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Role of Mn^{2+} ions on optical and luminescent properties of $LiF–Sb_2O_3–ZnO–B_2O_3–SiO_2$ glasses

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ABSTRACT

MnO doped $LiF–Sb_2O_3–ZnO–B_2O_3–SiO_2$ glasses were synthesized by melt quenching technique. Different physical parameters such as density, molar volume, electronegativity, optical basicity and refractive index were calculated. The non-crystalline nature of the samples was confirmed by XRD analysis. SEM images projected that the prepared glass materials were contain well defined and indiscriminately allocated grains. The chemical analysis of these materials was studied by energy dispersion spectrum. The glass transition and glass crystallization temperatures of the glasses were recorded by DTA. FT-IR, Raman and ESR studies were also carried out on the prepared glass samples. The optical absorption reports of these glass materials have suggested that the octahedral tendency of Mn^{2+} ions increases with increasing concentration of MnO. The optical bandgap, Urbach energy, transition probability and emission cross section of these glass materials were calculated. Photoluminescence studies were also performed on the glass samples. The outcomes on all the investigations of these glasses have suggested that the Mn^{2+} ions predominantly occupy octahedral sites at higher concentrations of MnO.

1. Introduction

The subject of MnO doped antimony borosilicate glass materials appeared to be most advantageous and speculative. Mn^{2+} metal ions involved glass materials exhibit different characteristics which are mainly used in developing electrooptical and semiconductive devices [1]. Almost all classes of MnO doped antimony borosilicate glass materials exhibit two and three fold oxidation states. Basically the material such as glass is an amorphous solid and it is often transparent and mainly used for different decorative applications like tableware and optoelectronic devices [2]. Glass can transmit, reflect and refract light. These qualities can be enhanced by cutting and polishing to make optical lenses, prisms, fine glassware and optical fibers for high speed data transmission [3]. Many applications of borosilicate glasses are derived from their optical transparency, giving rise to their primary use as window panels. Addition of Mn^{2+} ions to the present glass materials extensively enhances the optical characteristics, required to develop high efficient photosensitive waveguides. The supreme class of most advantageous glass materials are collectively made up through well regulated structural, mechanical and optical properties. The borosilicate glass materials have great benefits over classical silicate glass materials of rich characteristics such as abnormal transmission of UV rays and remarkable thermal expansion [4,5]. MnO doped antimony borosilicate glass materials have great importance in developing photoconductive and electrooptical devices. The polymeric anions of the present alkali borosilicate glass materials are influenced by Mn^{2+} metal ions which induce different properties such as hygroscopicity, volatile nature and chemical stability. The ESR records of MnO doped glasses were used to survey the glassy

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configuration to enhance different optical characteristics of various glass materials [6]. Different oxidation states of MnO such as Mn^{2+} and Mn^{3+} of these glass materials were acknowledged as luminescence activators. The existence of Mn^{3+} ions in borosilicate glasses provide a deep purple colour to the materials, indicate dualistic states varied together within the colour of the Mn^{3+} ions predominant throughout the other glassy materials [7,8]. The optical absorption spectra of MnO doped borosilicate glasses were acknowledged as prevailing tool, for probing the instinctive atmosphere of a paramagnetic impurity and characterising the crystal field. The Mn^{2+} ions of borosilicate glass materials exhibit emission peaks within the wavelength ranging from 530 to 610 nm. The bandwidth ranges of these materials effect the fluorescence of Mn^{2+} ions to examine the coordination in both crystalline and amorphous materials [9]. The Mn^{2+} ions of antimony borosilicate glass materials were extremely malleable and rich in emission cross-section value within green to red spectral range to advance their credibility in lasers. The Mn^{2+} ions of MnO were often used in magnetic inspections to explore the structure and durable photosensitive nature of various glass materials [10]. MnO doped glass materials exhibit laser emission of extremely strength and least beam divergence [11,12]. In the present investigation, we have chosen chemical composition of LiF–Sb_2O_3–ZnO–B_2O_3–SiO_2 in different concentrations of MnO for synthesis and characterization.

