Journal of Alloys and Compounds 663 (2016) 708–717

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Ionic conductivity, dielectric and optical properties of lithium lead borophosphate glasses combined with manganese ions

S. Yusub [a, *], P. Srinivasa Rao [b], D. Krishna Rao [c]

[a] Department of Physics, Sri Vasavi Institute of Eng. Tech., Nandamuru, 521369, A.P., India
[b] Department of Physics, S.V.R.M. College, Nagaram, 522268, A.P., India
[c] Department of Physics, Acharya Nagarjuna University, Nagarjunanagar, 522510, A.P., India

ARTICLE INFO

Article history:
Received 14 October 2015
Received in revised form
30 November 2015
Accepted 20 December 2015
Available online 23 December 2015

Keywords:
X–ray diffraction
Quenching
Optical properties
Electron paramagnetic resonance
Dielectric response
Ionic conduction

ABSTRACT

Multi–component transparent glasses of composition $20Li_2O–20PbO–45B_2O_3–(15–x)P_2O_5–xMnO$, with $0 \leq x \leq 3$ mol% (x = 0, 0.2, 0.4, 0.6, 1, 2 and 3), were fabricated by the melt quenching technique. The amorphous nature of the samples was asserted by X–ray diffraction. FTIR analysis disclosed the bands due to Mn–O specific vibrations along with conventional borate and phosphate groups. EPR and optical absorption spectra were recorded at ambient temperature. The results demonstrated that manganese ions exist in Mn^{2+} and Mn^{3+} states and occupy octahedral sites in the glass network. Dielectric studies such as dielectric constant (ε'), loss ($\tan\delta$) and a.c. conductivity (σ_{ac}) in the frequency range 10^3–10^6 Hz in the temperature range 30–300 °C were also carried out on these samples. These studies have revealed that the glasses exhibited semiconducting nature and such nature increases with increase in the concentration of MnO.

1. Introduction

B_2O_3 is one of the best essential glass formers, when alloyed with transition metal ions find potential applications for different domains of modern science and technology [1–3]. When P_2O_5 is incorporated in borate glasses, it reduces the melting and softening temperatures and decreases the optical band gap of the glasses. The phosphate ions enter the glass system with various structural units like P=O, $P–O^-$, PO_4^{3-} and PO_4 [4,5]. This structural group alters the physical characteristics of glasses vigorously. Nowadays, much attention is given to research on borophosphate glasses assorted with different transition metal ions, because of their tremendous technological importance in the production of tunable solid–state lasers, optical materials, solar energy converters, fiber optic communication devices, cathode electrodes in batteries and in number of electronic components [6–9]. Borate glasses combined with Li^+ ions are considered as the potential media for electrolytes as they show isotropic ion conductivity and stability at high voltage [10,11]. Lithium borophosphate glasses are venerable for their exceptional physical and chemical stabilities, combined with improved ionic conductivities, which makes their use as solid electrolytes [12,13].

PbO is a conventional glass modifier and invades the glass network by rupturing the B–O–B and P–O–P linkages. It is also assumed that PbO may take part in the glass system with $[PbO_{4/2}]$ pyramidal units attached in corrugated layers when the lead ion is attached to four oxygen atoms in a covalent Q^4 bond configuration [14]. The covalency of Pb–O bond is much stronger than B–O and P–O bond since electro negativity of Pb (2.33) is greater than that of B (2.04) and P (2.19). Due to this reason, the lead ions have the higher affinity towards oxygen atoms and engage with $[PbO_5]$ and $[PbO_6]$ structural units in the glass system [15–17]. Li^+ ions being strong modifiers are anticipated to occupy non–bridging oxygen (NBO) positions in the domain of BO_4, PO_4 structures [18–20].

