O_3 content. The dielectric parameters (viz., dielectric constant, loss and electrical modulus coefficients measured over a wide range of frequency and temperature) and also ac conductivity were found to increase with increase of Cr_2O_3 content. The reasons for such increase were discussed quantitatively in terms of various polarization mechanisms coupled with structural variations of the glass network.

1. Introduction

Investigation on spectroscopic and electrical properties of Cr_2O_3 doped glasses is still an interesting subject. Glasses doped with chromium ions are attractive as possible laser media, especially for tunable solid state lasers in the red and infrared spectral regions. It is quite possible for chromium ions to exist in different valence states simultaneously in the same glass host.

Materials containing mixed valence chromium ions are of recent interest as cathode materials in rechargeable batteries owing due to their very high energy density and high capacitance [1,2]. Among various oxidation states of chromium ions, Cr^{3+}, Cr^{4+}, Cr^{5+} and Cr^{6+} are most likely to be active and stable. Out of these, the Cr^{6+} (d^0) ions have the closed shell configuration, participate in the glass network with CrO_4^{2-} structural units and are expected to strengthen the host glass network. The Cr^{5+} (d^1) ions either participate in the glass network with CrO_4^{3-} complexes or go into the modifying positions with octahedral coordination. Similarly, Cr^{3+} ions occupy octahedral sites and this ion is well known due to its low crystal field strength that enables to give broad luminescence corresponding to $^4T_2 \rightarrow {}^4A_2$ transition. Several recent studies are available on the environment and oxidation states of chromium ion in various crystals, inorganic glass systems [3–5]. For example, Kaewkhao et al. [6] have recently reported that substitution of Cr_2O_3 in the place of SiO_2 in the silicate glasses, the network of glasses gets compressed but refractive index of glass samples gets increased. Similarly, Yano et al. [7] have reported surface composition and valence states of chromium ions in Cr_2O_3-doped iron-phosphate glasses at high temperature. Despite these

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studies, the review of several such studies on Cr^{3+} ions containing glasses has indicated that unexpected chromium ion effects on optical, dielectric as well as mechanical phenomena need still convincing explanation in the semiconducting glasses like GeO_2.

Germanium oxide glasses find several applications in IR technology, nonlinear optics, in the design of laser devices and as light guiding cores of optical fibers [8]. GeO_2 glasses also exhibit photo-structural effects, in particular photo-induced refractive index changes. Because of these qualities, GeO_2 based glasses are also being used to generate phase gratings directly in optical fibers by UV irradiation [9]. Addition of heavy metal oxides like PbO and Sb_2O_3 to these glasses further strengthen their second harmonic generation [10] capability and makes the glasses useful for nonlinear optical devices like ultrafast optical switches, power limiters and broad band optical amplifiers operating around 1.5 μm [11,12]. GeO_2 glasses are also well-known glasses for solid electrolyte applications [13] since they exhibit high ionic conductivity. The results of high real-space resolution neutron diffraction studies on PbO containing GeO_2 glasses have indicated that the glass structure consists of [GeO_4] and [GeO_6] units together with either [GeO_5] units or excess non-bridging oxygens. The average Pb–O coordination number is a little in excess of three, typical of Pb^{2+} with a sterically active lone-pair of electrons in these glasses. The variation in the concentration of such structural units in the glass network is expected to have profound influence especially on electrical properties of these glasses [14].

The addition of Li_2O to GeO_2 glass matrix containing Cr^{3+} ions is an added advantage especially for electrolytic applications. Substitution of Li sites by Cr^{3+} ions in these glasses is important for several reasons. Cr^{3+} centers whether they are in either in high-field sites (energy of $^4T_{2g} > {}^2E_g$) or in low-field sites (energy of $^4T_{2g} < {}^2E_g$) occupy Li^+ site and pave the way for the easy transport of Li^+ ions in the glass network [15–17]. This should lead to some unusual surface segregation effects for dopants occupying the Li^+ site [18]; such surface segregation, with an associated contribution to the ion conductivity in turn influences the electrical properties of these glasses. It is the interplay between spin polarization of Cr^{3+} and Li^+ migration that brings interesting changes in the conductivity mechanism. Thus the electronic properties of lithium containing germanate glasses doped with chromium ions may be manipulated by the direct inclusion of dopants, as well as, by the presence of Li^+, O^- ions, and dopant vacancies to serve as trap sites [2,19].

