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The role of chromium ions on dielectric and spectroscopic properties of Li_2O–PbO–B_2O_3–P_2O_5 glasses

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ABSTRACT

Li_2O–PbO–B_2O_3–P_2O_5 glasses containing different concentrations of Cr_2O_3 ranging from 0 to 1 mol% were synthesized by melt quenching technique. The amorphous nature of the glasses was asserted by X-ray diffractometry. The dielectric properties i.e., dielectric constant (ε'), loss factor ($\tan\delta$) and a.c. conductivity (σ_{ac}) over a range of frequency 10^3–10^6 Hz in the temperature range 303–573 K have been carried out on these samples. The results have been analyzed in the light of different oxidation states of chromium ions with the help of data on infrared, optical absorption and ESR spectra. The analysis of the results indicates that when the concentration of Cr_2O_3 is increased in the glass matrix the Cr^{3+} ions which act as modifiers with CrO_6 structural units increase. The Cr^{6+} ions which enter the network as glass formers with CrO_4^{2-} structural units decrease with increase in dopant concentration.

1. Introduction

Nowadays much attention is paid towards borophosphate glasses due to their low refractive index, menial dispersion, remarkable optical properties and high transparency from the ultraviolet to the near-infrared region [1,2]. The chemical durability of borophosphate glasses doped with transition metals is greater than that of phosphate glasses due to the composition boron oxide in the glass network, mostly in the form of BO_4 tetrahedral, which transforms metaphosphate chain into three-dimensional network [3]. Due to these special properties, these glasses are used as materials for optical components such as tunable solid state lasers, optical materials, optical filters, IR domes, memories, modulators, luminescence materials, phosphors, solar energy converters, fiber optic communication devices, radiation dosimetry, cathode materials in batteries and in a number of electronic gadgets [4–10]. The conductivity of borate glasses integrated with multivalent transition metal ions can be enhanced by adding Li_2O to the glass network. The mixed electronic and ionic conduction of these glasses depend on the glass composition.

Among all the transition metal ions, chromium ions have attracted the attention of researchers due to their extraordinary absorption and emission properties when they occupy the octahedral positions in the host glass [11]. Chromium, a quite economical ion when dissolved in the glass network even in a very small concentration makes the glass colored and influences the optical and dielectric properties very strongly [12]. Cr^{3+} ion is used to explore the structure and local symmetry of new glass materials. In glass phases these ions occupy different sites with different field strengths due to changes in position and compositional disorder. Glasses combined with mixed valence chromium ions are used as cathode materials in rechargeable batteries because of their high energy density and lofty capacitance [12,13]. Chromium ions are expected to increase or decrease the chemical durability, mechanical strength and conductivity of the glasses hence they occupy in different oxidation states. These ions exist in glasses in Cr^{3+} states with CrO_6 structural units (acting as modifiers), Cr^{5+} and Cr^{6+} states with CrO_4^{3-} and CrO_4^{2-} structural units respectively (playing the role of glass formers) basing on the quantitative properties of glass formers, modifiers, size of the ions in the glass network, their field strength and mobility of the modifying cation [14–16].

Literature survey on borophosphate glasses reveals that most of the studies on these glasses are confined to structural investigation by means of DSC, spectroscopic studies etc. Particularly, no considerable studies on dielectric properties (dielectric constant ε', loss factor $\tan\delta$, a.c. conductivity σ_{ac} and dielectric breakdown strength) of chromium doped lithium lead borophosphate glasses are available. These studies are vital in estimating the conductivity and topology of the glasses. The main objective of the present investigation is to make a comprehensive study on the influence of chromium ions on the structural aspects of lithium lead borophosphate glasses from a systematic study on dielectric properties and spectroscopic studies such as optical absorption, FTIR and ESR spectra.

2. Experimental details

In the present investigation, the particular glass composition $20Li_2O$–$20PbO$–$45B_2O_3$–$(15 - x)$ P_2O_5: xCr_2O_3 (x ranging from

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0 to 1 mol%) was chosen. The glass samples are labeled as follows.

