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Influence of Ga^{3+} ions on spectroscopic and dielectric features of multi component lithium lead boro bismuth silicate glasses doped with manganese ions

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ABSTRACT

Multi-component glasses of the chemical composition $19.5Li_2O–20PbO–20B_2O_3–30SiO–(10-x)Bi_2O_3–0.5MnO{:}xGa_2O_3$ with $0 \leq x \leq 5.0$ have been synthesized. Spectroscopic (optical absorption, IR, Raman and ESR) and dielectric properties were investigated. Optical absorption and ESR spectral studies have indicated that managanese ions do exist in Mn^{3+} state in addition to Mn^{2+} state in the samples containing low concentration of Ga_2O_3. The IR and Raman studies indicated increasing degree of disorder in the glass network with the concentration of Ga_2O_3 up to 3.0 mol%. The dielectric constant, loss and ac conductivity are observed to increase with the concentration of Ga_2O_3 up to 3.0 mol%. The quantitative analysis of the results of dielectric properties has indicated an increase in the insulating strength of the glasses as the concentration of Ga_2O_3 is raised beyond 3.0 mol%. This has been attributed to adaption of gallium ions from octahedral to tetrahedral coordination.

1. Introduction

Ga_2O_3 is a heavy metal oxide and when introduced in the glass matrix it is expected to influence the physical properties (*viz.*, refractive index, thermal expansion coefficient, chemical resistance, glass transition temperature, infrared transmittance and the electrical properties) of the glass to a large extent. In view of these qualities the glasses containing Ga_2O_3 are suitable for use as infrared windows, ultrafast optical switches, optical isolators and other photonic devices for communication and advanced computer applications. Many recent investigations on the role of Ga_2O_3 in various glass matrices are available in the literature [1–5].

Manganese ion is an interesting transition metal ion and is extensively investigated in various glasses. This ion exists in Mn^{2+} and Mn^{3+} stable states. Mn^{2+} ion contains half filled *d* orbital with d^5 configuration with ^6S as the ground state. For these reasons, the total orbital angular momentum for Mn^{2+} ion is zero. Since the total spin is 5/2, this ion exhibits zero field splitting which is sensitive to the local environment. Both Mn^{3+} and Mn^{2+} ions are well known paramagnetic ions. Mn^{3+} ion exhibits large magnetic anisotropy due to its strong spin–orbit interaction of the 3d orbital, whereas such anisotropy energy of Mn^{2+} ion is small because its orbital angular momentum is zero. Recently, lasing action of Mn^{2+} ions has also been reported in some inorganic glasses [6–8] with large quantum luminescence efficiencies even at room temperature. The studies on up-conversion emission with manganese ion as sensitizer and rare-earth ions as activators in some glasses have also been reported earlier [9,10]. The manganese ions have larger oscillator strengths than rare-earths and can therefore absorb more of the input energy and fluorescence strongly in green and red regions [6–8]. Ga_2O_3 is considered to act as a network former if Ga^{3+} ion takes fourfold coordination in oxide glasses. The excess negative charges on GaO_4 tetrahedrons are compensated either by localization of a modifier ion nearby or by generation of threefold oxygens. The GaO_4 tetrahedrons may enter the glass network and alternate with BO_4 and SiO_4 tetrahedrons in borosilicate glasses. Gallium ions also take part modifier positions with GaO_6 structural units depending upon its concentration and other constituents of the glass matrix [11]. Overall, the variation of Ga_2O_3 content in glass network is expected to change the local environment of the manganese ions in the glass network and there by influences the spectroscopic properties of manganese ions.

