



Optical properties and spectroscopic study of different modifier based Pr^{3+} :LiFB glasses as optical amplifiers

A. Balakrishna^{a,b,*}, S. Babu^a, Vinod Kumar^b, O.M. Ntwaeaborwa^{b,**}, Y.C. Ratnakaram^{a,**}

^a Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

^b Department of Physics, University of the Free State, Bloemfontein ZA9300, South Africa

ARTICLE INFO

Article history:

Received 17 October 2015

Accepted 7 July 2016

Available online 8 July 2016

Keywords:

Judd-Ofelt theory

Luminescence

Stimulated emission cross-sections

Branching ratios

ABSTRACT

In this paper, we report the preparation and optical characterization of Pr^{3+} doped lithium fluoro borate (LiFB) glasses for six different chemical compositions of $\text{Li}_2\text{B}_4\text{O}_7$ - BaF_2 - NaF -MO (where M = Mg, Ca, Cd and Pb), $\text{Li}_2\text{B}_4\text{O}_7$ - BaF_2 - NaF -MgO-CaO and $\text{Li}_2\text{B}_4\text{O}_7$ - BaF_2 - NaF -CdO-PbO. The structural and optical properties of these glasses were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), optical absorption and photoluminescence techniques. The optical absorption spectra of Pr^{3+} ions in LiFB glasses have been recorded in the UV-VIS-NIR region. The optical absorption data are used to calculate various spectroscopic parameters such as Racah (E^1 , E^2 , E^3) and spin-orbit interaction (ξ_{4f}) parameters. Judd-Ofelt (J-O) (Ω_λ where $\lambda = 2, 4$ and 6) intensity parameters were determined by applying J-O theory, which in turn used to calculate the radiative properties such as radiative transition probabilities (A), radiative lifetimes (τ_R), integrated absorption cross-sections (Σ) and branching ratios (β_r) for all emission levels of Pr^{3+} ion in different LiFB glass matrices. By using the J-O theory and luminescence parameters, stimulated emission cross sections (σ_p) of prominent transitions, $^3\text{P}_0 \rightarrow ^3\text{H}_4$ and $^1\text{D}_2 \rightarrow ^3\text{H}_4$ of Pr^{3+} ion in all LiFB glasses were calculated. $^3\text{P}_0 \rightarrow ^3\text{H}_4$ possesses higher branching ratios and stimulated emission cross-sections for the Pr^{3+} :LiFB(Mg-Ca) glass, which can be used as a best laser excitation. The optical gain parameter ($\sigma_p \tau_R$) was noticed higher in Pr^{3+} :LiFB(Mg-Ca) and Pr^{3+} :LiFB(Cd-Pb) glasses for the transition $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition, and these glasses have potential for optical amplification at 488 nm wavelength.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Rare-earth (RE) ions doped glasses with efficient frequency upconversion have received considerable attention due to solid state lasers emitting in the blue to green region of the optical spectrum. Among these rare-earth ions, Pr^{3+} is an attractive optical activator, because its energy level spectrum contains several meta-stable multiplets $^3\text{P}_{0,1,2}$, $^1\text{D}_2$, $^1\text{G}_4$ that offer the possibility of simultaneous blue, green and red emission for laser action, as well as infrared emission for optical amplification at 1.3 μm [1,2]. Pr^{3+} systems are also interesting as short-wavelength upconversion laser materials [3–5]. In recent years, studies on luminescence features of trivalent praseodymium ions have become more popular because of its $4f^2$ configuration, which possesses 91 fold degenerate orbitals [6]. Spectroscopic properties of Pr^{3+} and Er^{3+} ions in lead-free borate glasses modified by BaF_2 were studied by Pisarska et

al. [7]. Mazurak et al. [8] reported optical properties of the Tm^{3+} and energy transfer between Tm^{3+} and Pr^{3+} ions in P_2O_5 -CaO-SrO-BaO phosphate glass. Orange emission in Pr^{3+} -doped fluoro-indate glasses studied by Manzani et al. [9]. Visible upconversion emissions in Pr^{3+} -doped TeO_2 -ZnO glass were studied by Rai [10]. The luminescent properties of Pr^{3+} -doped transparent oxyfluoride glass-ceramics containing BaYF_5 nanocrystals were studied by Gu et al. [11]. Hu et al. [12] reported the synthesis and efficient near-infrared quantum cutting of $\text{Pr}^{3+}/\text{Yb}^{3+}$ codoped LiYF_4 single crystals. The luminescence of rare-earth ions in glass-ceramics such as $\text{LaF}_3:\text{Pr}^{3+}$ [13] has been intensively investigated. In 2009, the photoluminescence of Pr^{3+} -doped SiO_2 - Al_2O_3 - BaF_2 - GdF_3 glasses [14] and the photo-luminescence of Pr^{3+} in glass ceramic containing LiGdF_4 were reported [15]. Rai et al. [16] reported the frequency upconversion involving quarters of ions in a $\text{Pr}^{3+}/\text{Eu}^{3+}$ oxyfluoroborate glass. The spectroscopic features of Pr^{3+} , Nd^{3+} , Sm^{3+} and Er^{3+} ions in Li_2O -MO (Nb_2O_5 , MoO_3 and WO_3)- B_2O_3 glass systems were studied by Srinivasa Rao et al. [17].