C0: $20Li_2O–20PbO–45B_2O_3–15P_2O_5$
C1: $20Li_2O–20PbO–45B_2O_3–14.9P_2O_5$: $0.1Cr_2O_3$
C2: $20Li_2O–20PbO–45B_2O_3–14.7P_2O_5$: $0.3Cr_2O_3$
C3: $20Li_2O–20PbO–45B_2O_3–14.5P_2O_5$: $0.5Cr_2O_3$
C4: $20Li_2O–20PbO–45B_2O_3–14.2P_2O_5$: $0.8Cr_2O_3$
C5: $20Li_2O–20PbO–45B_2O_3–14.0P_2O_5$: $1.0Cr_2O_3$

Analytical grade reagents of Li_2CO_3, PbO, H_3BO_3 and Cr_2O_3 were taken in proportionate amounts and amalgamated stoichiometrically in an agate mortar and melted in a porcelain crucible at 1223 K for 40 min in an automatic temperature controlled furnace. The bubble free, transparent melt was poured in a brass mold and subsequently annealed at 573 K. The dopant free sample (C0) was appeared to be clear, transparent and white in color; thereafter the color of the samples (from C1 to C5) was noticed to change from light green to dark green. The amorphous nature of the glasses was reflected from the X-ray diffraction spectra of the specimen recorded with Philips X-pert system using the step-scan method with Cu-K_α radiation ($\lambda = 1.5406$ Å) operated at 40 kV, 25 mA; a step size of 0.04° and a collection time of 2 s per point over the 2θ range. The density of the samples was estimated to an accuracy of ± 0.0001 g/cm^3 using the VIBRA HT Model a programmable density measurement kit using O-xylene (99.99% pure) as an immersion liquid. The refractive index of the glasses was determined by the Abbe refractometer NAR-4T Atago model, Japan, using methyl iodide containing sulfur solution ($\mu_D = 1.78$) as contact liquid, with light source of LED lamp (approximating to yellow color wavelength). The glass samples of 1 mm thickness were devised by cutting, grinding and polishing for recording the optical absorption spectra in the wavelength range 200–1000 nm with a resolution of 0.1 nm using the double beam UV–VIS–NIS spectrophotometer. The powdered samples of 100 mg were taken in a quartz tube for ESR studies. The ESR spectra of the samples were obtained using JOEL-FE-1X operating at the X-band frequency ($\nu \sim 9.154$ GHz) with field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and micropower of 10 mW was used. The FTIR spectra of the glasses were recorded in the wavenumber range from 400 to 1250 cm^{-1} with the help of a JASCO FTIR 6200 spectrophotometer by the KBr pellet method.

For dielectric measurements, the samples were ground flat to the dimensions of 1 cm × 1 cm × 0.2 cm and polished to higher extent. A thin layer of silver paint was applied on both sides of the samples, in order to serve as electrodes for dielectric studies. LF-impedance analyzer (Hewlett-Packard model 4192A) was used in the frequency range 10^3–10^6 Hz to measure the dielectric constant (ε'), loss factor ($\tan\delta$) and a.c. conductivity (σ_{ac}) over a range of temperature 303–573 K. The accuracy in the measurement of dielectric constant is ~0.01 and dielectric loss is ~0.001. The dielectric breakdown strength of all the samples was estimated at room temperature in air medium using a high ac voltage breakdown tester (ITL Model BOV-7, Hyderabad) operated with an input voltage of 230 V at a frequency of 50 Hz.

