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Spectroscopic properties of Pr^{3+} ions embedded in lithium borate glasses

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ABSTRACT

A series of lithium borate glasses with different Pr^{3+} contents were prepared by the melt quench technique to explore the new material for solid state light applications. We found that the addition of Pr^{3+} ions in the glass matrix has a profound effect on the properties of the glasses. The presence of Pr^{3+} ions in the glass matrix created various absorption bands compared to the base glass. These bands were due to the ground state ($^3H_4$) of the Pr^{3+} to the various excited states. Optical energy band gap was calculated by Tauc's method which showed a decreasing trend with an increase in the Pr^{3+} content. This might be due to structural changes when the glass structure became rigid due to the Pr^{3+} ions and this was confirmed by the density results. Rigidity of the glass structure was further confirmed by the Fourier transformed infrared results. The excitation spectra showed bands at $^3H_4 \rightarrow {}^3P_2$, $^3P_1$ and $^3P_0$ nm. The $^3H_4 \rightarrow {}^3P_2$ band was used to study the unresolved $^1D_2 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3H_6$ transitions of the Pr^{3+} ions.

1. Introduction

The days have passed since glasses were remembered only as window and bottle material. The fascinating aspect about the glasses is that they can be fabricated over a wide compositional range with any desired shape. The recent development and studies on glasses offer immense technological promises such as laser, optoelectronic devices, electro-chromic devices and solid state lighting [1–7]. Lithium borate glasses are the most versatile glass system within the family of glass systems. With the properties like strength, formability over a wide range of composition, good rare earth solubility and unique boron anomaly of these glasses established them as a potential material for emerging technologies. These glasses are mainly known as solid electrolytes but introducing rare earth oxide in these glass systems allows one to study and develop new material for optical applications [8–10].

Rare earth elements are rigorously studied and are interesting class materials, promising exciting new areas of spectroscopy. The position of an electron in the 4*f* and 5*d* orbitals of these elements produces extremely exciting spectral characteristics. These spectral characteristics are very useful for designing various optical devices and materials [11,12]. Pr^{3+} differs from the rare earth family because its energy level contains many metastable multiples $^3P_{0,1,2}$, $^1D_2$, $^1G_4$ that offer the emission in the blue, green, orange and red wavelengths [13]. Also, by using Pr^{3+} ions in the material one can achieve simultaneous blue and red emissions in the visible region for laser action and near infrared emission at 1.3 μm for optical amplification [14]. The energy level scheme of Pr^{3+} supports an efficient energy transfer and up conversion process, which is beneficial for various potential applications [15]. Gu et al. [13] studied the Pr^{3+} containing SiO_2–Al_2O_3–Na_2O–BaF_2–Y_2O_3 glasses. They incorporated Pr^{3+} ions in $BaYF_5$ nanocrystals by heat treatment to the glasses, which was confirmed by the intensity of the emission spectra. Addition of Pr^{3+} ions in the zinc alumino bismuth borate glasses showed the enhancement in the emission up to 1 mol% and further decreased due to fluorescence quenching [16]. These glasses also emitted reddish orange light on excitation of 445 nm. Pr^{3+} also shows a super broadband emission in a low phonon host such as Tellurite–tungstate [17], bismuth–gallate [18], fluorotellurite [19], tellurite–germanate [20] and borophosphate [21]. Pr_6O_{11} also has a promising influence on the physical properties of glasses. The density and molar volume of Pr_6O_{11} containing $Na_2B_4O_7$–V_2O_5 glasses increased with the increase in the Pr_6O_{11} content [22].

Motivated by the emission properties of Pr^{3+} ions, the spectroscopic properties of Pr^{3+} ions in lithium borate glasses were reported with the support of the physical properties of these glasses. The influences of various factors on these properties are also discussed to get a better insight of the obtained results.

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2. Materials and method

Pr^{3+} doped lithium borate glasses in the composition of (mol %) 27.5 Li_2O–(72.5–X) B_2O_3–X Pr_6O_{11} (X=05, 1, 1.5 and 2) were prepared by the quenching method. The glasses were synthesized using high purity raw materials like Li_2CO_3 (99.99%, Merck, Germany), B_2O_3 (99.99%, Merck, Germany) and Pr_6O_{11} (99.9%, Alfa Aesar, Germany). Batches of about 15 g glasses were melted in an alumina crucible in air at 1000 °C for 1 h. The homogenization of the melt was achieved by an intermittent stirring and then cast into an aluminum mold of a rectangular shape. The quenched samples were annealed at 300 °C for 3 h in a preheated annealing furnace followed by cooling to room temperature. Parallel faces of rectangular samples were polished to optical quality. The density of the glasses was measured by Archimedes principle by using toluene as an immersion liquid. Fourier transformed infrared (FTIR) spectroscopy measurements have been carried out with an IR-Affinity-1, Shimadzu. Small quantity of sample was ground with anhydrous KBr and the IR spectra were recorded between 4000 and 400 cm^{-1} in the absorbance mode, by averaging 45 scans for each spectrum. Optical absorption spectra of glasses were recorded at room temperature using a fiber optics UV–vis spectrometer (Model-AVASPEC 3648) in the 300–950 nm wavelength range which further normalized with sample thickness. The samples were crushed in powder form and Photoluminescence (PL) spectra were recorded at room temperature using a spectroflurometer (JASCO FP-8200, Japan) with 150 W Xe lamp as light source.