Pr^{3+} -doped glasses have potential applications as UV-VIS-NIR lasers, upconverters, optical fibers and optical amplifiers [18]. Studies on Pr^{3+} ion are ideal for the comparison of different relaxation processes such as multi phonon relaxation and cross relaxation due to numerous energy

* Correspondence to: A. Balakrishna, Department of Physics, Sri Venkateswara University, Tirupati 517 502, India.

** Corresponding authors.

E-mail addresses: balakrishna.veera@gmail.com (A. Balakrishna), ntwaeab@gmail.com (O.M. Ntwaeaborwa), ratnakaramsvu@gmail.com (Y.C. Ratnakaram).

levels [19]. Over the past few years, there has been a considerable interest in the study of borate based glasses due to their structural and optical properties. Luminescence of RE ions depends more on the nature of the host and the ambient temperature [20]. An interesting characteristic of the borate glasses is the appearance of variations in its structural properties, when different modifier oxides (MgO, CaO, CdO and PbO) are introduced. The fluoride compounds (BaF₂ and NaF) are usually used as minor addition to enhance the luminescence properties. The differences in spectroscopic investigations depend upon the introduction of modifier oxides. The addition of alkali earth oxides (MgO and CaO) into the glass structure leads to disruption of the glass network and promotes the formation of non-bridging oxygen groups [21]. In contrast to alkaline earth oxides, PbO has the ability to form stable glasses due to its dual role, one as modifier (if Pb–O is ionic) and the other as glass former (if Pb–O is covalent) depending upon the structural units [22]. It is well established that the radiative parameters associated with luminescence transitions of Ln³⁺ ions in glass lattice are highly sensitive even for small changes in the chemical environment. Network modifiers also change the local environment of Ln³⁺ ions to some extent [23,24]. It is for this reason we have chosen PbO which acts both as network former and modifier.

The objective of the present work is to investigate the rare earth chemical bond environment changes that take place due to the presence of different modifier oxides in the Li₂B₄O₇–BaF₂–NaF–MO (where M = Mg, Ca, Cd and Pb) glass network by applying the Judd–Ofelt (J–O) theory. However, it is well known that the application of J–O theory to Pr³⁺ ion presents some problems due to the small energy difference between the ground configuration 4f² and the first-excited state configuration 4f¹5d¹ [25]. This manifests itself both as a large deviation between the measured and calculated oscillator strengths and as such the difficulty experienced to fit the ³H₄–³P₂ hypersensitive transition [26]. The present study includes FT-IR, optical absorption and photoluminescence studies. The J–O parameters are obtained from UV–VIS–NIR absorption spectra and then used to evaluate radiative parameters and the luminescence properties such as transition probabilities (A_R), branching ratios (β_R), radiative lifetimes (τ_R) and stimulated emission cross-sections (σ_p) for different emission transitions of Pr³⁺ ions in lithium fluoro-borate glasses.

2. Experimental details

Nominal composition of the glass specimens are 49Li₂B₄O₇ + 20BaF₂ + 10NaF + 20RO (where R = Mg, Ca, Cd and Pb) + 1.0Pr₆O₁₁, 49Li₂B₄O₇ + 20BaF₂ + 10NaF + 10MgO + 10CaO + 1.0Pr₆O₁₁ and 49Li₂B₄O₇ + 20BaF₂ + 10NaF + 10CdO + 10PbO + 1.0Pr₆O₁₁. The starting materials used in the glass preparation are Li₂B₄O₇, BaF₂, NaF, MgCO₃, CaCO₃, CdCO₃, Pb₃O₄ and Pr₆O₁₁. The appropriate mixtures of these compounds were thoroughly ground in an agate mortar in order to have proper mixing and homogeneity. The homogeneously mixed chemicals were then melted in porcelain crucible at 950 °C for 1 h in electrical furnace and then subsequently quenched on to preheated brass mould. The specimens were annealed for 3 h, cut and polished for optical measurements.

