Characterization and optical properties of Pr₂O₃-doped molybdenum lead-borate glasses

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Abstract. Pr³⁺ doped molybdenum lead-borate glasses with the chemical composition 75PbO–[25–(x+y)B₂O₃]–yMoO₃–xPr₂O₃ (where $x = 0.5$ and 1.0 mol% and $y = 0$ and 5 mol%) were prepared by conventional melt-quenching technique. Thermal, optical and structural analyses are carried out using DSC, UV and FTIR spectra. The physical parameters, like glass transition (T_g), stability factor (ΔT), optical energy band gap (E_{gopt}), of these glasses have been determined as a function of dopant concentration. The T_g and optical energy gaps of these glasses were found to be in the range of 290–350°C and 2.45–2.7 eV, respectively. Stability of the glass doped with Pr³⁺ is found to be moderate (~ 40). The results are discussed using the structural model of Mo–lead-borate glass.

Keywords. Praseodymium-doped glasses; optical energy band gap; absorption spectrum.

1. Introduction

Characterization and study of properties of glasses provide useful information to design the materials for specific application. Optical properties of rare-earth ions in glasses vary in a wide range that depends on the chemical composition of glass former and glass modifier. Study of the optical properties of the rare-earth ions in glasses provides fundamental data that includes transition positions and cross-sections, transition probabilities, radiative and non-radiative decay rates, branching ratios, etc. for the excited states. These data are essential to estimate/design optical devices such as lasers, colour displays, upconverters, fibre amplifiers, etc. [1]. Specifically, heavy metal oxide (HMO) glasses doped with trivalent rare-earth ions are very important because they show strong luminescence due to their small cutoff phonon frequencies. However, to make devices with enhanced optical characteristics, the concentration of rare-earth ions has to be low enough, so that luminescence quenching is minimized. Praseodymium-doped glasses are being widely investigated, such glasses which exhibit very rich emission spectra extending from UV to IR [2]. Molybdenate glasses, a host of borate glasses containing alkaline earth oxides along with PbO, ZnO, TeO₂ and BaO as glass modifiers are promising materials for their probable applications in the fields of optical fibres, laser hosts, optical filters, X- and γ -ray absorbers, photonic devices [3]. In the present work, we report the characterization and optical

properties of lead-borate glasses doped with Pr³⁺ with and without molybdenum (MoO₃).

2. Experimental

Analytical grade compounds of PbO, H₃BO₃, MoO₃ and Pr₂O₃ were used as starting materials. A mixture of these compounds was powdered in a agilent mortar to get a homogeneous mixture. This mixture was taken in a ceramic crucible and heated at 650°C for 1 h to remove moisture and then the temperature was raised to 1000°C and heated in Muffle furnace up to 1000°C for 2 h [4]. The glass samples were obtained by quenching the molten liquid between two brass moulds. Transparent yellowish and greenish coloured glasses were obtained. X-ray diffraction (XRD) study of these samples using X-ray diffractometer reveals the amorphous nature of these samples. The XRD pattern does not show any sharp peaks. This confirms the amorphous nature of the glasses investigated. The glass transition temperatures were measured using differential scanning calorimeter (DSC). In the temperature range of 50–500°C with the heating rate of 10°C min^{−1}, the Fourier transform infrared (FTIR) spectra of glasses were recorded on a Perkin Elmer spectrometer in the region from 400 to 1600 cm^{−1} by KBr pellet technique. The optical absorption studies were performed on the polished glass samples, using UV–Visible spectrometer (Perkin Elmer Lambda 35) in the wavelength region of 500–900 nm.

Table 1. Glass compositions of prepared glasses with their codes.

Sample code	Concentration (mol%)			
	PbO	B ₂ O ₃	MoO ₃	Pr ₂ O ₃
1PBMPR	75	24.5	0	0.5
2PBMPR	75	19.5	5	0.5
3PBMPR	75	24	0	1
4PBMPR	75	19	5	1

Figure 1. Optical absorption spectra of 1PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses.

The details of the glasses investigated along with their code are given in table 1.