3. Results

3.1. Characterization and physical parameters

The fabricated glasses are free from visible defects like bubbles, cracks and inclusions. The X-ray diffraction spectra of C0, C1 and C4 glasses are shown in Fig. 1. No sharp Bragg peaks are observed in the spectra which indicate the amorphous nature of the glasses. However, a small hump in the spectra reveals the short range order of the glass samples. The physical parameters such as chromium ion concentration N_i, mean chromium ion separation r_i, polaron radius r_p and molar volume V_m are evaluated and mentioned in Table 1 along with the refractive indices of glasses. The measured density of chromium free sample is found to be 3.564 g/cm^3 and is found to increase with increase in the dopant concentration. A similar trend in refractive index and a reverse trend in molar volume of samples are noticed and recorded in Table 1. Among all the prepared glass samples the maximum value of density is 3.621 g/cm^3 for C5 glass.

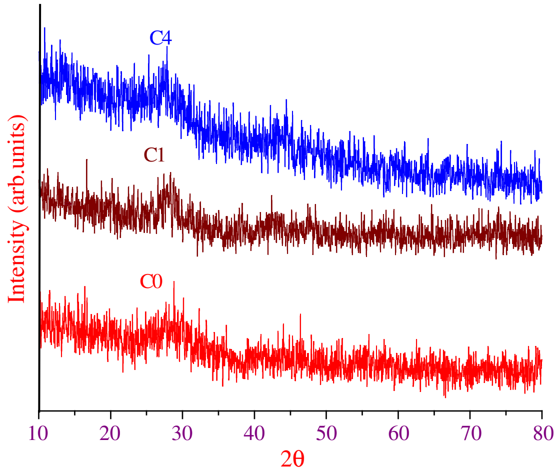

Fig. 1. X-ray diffraction pattern of $Li_2O–PbO–B_2O_3–P_2O_5$: Cr_2O_3 glasses.

3.2. Optical absorption

Fig. 2 shows the optical absorption spectra of $Li_2O–PbO–B_2O_3–P_2O_5$ glasses added with different concentrations of Cr_2O_3, at room temperature in the wavelength range 250–850 nm. No absorption peaks are found in the spectrum of pure sample C0 as it is radical free. When chromium ions are incorporated in the glass system then the spectra exhibit two intense absorption bands, with band positions at 438 nm (22,831 cm^{-1}), 625 nm (16,000 cm^{-1}). Besides this another three feeble bands are identified at 351 nm (28,490 cm^{-1}), 644 nm (15,528 cm^{-1}) and 691 nm (14,472 cm^{-1}). All these bands are noticed to shift to higher wavelength side. The intensity of the bands at 438 and 625 nm is observed to increase with increase in dopant concentration. The fundamental absorption edge reveals the band structure around the energy gap.

The absorption edge at 299 nm for C0 glass is red shifted to 342 nm (C5 glass) with gradual increase in concentration of chromium ions. Optical energy band gap E_g of the glasses is determined from the Tauc plots drawn between $h\nu$ and $(\alpha h\nu)^{1/2}$ by extrapolating the linear region to x-axis where $(\alpha h\nu)^{1/2} = 0$ as shown in Fig. 3. The gradual decrease in optical band gap is noticed with increase in the concentration of Cr_2O_3. The optical band gap is observed to be high for C0 glass (4.29 eV) and low for C5 glass (3.37 eV). Urbach energy (ΔE) which gives the crucial information about the density of energy states in the band gap is evaluated from the plots drawn between photon energy $h\nu$ versus ln $\alpha(\nu)$ values. The relation between $\alpha(\nu)$ and Urbach energy (ΔE) is given by the Urbach law as follows [17]

$$\alpha(\upsilon) = C \exp(h\upsilon/\Delta E) \quad (1)$$

where C is constant and ΔE is the Urbach energy interpreted as the energy gap between localized tail states in the forbidden region. ΔE values are acquired by taking the reciprocals of the slopes of the linear region of the ln $\alpha(\upsilon)$ versus $h\upsilon$ plots as shown in Fig. 4. The evaluated ΔE values which are found to increase with the concentration of chromium ions are mentioned in Table 2. The minimum and maximum values of ΔE for C0 and C5 glasses are 0.2536 eV and 0.6015 eV respectively. Inset of Fig. 4 shows the variation of optical band gap and Urbach energy with concentration of dopant.