2. Experimental

The chemical compositions of (25-x)LiF–10Sb_2O_3–05ZnO–20B_2O_3–40SiO_2: x MnO have been chosen for the present synthesis in which ‘x’ is a variable concentration ($0 < x < 0.5$). The glass samples were synthesized by melt quenching technique. The chosen chemical composition series of present glasses are as follows:

$M_0$25.00LiF–10Sb_2O_3–05ZnO–20B_2O_3–40SiO_2
$M_1$24.90LiF–10Sb_2O_3–05ZnO–20B_2O_3–40SiO_2: 0.1MnO
$M_2$24.80LiF–10Sb_2O_3–05ZnO–20B_2O_3–40SiO_2: 0.2MnO
$M_3$24.70LiF–10Sb_2O_3– 05ZnO–20B_2O_3–40SiO_2: 0.3MnO
$M_4$24.60LiF–10Sb_2O_3–05 ZnO–20B_2O_3–40SiO_2: 0.4MnO
$M_5$24.50LiF–10Sb_2O_3–05ZnO–20B_2O_3–40SiO_2: 0.5MnO

The precise quantities (all in mole percent) of analytic grades of SiO_2, B_2O_3, Sb_2O_3, ZnO, LiF and MnO chemicals were methodically varied in an agate mortar and quenched in a dense walled platinum crucible in the temperature ranging from 1410 to 1430 °C in an automatic maintained temperature furnace for about 30 min, until a void free transparent liquid was formed. The final melt was discharged in a brass cast and successively annealed at 300 °C in a muffle furnace.

The mass of the prepared glass materials was measured through Oahu’s digital balance with a precision of 10^{-4} gm. The densities of these glass materials were also measured by Archimedes principle with an accuracy of 0.001 g/cm^3, by using O-xylene buoyant liquid. XRD-7000 (Shimadzu) was used to conform the different crystalline phases within the glass materials. S-3700 N (Hitachi) was used to record the SEM images of the prepared glass materials. The differential thermal analysis was carried out by DTG – 60H (Shimadzu) with programmed heating rate of 5 °C per min, in the temperature ranging from 27 to 1200 °C. FT-IR spectrum was recorded by using 8400S model (Shimadzu). Raman spectra of the glasses were recorded in the wavelength ranging from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} by using BWTeki Raman plus spectrometer. The optical absorption spectra of the glasses were recorded at room temperature by 8400S UV-VIS Spectrometer (Shimadzu) with a precision of 0.1 nm in the wavelength ranging from 200 to 1100 nm. ESR spectra of the prepared glass samples were recorded at room temperature on E11Z Varian X–band (ν = 9.5 GHz) ESR Spectrometer. QE PRO-FL Spectrometer was used to record the emission spectrum.

3. Results and discussion

3.1. Physical parameters

The different physical parameters of LiF–Sb_2O_3–ZnO–B_2O_3–SiO_2: MnO glass materials were calculated and furnished in Table 1. The observed density (ρ) and refractive index (μ) of the present glasses were decreased with increasing concentration of MnO, whereas the quantity molar volume (V_m) increases with increasing concentration of MnO. The observed electronegativity (χ_{th}) of the present glass materials increases with increasing concentration of MnO, where as the quantity optical basicity (Λ_{th}) decreases. Mostly the variation in degree of compactness, the dimensions of the microcrystals produced, variation in the coordination of glass forming

Table 1
Summary on physical properties of LiF–Sb_2O_3–ZnO–B_2O_3–SiO_2: MnO glasses.

Glass	Density (ρ) (gm/cm^3)	molar volume (V_m)	Refractive index (μ)	Electro- negativity (X_{th})	Optical basicity (Λ_{th})
M_0	2.8651	29.332	1.6841	5.476	0.1723
M_1	2.8549	29.425	1.6830	5.962	0.1601
M_2	2.8428	29.536	1.6821	6.348	0.1491
M_3	2.8309	29.647	1.6805	6.734	0.1327
M_4	2.8203	29.751	1.6791	7.125	0.1237
M_5	2.8175	29.831	1.6785	7.506	0.1158