Lithium borosilicate glasses containing heavy metal oxides like Bi_2O_3 are useful particularly in optical and optoelectronic devices such as ultrafast switches, infrared windows, optical isolators, thermal and mechanical sensors [12–14]. The most stable valence of the bismuth ion is the positive tri-valence state (Bi^{3+}) and its electronic configuration is $4f^{14}5d^{10}6s^2$. Bismuth ion exists in various valence states from positive valence to negative valence in

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different compounds (*e.g.* Bi^{3+}, Bi^{2+}, Bi^{+}, Bi^{0}, Bi^{2-}). Further, bismuth ion exhibit emission in various wavelength regions from visible to near-to-mid infrared region and even far-infrared, depending on its valence states. In view of such peculiarities, Bi_2O_3 containing glasses also offer highly suitable environment for hosting transition metal ions like manganese ions that exhibit luminescence in the green and yellow regions and bismuth ions may also act as sensitizers for up-conversion [15–19].

In the present study we have synthesized multi-component Li_2O–PbO–B_2O_3–SiO_2–Bi_2O_3:MnO glasses mixed with different contents of Ga_2O_3 and investigated the influence of variation of Ga_2O_3 concentration on spectroscopic characteristics of manganese ions. Studies are also extended to dielectric properties of the bulk material.

2. Experimental

For the present study, a particular composition $19.5Li_2O$–$20PbO$–$20B_2O_3$–$30SiO_2$–$(10–x)Bi_2O_3$–$0.5MnO$:xGa_2O_3 with six values of *x* ranging from 0 to 5 is chosen. The detailed compositions of the glasses used in the present study are as follows:

$$G_0 : 19.5Li_2O - 20PbO - 20B_2O_3 - 30SiO_2 - 10Bi_2O_3 - 0.5MnO$$
$$G_1 : 19.5Li_2O - 20PbO - 20B_2O_3 - 30SiO_2 - 9Bi_2O_3 - 0.5MnO : 1.0Ga_2O_3$$
$$G_2 : 19.5Li_2O - 20PbO - 20B_2O_3 - 30SiO_2 - 8Bi_2O_3 - 0.5MnO : 2.0Ga_2O_3$$
$$G_3 : 19.5Li_2O - 20PbO - 20B_2O_3 - 30SiO_2 - 7Bi_2O_3 - 0.5MnO : 3.0Ga_2O_3$$
$$G_4 : 19.5Li_2O - 20PbO - 20B_2O_3 - 30SiO_2 - 6Bi_2O_3 - 0.5MnO : 4.0Ga_2O_3$$
$$G_5 : 19.5Li_2O - 20PbO - 20B_2O_3 - 30SiO_2 - 5Bi_2O_3 - 0.5MnO : 5.0Ga_2O_3$$

Analytical grade reagents of Li_2CO_3, PbO, H_3BO_3, SiO_2, Bi_2O_3, MnO and Ga_2O_3 powders in appropriate amounts (all in mol%), where thoroughly mixed in an agate mortar and melted in a silica crucible at 1300 °C in an automatic temperature controlled furnace for about ½ h. The resultant bubble free transparent liquid formed was then poured in a brass mold and subsequently annealed about 350 °C. The photographs of transparent samples synthesized were shown in Fig. 1. The pictures clearly indicate that with increase in the concentration of Ga_2O_3 the color of the samples changed gradually to thick black.

The amorphous nature was identified by X-ray diffraction using X'pert system using the step scan method with Cu K_α radiation (λ = 1.5406 Å), a step size of 0.04 Å and a collection time of 2 s per point over 2θ range, 0–90°. The density '*d*' of the glasses is determined to an accuracy of ($\pm$0.0001 g/cm^3) by the standard principle of Archimedes' using O-xylene (99.99% pure) as the buoyant liquid with a programmable VIBRAHT density measurement Kit.

The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 300–800 nm up to resolution of 0.1 nm using JASCO Model V-670 UV-vis-NIR spectrophotometer. The ESR spectra of the fine powders of the samples were recorded at room temperature on (JEOL-FE-IX) operations at X-band frequencies ($\sim$9.4 GHz) with a field modulation frequency of 100 kHz.