Glasses doped with manganese ions find stupendous industrial and scientific applications [3]. These manganese ions form the link with borate and phosphate groups and strengthen its structure and may enhance the chemical resistance of the glass network. These ions exist in divergent valence states in different glass systems [21]. For example, Mn^{2+} ions exist with both octahedral and tetrahedral coordination's in silicate and germanate glasses whereas Mn^{3+} ions occupy octahedral positions in borate glasses. Further, among different manganese ions Mn^{2+} and Mn^{3+} are well–known

* Corresponding author.
E-mail address: syedyusuf1985@gmail.com (S. Yusub).

http://dx.doi.org/10.1016/j.jallcom.2015.12.147
0925-8388/

paramagnetic ions. Interestingly Mn^{2+} and Mn^{4+} ions are noticed as luminescence activators [22]. The content of manganese in different forms in different valence states existing in the glass depends on the size of the ions in the glass network, their field strength, mobility of the modifier cation, quantitative properties of modifiers and glass formers, etc [5,7,14]. The Mn^{2+} ion has the electronic configuration of $3d^5$, which leads to a half filled d shell. Most of the Mn^{2+} ions occupy the octahedral sites and have a high spin arrangement with five unpaired electrons [23,24]. The Mn^{2+} ions are widely used as acceptable structural probes in the glasses because their EPR spectrum can be easily identified at room temperature.

The manganese ions are assumed to influence the physical, optical and dielectric properties of Li_2O–PbO–B_2O_3–P_2O_5 glass network and have the strong bearing on them. Most of the studies on these glasses are confined to the structural investigation by means of spectroscopic, differential scanning calorimetry and ion transport studies etc. Particularly, no considerable research on dielectric properties of manganese ions doped lithium lead borophosphate glasses is available. These studies evaluate the conductivity and topology of the glass network. The main objective of the present work is to make a comprehensive analysis on the role of manganese ions on the structural aspects of lithium lead borophosphate glasses from a systematic study on dielectric properties and spectroscopic studies.

2. Material and methods

The multi–component glasses of the composition $20Li_2O$–$20PbO$–$45B_2O_3$–$(15-x)P_2O_5$–$xMnO$, with $0 \leq x \leq 3$ mol% ($x = 0, 0.2, 0.4, 0.6, 1, 2$ and 3), were synthesized by melt quenching technique. Basing on the concentration of dopant, the samples were designated as M0 (pure), M1($x = 0.2$), M2 ($x = 0.4$), M3 ($x = 0.6$), M4 ($x = 1$), M5 ($x = 2$) and M6 ($x = 3$). The basic chemicals viz., Li_2CO_3, PbO, H_3BO_3, P_2O_5 and $MnCO_3$ used in the fabrication of glasses were of Analar (AR) grade quality. Using the electrical balance, the chemicals were weighed to an accuracy of 0.0001 g and mixed in an agate mortar. The mixture of the chemicals were taken in a porcelain crucible and melted at a temperature of 950 °C for 40 min till a bubble–free liquid was formed. The melt of the sample was spilled on a brass slab kept at ambient temperature and afterward annealed at 300 °C. It was observed that the pure glass was colorless. With the hike in the concentration of MnO, the color of the glass was noticed to change from light purple to dark purple.

The X–Ray diffraction spectra of the MnO doped lithium lead borophosphate glasses were recorded in the range of 10 to 80° using SO–DEBYE FLUX 202 fitted with the copper target and nickel filter working at 40 KV, 30 mA. The density of the glasses was estimated by the VIBRA HT density measurement kit. Archimedes' principle was used in the measurement density using O–xylene (99.99% pure) as a buoyant liquid. The accuracy in the measurement of density was ±0.0001. The refractive index of the samples was evaluated by Abbe refractometer NAR–4 T Atago model, Japan. Methyl iodide, containing the sulphur solution ($\mu_D = 1.78$) as contact liquid, with the light source of LED lamp (yellow color of D–line) was used for estimating the refractive index of the prepared glasses. The FTIR transmission spectra of the glasses were recorded in the wavenumber range 400–1250 cm^{-1}, using JASCO–FTIR–5300 Fourier Transform Infrared spectrometer. The powdered glass samples of 100 mg were taken in a quartz tube for EPR studies. The EPR spectra of the glasses were obtained on 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 micro power of 10 mW was used. For optical absorption studies, samples of about 1 mm thickness were prepared by cutting, grinding and polishing. The double beam UV–Visible–NIR spectrophotometer (JASCO V–670) at an error of ±0.1 nm was used for recording the optical absorption spectra in the wavelength range 200–1000 nm.