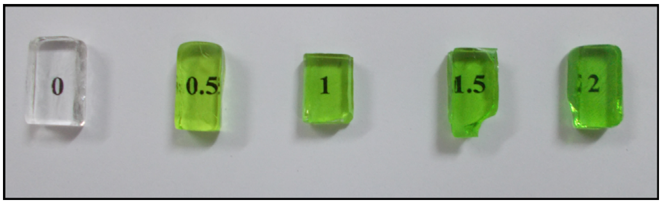

Fig. 2. Glasses with different mol% Pr_6O_{11}.

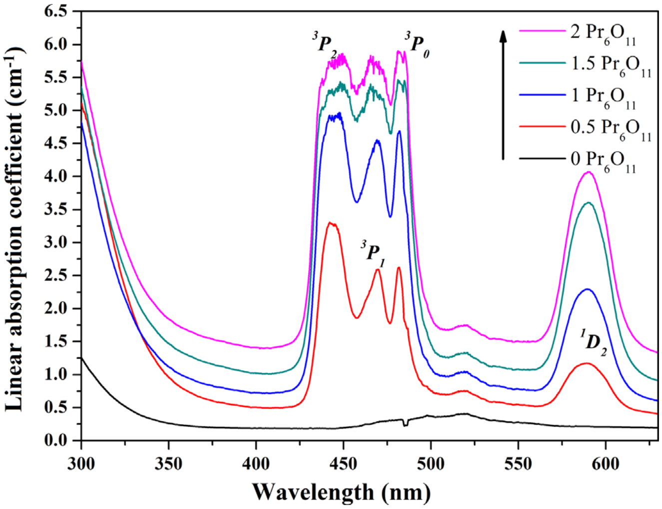

Fig. 3. Linear absorption spectra of prepared glasses.

3. Results and discussions

Fig. 1 shows the XRD patterns for the prepared glass series. The patterns show only humps and the absence of any crystalline sharp peak confirms the amorphous nature of the glasses. The base glass and Pr^{3+} ion containing glasses were transparent as shown in Fig. 2. The Pr^{3+} containing glasses were of green color because of a uniform distribution of the Pr^{3+} ions in the glass matrix. These samples were further used for the optical absorption measurements. The variation of linear absorption spectra is shown in Fig. 3. Due to the amorphous nature of the glasses the absorption edge was not sharply defined. Pr^{3+} ion containing glasses showed many absorption peaks as compared to the base glass. It is observed from the absorption spectra that the absorbance increases with the addition of Pr_6O_{11} due to structural changes caused by the Pr_6O_{11} in the glasses. This spectra shows absorption bands at 443, 469, 481 and 589 nm which were assigned to transitions $^3H_4 \rightarrow {}^3P_{2,1 \text{ and } 0}$ and $^3H_4 \rightarrow {}^1D_2$ respectively [23]. These bands correspond to the $^4f_2$-configuration electric dipole transitions from the ground state ($^3H_4$) to the various excited states and the band widths were due to the combination of inhomogeneous broadening and unresolved stark splitting [23].

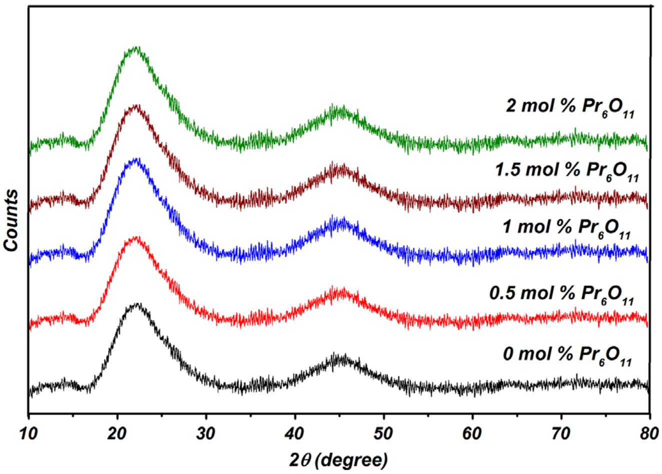

Fig. 1. XRD pattern of glass sample.

The values of indirect (n=2) and direct (n=1/2) band gaps were calculated by using Tauc's method for indirect and direct transitions as described in Refs. [1,2]. Variation of the obtained values for E_g^{Opt} is shown in Fig. 4 for the different glass samples used in the present investigation. It is observed from this figure that the band gap decreases with the increase in Pr_6O_{11}. This decrease in band gap can be correlated with structural changes that occured due to the addition of Pr^{3+} ions in the glass matrix. These structural changes were evident from the variation of density and molar volume as shown in Fig. 5. The density of the glasses was

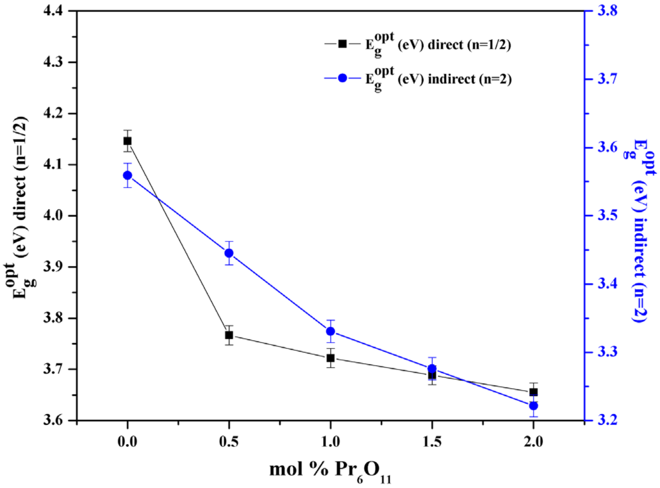

Fig. 4. Optical energy band gap of glasses.