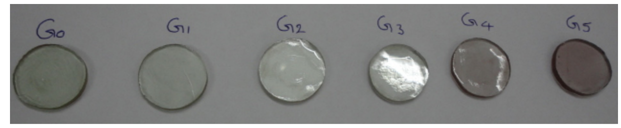

Fig. 1. Physical appearance of Li_2O–PbO–B_2O_3–SiO_2–Bi_2O_3–MnO:Ga_2O_3 glasses.

The samples used for optical and dielectric studies were prepared by suitable grinding and optical polishing to the dimensions of 1 cm × 1 cm × 0.2 cm. A thin layer of silver paint was applied on either side of the large faces of the samples, in order to serve as electrode for dielectric measurements. The dielectric measurements were made on LF-impedance analyzer (Hewlett-Packard Model 4192A) in the frequency range 10^3–10^6 Hz and in the temperature range of 30–300 °C. The accuracy in the measurement of dielectric constant ε' is $\sim\pm$0.01 and the dielectric loss (tan δ) is $\sim\pm$0.001. The dielectric breakdown strength of all these glasses was determined 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 frequency of 50 Hz.

3. Results

The density '*d*' of the Ga_2O_3 free glass was measured to be 4.41 g/cm^3 and it is found to increase with increasing concentration of Ga_2O_3 up to 3.0 mol%; beyond this concentration a slight decrease in the value of '*d*' is observed (Table 1). From the measured values of the density and average molecular weight $\overline{M}$ of the samples, various other physical parameter such as manganese ion concentration, N_i, and mean manganese ion separation, r_i, in the Li_2O–PbO–B_2O_3–SiO_2–Bi_2O_3–MnO:Ga_2O_3 glass samples were computed and are presented in Table 1.

Fig. 2 shows X-ray diffraction pattern of some glass samples. The pattern shows absence of sharp Bragg peaks confirming the amorphous nature of the prepared samples.

The optical absorption spectra of Li_2O–PbO–B_2O_3–SiO_2–Bi_2O_3–MnO:Ga_2O_3 glasses recorded in the wavelength region of 300–800 nm are shown in Fig. 3. The absorption edge observed at 333 nm for G_0 glass sample is found to be shifted gradually toward higher wavelength with increase of the concentration of Ga_2O_3 up to 3.0 mol%. Above this concentration, the absorption edge exhibited spectrally blue shift. The spectrum of this glass showed an intense absorption band at 534 nm corresponding to $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ octahedral transition of Mn^{2+} ions and a weak kink at about 422 nm, due to $^6A_1(S) \rightarrow {}^4T_1(G)$ tetrahedral transition of Mn^{2+} ions [20,21]. Additionally, a weak absorption band with a peak at about 485 nm due to $^5E_g \rightarrow {}^5T_{2g}$ octahedral transition of Mn^{3+} ions [22] is also observed in the spectrum of this glass. With an increase in the concentration of Ga_2O_3 up to 3.0 mol%, the octahedral band is observed to grow gradually at the expense of the tetrahedral band with minor red shift. The summary of data on the position of various bands in the optical absorption spectra of

Table 1
Physical Parameters of Li_2O–PbO–B_2O_3–SiO_2–Bi_2O_3–MnO: Ga_2O_3 glasses.

Sample	Conc. Ga_2O_3 (mol%)	Avg. mol. wt. $\bar{M}$	Density ρ (g/cm^3) ($\pm$0.01)	Molar volume V_m (cm^3) ($\pm$0.001)	Conc. Mn ions N_i ($\times 10^{21}$ ions/cm^3) ($\pm$0.01)	Inter ionic distance of Mn ions R_i (Å) ($\pm$0.01)	Polar on radius R_p (Å) ($\pm$0.01)
G_0	0	129.28	4.41	0.515	10.28	4.60	1.85
G_1	1	126.50	4.42	0.516	10.53	4.56	1.84
G_2	2	123.71	4.44	0.519	10.82	4.52	1.82
G_3	3	120.93	4.47	0.430	11.12	4.48	1.81
G_4	4	118.14	4.31	0.418	10.97	4.50	1.82
G_5	5	115.36	4.16	0.487	10.87	4.52	1.83