3. Results and discussion

3.1 Optical properties

Figure 1 shows the typical optical spectra of 1PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses. The optical absorption coefficient $\alpha(\nu)$ was calculated for each sample at different photon energies by using the relation;

$$\alpha(\nu) = 2.303 \frac{A}{d}, \quad (1)$$

where A is the absorbance and d the thickness of the samples. Optical energy band gap (E_{gopt}) was calculated by the interpolation of the linear region to meet $h\nu$ axis at $(\alpha h\nu)^{1/2} = 0$ (α = absorption coefficient) [5]. The absorption coefficient, $\alpha(\nu)$ and E_{gopt} , in many amorphous materials are related as [6],

$$\alpha(\nu) = B(h\nu - E_g)^n / h\nu, \quad (2)$$

where B is a constant called band-tailing parameter, n the index which can have the values (1/3, 1/2, 2 and 3) corresponding to indirect forbidden, indirect allowed, direct allowed, direct forbidden transitions, respectively. E_{gopt} is the optical

Figure 2. Tauc's plots of optical energy indirect band gap of 1PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses. **Figure 3.** Variation of energy band gap in 1PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses with MoO₃ and Pr₂O₃ concentrations.

energy band gap and $h\nu$ the incident photon energy. Here the optical bandgap refers to photons assisting the electrons to move from valence band to conduction band [5]. Refractive index n can take values between 0.5 and 2 depending on the nature of the inter-band electronic transitions. It has been observed that for direct and indirect allowed transitions, the measured absorption fits well to the above Eq. (2) for $n = 2$ and $n = 1/2$. A graph between $(\alpha h\nu)^n$ and $(h\nu)$ is called Tauc's plot [7]. A plot of $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$) for indirect allowed transitions to find the values of the optical band gap E_{gopt} is shown in figure 2. The value of E_{gopt} decreases with increase in Pr³⁺ and MoO₃ concentrations.

Figure 3 shows the variation of energy bandgap in 1PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses with MoO₃ and Pr₂O₃ concentrations.

3.2 Urbach energy

The exponential dependence of $\alpha(\nu)$ on the $h\nu$ in many amorphous solids is known as Urbach rule, can be written as [8],

$$\alpha(\nu) = B \exp\left(\frac{h\nu}{\Delta E}\right), \quad (3)$$

where B is constant and ΔE the Urbach energy (width of the band tails of the localized states). ΔE provides a measure of disorder in the amorphous and crystalline solids [8,9]. The values of Urbach energy ΔE were calculated by taking the reciprocal of the slopes of the linear portion of the $\ln(\alpha)$ vs. $h\nu$ curves in the lower photon energy regions as shown in figure 4. The values of ΔE for the prepared glass lie between 0.18 and 0.3 eV and values are listed in table 2. Obtained values of ΔE show that these samples obey Urbach rule [10].

Figure 4. Plot of $\ln(\alpha)$ vs. $h\nu$ for Urbach energy of 1PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses.

3.3 FTIR analysis

The structural features of the glasses were studied using FTIR analysis in the wavenumber range of 500–1600 cm⁻¹. Figure 5 shows FTIR spectra of 1 PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses in the range of 500–1600 cm⁻¹. A frequency band at 579 cm⁻¹ corresponds to Pb–O asymmetrical bending vibrations. Borate glasses exhibit broad absorption peaks in three regions. The absorption band at 706 cm⁻¹ is assigned to B–O–B bending vibration, the band between 1100 and 800 cm⁻¹ is due to the stretching modes of [BO₄]⁻ tetrahedral borons and broad absorption band in the region of 1200–1440 cm⁻¹ is due to a stretching vibration of [BO₃] trigonal borons [11–13]. The symmetric stretching modes of the terminal Mo–O bond of crystalline MoO₃ appears at 1050 cm⁻¹. An absorption peaks at lower wavenumber side attributed to vibration of metal cation such as Pb²⁺ and Mo [11]. With the increase of Pr₂O₃, the spectrum exhibits a shift to longer wavelength [14].

3.4 DSC analysis

DSC thermograms were recorded for samples under study as shown in figures 6 and 7. The thermograms reveal an endothermic baseline shift corresponding to the glass transition followed by an exothermic peak due to crystallization of glassy phase. The values of glass transition (T_g) and crystallization (T_c) temperatures are listed in table 2. The DSC curves for the glasses show a glass transition corresponding to temperature T_g that we usually, just take the middle of the incline to be the T_g . The variation of the glass transition temperature of 1PBMPR and 3PBMPR are shown in figure 6, without MoO₃ content and figure 7 shows the variation of T_g for 2PBMPR and 4PBMPR glasses with MoO₃ content. The variation in glass transition temperature is such that, with increase in Pr₂O₃ with MoO₃ content, the glass transition temperature also increases. It is found that T_g decreases in the samples without MoO₃ content. Thus, transition temperature is very sensitive to MoO₃ and Pr₂O₃ concentrations. The value of T_g ranges from 290 to 350°C. From the results, it is clear that the strength of the glass remains almost constant with the addition of MoO₃ and Pr₂O₃ contents.