The glass samples were optically polished, ground flat and reduced to the final dimension of 1.0 cm × 1.0 cm x 0.2 cm. A silver coating was given to these glasses on both sides so as to act as electrodes for dielectric measurements. LF–impedance analyzer (Hewlett–Packard model 4192A) operated in the frequency range 10^3–10^6 Hz was used for measuring a.c. conductivity (σ_{ac}), loss ($\tan\delta$) and dielectric constant (ε') of the prepared glasses. These values were measured in the temperature range 30–300 °C. Accuracy in the measurement of dielectric loss was ~0.001 and that of dielectric constant was ~0.01. An ac voltage breakdown tester (ITL Model BOV–7, Hyderabad) working with an input voltage of 230 V at a frequency of 50 Hz was used to estimate the dielectric breakdown strength of all the samples in the air medium and at room temperature.

3. Results

3.1. Characterization and physical parameters

The fabricated glasses are free from defects like inhomogeneities, bubbles, cracks and the inclusions. The absence of sharp Bragg peaks in the X–ray diffraction pattern of M0, M1 and M6 glasses as shown in Fig. 1 revealed the amorphous nature of the glasses. However, a small hump in the diffraction pattern indicates the presence of short–range order for the present glasses. The measured density 'ρ' values and the average molecular weight 'M' of the samples is used to obtain the various physical parameters such as manganese ion concentration N_i, mean manganese ion separation 'R_i', polaron radius 'R_p' and molar volume 'V_m' presented in Table 1 along with refractive index 'n' of the samples. The estimated density of M0 glass is 3.5642 g/cm^3. This value is noticed to increase gradually from the increase in the concentration of MnO. A similar trend in refractive indices and a reverse trend in molar volume are observed; such changes are expected due to variations in the structural compactness/softening i.e. the change in geometrical configurations, co–ordination number and cross–link density, etc. in the glass samples with increase in the concentration

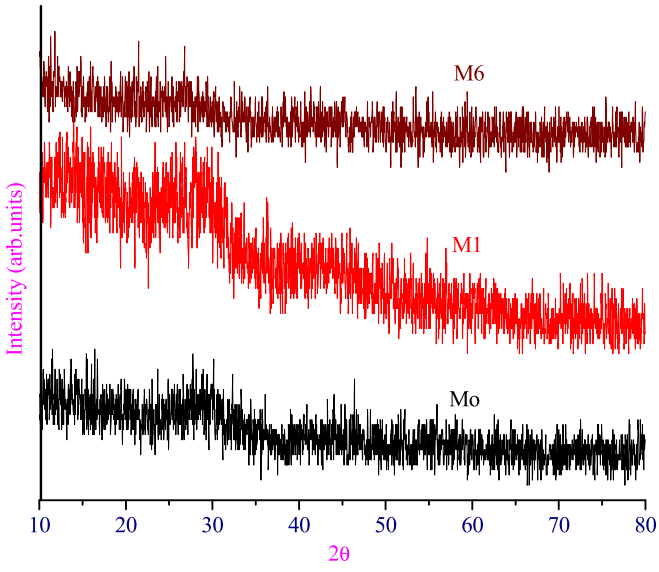

Fig. 1. X–ray diffraction pattern of Li_2O–PbO–B_2O_3–P_2O_5: MnO glasses.