Several recent studies on Li_2O–GeO_2 glasses mixed with various other glass formers like P_2O_5, SiO_2 are available. For example, Mogus-Milankovic et al. [20] have reported lithium ion transport upon the addition of germanium oxide in lithium borophosphate glasses. In this study the authors have observed increase of electrical conductivity with the addition of GeO_2 and it was attributed to the formation of ion conducting channels arising from the structural modification and formation of the P–O–Ge linkages, resulting in an easy migration of Li^+ ions along these bonds. Feltri et al. [21] have studied the ac conductivity of GeO_2-doped silica glasses. In this study the authors have found that the variations of conductivity due to doping with GeO_2 are smaller than one order of magnitude. Their studies have also revealed that the substitution of Si units with Ge units did not affect the microscopic structure of the glass. Henderson et al. [22] have reported detailed studies on the structure of alkali germinate glasses mixed with P_2O_5 using Raman spectroscopy. In this study it was found that at high Ge:P ratios the glasses exhibit a density anomaly. The anomaly is attributed to the formation of small three-membered GeO_4 rings and alkali cation size and mass were reported as contributing factors to this anomaly. In spite of the availability of several such studies on GeO_2 glasses, the studies on heavy metal oxides viz. PbO, Sb_2O_3 mixed lithium germinate glasses that have got tremendous practical applications are very rare. Motivated by these facts, the present investigation is mainly devoted to have a comprehensive understanding over the influence of site and valence variations of chromium ions on electrical properties of $Li_2O-Sb_2O_3-PbO-GeO_2$ glasses with the support of the experimental data on spectroscopic (IR, Raman, ESR and optical absorption) properties. Such studies are expected to be useful for considering this material useful for solid electrolyte applications.

2. Experimental

The chemical compositions of the glasses, together with the sample identification nomenclature used in the present study are as follows:

C_0: $10Li_2O–30Sb_2O_3–20PbO–40GeO_2$;
C_1: $10Li_2O–29.9Sb_2O_3–20PbO–40GeO_2$: $0.1Cr_2O_3$;
C_2: $10Li_2O–29.8Sb_2O_3–20PbO–40GeO_2$: $0.2Cr_2O_3$;
C_3: $10Li_2O–29.7Sb_2O_3–20PbO–40GeO_2$: $0.3Cr_2O_3$;
C_4: $10Li_2O–29.6Sb_2O_3–20PbO–40GeO_2$: $0.4Cr_2O_3$;
C_5: $10Li_2O–29.5Sb_2O_3–20PbO–40GeO_2$: $0.5Cr_2O_3$.

Analytical grade reagents of Li_2CO_3, Sb_2O_3, GeO_2, PbO, Cr_2O_3 (Sigma Aldrich 99.99% pure) powders in appropriate proportions were thoroughly mixed in an agate mortar and melted in a thick-walled silica crucible at 1300 °C in a PID temperature controlled furnace for about 20 min. The resultant bubble free transparent liquid was then poured in a brass mold and subsequently annealed at 400 °C.

The X-ray diffraction patterns of the samples were recorded on a Philips Xpert system using the step scan method with Cu-Kα radiation ($\lambda = 1.5406$ Å), a step size of 0.04° 2θ and a collection time of 2 s per point over 2θ range to confirm the amorphous nature of the samples. A programable VIBRA HT density measurement kit was used to determine the densities of the bulk samples automatically (with readability 0.0001 g/cm^3) by means of Archimedes' principle with O-Xylene (99.9% pure) as buoyant liquid.

The samples were then ground and optically polished. The final dimensions of the samples used for the present measurements were about 1.0 cm × 1.0 cm × 0.1 cm. The optical absorption spectra of the samples were recorded in the wavelength range of 300–800 nm up to a resolution of 0.1 nm using a JASCO V-670 UV–vis NIR spectrophotometer. FTIR transmission spectra were recorded on a JASCO-FT/IR-5300 spectrophotometer to a resolution of 0.1 cm^{-1} in the range of 400–1200 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). Micro-