Table 2. Transition temperature (T_g), crystallization temperature (T_c), glass stability (ΔT), optical band gap energy (E_{gopt}) and Urbach energies (ΔE) of 1PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses.

Sample code	Concentration (mol%)				Transition temperature T_g (°C)	Crystallization temperature T_c (°C)	Glass stability $\Delta T = (T_c - T_g)$ (°C)	Indirect band gap energy E_{gopt} (eV)	Urbach energy ΔE (eV)
	PbO	B ₂ O ₃	MoO ₃	Pr ₂ O ₃					
1PBMPR	75	24.5	0	0.5	290	330	40	2.55	0.25
2PBMPR	75	19.5	5	0.5	330	370	40	2.45	0.30
3PBMPR	75	24	0	1	310	350	40	2.70	0.18
4PBMPR	75	19	5	1	350	390	40	2.65	0.20

Figure 5. FTIR plot of 1PBMPR, 2PBMPR, 3PBMPR and 4PBMPR glasses.

Figure 6. DSC curves 1PBMPR and 3PBMPR glasses without MoO₃ content.

3.5 Glass stability

Thermally stable glasses exhibit closed packed structure, while the unstable glasses exhibit loose packed structure [15]. Here, glass stability was calculated by taking the difference of T_c and T_g . Higher the value, higher is the glass stability. The stability of the glass doped with Pr₂O₃ with 5 mol% MoO₃ is found to be moderate (~ 40) of these glasses.

4. Conclusion

Using characterizations like DSC, UV and FTIR; thermal, optical and infrared properties of $(75\text{PbO}-(25-(x+y))\text{B}_2\text{O}_3-y\text{MoO}_3-x\text{Pr}_2\text{O}_3)$ glass system have been investigated. Addition of Pr₂O₃, changes the colour of the glass from yellow to green. Yellowish and greenish coloured glasses are formed. The energy band gap found to decrease in glasses with MoO₃ content. Urbach energy values show that materials

Figure 7. DSC curves of 2PBMPR and 4PBMPR glasses with MoO₃ content.

obey Urbach rule. FTIR study reveals that with increase in Pr₂O₃ content, the spectrum exhibits a shift to longer wavelength. The value of T_g found to increase with Pr₂O₃ for the glasses containing MoO₃. Stability of the investigated glass seems to be almost moderate (~ 40). Investigated glasses find their applications in both photonics and optoelectronics fields.

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References

- [1] Babu P and Jayasankar C K 2000 *Physica B* **279** 262
- [2] Srinivasarao L, Venkatapparao T and Syam Prasad P 2009 *IOP Conf. Ser.: Mater. Sci. Eng.* **2** 1
- [3] Gautam C, Yadav A K and Singh A 2012 *ISRN Ceram.* **2012** 69
- [4] Eraiah B and Anavekar R V 2001 *Phys. Chem. Glasses* **42** 121
- [5] Ghosh A, Bhattacharya S and Ghosh A 2007 *J. Appl. Phys.* **101** 083511
- [6] Davis E A and Mott N F 1970 *Philos. Mag.* **22** 903
- [7] Tauc J 1970 *Mater. Res. Bull.* **5** 721
- [8] Urbach F 1953 *Phys. Rev.* **92** 1324
- [9] Redfield D 2013 *Phys. Rev.* **130** 916
- [10] Ebraheem S and El-Saied A 2013 *Mater. Sci. Appl.* **4** 324
- [11] Lucacel R C and Ardelean I 2006 *Optoelectron. Adv. Mater.* **8** 1124
- [12] Selvaraj U and Rao K J 1984 *Spectrochim. Acta* **40** 1081
- [13] Raghavendra Rao T, Venkatreddy C, Ramakrishna C, Satish D V, Sambashiv Rao P and Ravikumar R V S S N 2011 *Mater. Res. Bull.* **46** 2222
- [14] Chen Q, Chen Q and Wang S 2011 *Open J. Inorg. Non-Metal. Mater.* **1** 1
- [15] Sinclair R N, Wright A C, Bachra B, Dimitriev Y B and Arnau-dov M G 1998 *J. Non-Cryst. Solids* **232–234** 38