The density of the samples was measured from Archimedes principle using mono-bromo-naphthalene as an immersion liquid. The refractive indices were measured using an Abbe refractometer at sodium wavelength for all glasses. The nature of glasses was confirmed by X-ray powder diffraction patterns (PAN analytical X'pert PRO). The SEM images along with energy-dispersive X-ray spectroscopy (EDS) spectra were recorded using the Carl Zeiss EVO-MA15 scanning electron microscope. The FTIR spectrum in the range 500–4000 cm⁻¹ was recorded for all the prepared glass matrices using ALPHA interferometer FTIR spectrophotometer. The absorption spectra were measured using JASCO V-570 spectrophotometer. The emission spectra were obtained using Fluoro Max-3 spectrofluorimeter (excited with xenon lamp at 445 nm wavelength).

3. Results and discussion

3.1. XRD and surface morphology analysis

Fig. 1 shows the XRD patterns of different (Mg–Ca and Cd–Pb) Pr³⁺ doped LiFB glass matrices. The XRD patterns of Pr³⁺ doped other glass matrices are similar in shape, hence they are not shown. The spectra does not consist any sharp peaks which indicate the amorphous nature of glass samples. Fig. 2(A) and (B) show the SEM images of Pr³⁺ doped Mg–Ca and Cd–Pb LiFB glass matrices along with their respective EDS spectra. The SEM image shows clear and smooth surface morphology with no clustering formation. SEM images were also confirmed the bubble free-amorphous nature of the present glass samples. The EDS spectra gives identification of all elements (O, F, Mg, Ca, Cd, Pb, Ba and Pr) present in the samples.

3.2. IR-structural analysis

The FTIR spectra of Pr³⁺ doped different LiFB glasses are shown in Fig. 3 and the functional groups identified from the spectra are presented in Table 1. Multicomponent borate glasses are known to have relatively large structural units like boroxol rings, penta-, tri-, di- and meta-borate groups with bridging or non-bridging oxygen ions [27–29]. The IR spectral vibrations of the borate based glasses are divided into three main regions. The first region lies between 1200 (C) and 1600 cm⁻¹ (C) which is due to the asymmetric stretching relaxation of the B–O bond in trigonal BO₃ units. It is represented by C in the figure. The different vibrational bands corresponding to molecular bonds present in the infrared spectra include metal-oxygen bond vibrations of Mg–O, Ca–O, Cd–O and Pb–O (A) [30,31]. The bands at 708 (B) and 975 cm⁻¹ (C) could be due to the bending and stretching vibrations of BO₄ units, respectively [32]. The peak around 2930 cm⁻¹ is due to hydrogen bonding [33]. The infrared absorption band around 3440 cm⁻¹ (F) in all the lithium fluoro-borate glasses is due to the hydroxyl groups, O–H stretching vibrations [34].

3.3. Optical absorption spectra and energy level analysis

The optical absorption spectra of the Pr³⁺ doped different LiFB glasses for ultraviolet (UV), visible (VIS) and near infrared (NIR) regions recorded at room temperature in the range 300–1800 nm are shown in

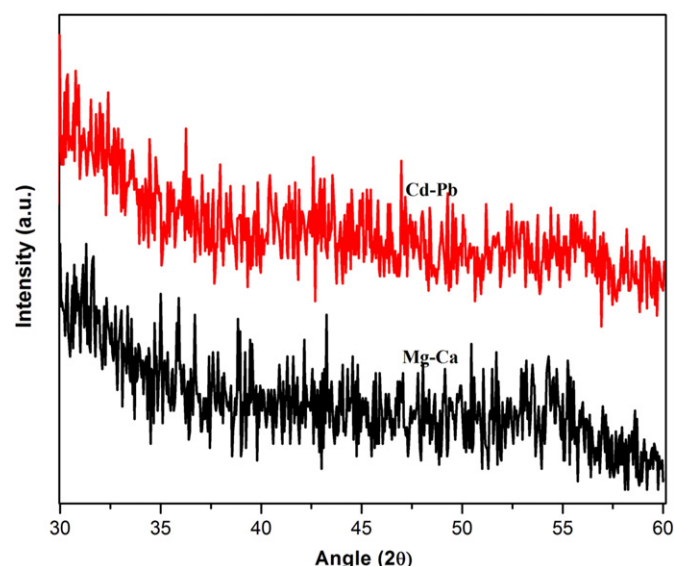


Fig. 1. XRD profiles of (Mg–Ca) and (Cd–Pb) lithium-fluoro-borate glasses.

Download English Version:

<https://daneshyari.com/en/article/1230804>

Download Persian Version:

<https://daneshyari.com/article/1230804>

[Daneshyari.com](https://daneshyari.com)