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Investigations on structural and luminescence behavior of Er^{3+} doped Lithium Zinc borate glasses for lasers and optical amplifier applications

K. Annapoorani [a], Ch. Basavapoornima [b], N. Suriya Murthy [c], K. Marimuthu [a,*]

[a] Department of Physics, Gandhigram Rural University, Gandhigram 624 302, India
[b] Department of Physics, Sri Venkateswara University, Tirupati 517 502, India
[c] Radiological Safety Division, IGCAR, Kalpakkam 603 102, India

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ABSTRACT

Trivalent Erbium doped Lithium Zinc borate glasses were prepared with the chemical composition (55–x)H_3BO_3 + 20Li_2CO_3 + 20ZnO + 5LiF + xEr_2O_3 (where x = 0.01, 0.05, 0.1, 0.5, 1.0 and 2.0 mol%) following the melt quenching technique. The different B—O vibrational bands and the change in coordination number of the boron with the addition of Er^{3+} ions in the prepared glasses were analyzed through FTIR and Raman spectra. The decreasing ionic nature was confirmed through Nephelauxetic ratios (β) and bonding parameter values (δ) from the absorption spectral measurements. The oscillator strengths and Judd-Ofelt parameters (Ω_2, Ω_4, Ω_6) were calculated on the basis of Judd-Ofelt theory. The dependency of Ω_2 parameter on the oscillator strengths of the hypersensitive transition has been studied. The radiative parameters such as transition probability (A), branching ratio (β_R) and radiative lifetime (τ) which characterizes the luminescence behavior were determined from the JO parameters and refractive index values. The luminescence from the thermally coupled energy level $^2H_{11/2}$ + $^4S_{3/2}$→$^4I_{15/2}$ was observed under 379 nm excitation and is inhomogeneously broadened ($\Delta\lambda_{eff}$ = 14 nm) due to the structural disorder in the prepared glasses. The stimulated emission cross-section corresponding to the $^4S_{3/2}$→$^4I_{15/2}$ transition is found to be higher for the LZB0.5E glass compared to the other reported literature thus it is suggested for suitable green laser applications. The luminescence behavior in the wavelength region 1400–1700 nm corresponding to the $^4I_{13/2}$→$^4I_{15/2}$ transition at 980 nm excitation was also observed and its suitability for optical amplifier applications and NIR laser have been discussed with parameters such as optical gain bandwidth (ΔG), Figure of Merit (FOM) and stimulated emission cross-section (σ_e). Of all the studied glasses, LZB0.5E glass possesses higher values of ΔG = 613.8 × 10^{-28} cm^3, FOM = 40.9 × 10^{-24} cm^2 s and σ_e = 93 × 10^{-22} cm^2 compared to the reported literature thus suggesting its suitability for optical amplifier and NIR laser applications.

1. Introduction

Lanthanide doped glasses have wide applications in various fields such as optical amplifiers, optical materials, temperature sensors and solar concentrators [1–4]. Generally glass host is more preferable than crystalline host because of the fact that glass can be produced in large volumes with high optical homogeneity and free of absorbing particle; it possesses low non-linear refractive indices and acts as a good elastic matrix by accepting large concentration of RE ions. Moreover crystalline matrices possess unfavorable properties like splitting of crystals in preferential directions, low chemical resistance, double refraction and low hardness which favors the development of glass matrices as a good optical medium. Nowadays studies on borate based glasses such as (30–x)Li_2O–xK_2O–10CdO/ZnO–59B_2O_3 [5], 60B_2O_3–(20–x)Na_2O–10PbO–10Al_2O_3:xTiO_2:yNd_2O_3 [6], PbO–Bi_2O_3–B_2O_3 [7], Bi_2O_3–B_2O_3–ZnO–Li_2O [8], and Gd_2O_3–MoO_3–B_2O_3 [9] find number of applications such as thin amorphous films for battery applications, bioactive glasses for tissue engineering, nuclear waste disposals, photonic applications, development of tuneable or short pulse lasers, optic fibre amplifiers and fibre lasers [10,11].

Since alkali ions can be thermally activated this can move easily from one side to another within a glass, thus it helps in the replacement of alkali ions near the glass surface by other ions of the same valence. Further, addition of alkali ions into the borate network increases the T_g and decreases the thermal expansion co-efficient [12]. When transition metal ions like ZnO are added into the glassy systems, it could generate different dopant sites by creating strong interaction thereby resulting in high intense optical and spectral properties [13]. Due to its optical, electrical and magnetic properties in combination with its non-toxicity and

* Corresponding author.
E-mail address: mari_ram2000@yahoo.com (K. Marimuthu).

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non-hygroscopic nature, ZnO doped glasses are used in the development of opto-electronic devices, solar convertors, ultraviolet emitting lasers and gas sensors [14].

In the present B_2O_3–Li_2CO_3–LiF–ZnO system, trivalent Erbium ion is doped at different concentrations to explore the optical properties in the wavelength region 500–600 nm corresponding to the thermally coupled $^2H_{11/2} + {}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition and in the wavelength region 1400–1700 nm corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. The spectroscopic properties of these transitions were highly dependent upon Ω_6 intensity parameters which have direct influences on the spontaneous transition probability and stimulated emission cross-section. Generally borate based glasses possess high Ω_6 value compared to the tellurite, germinate and fluoride [15,16] glasses. Thus Er^{3+} doped Lithium Zinc borate glasses were prepared to study its structural and optical properties.

The aim of the present work is (i) to prepare Er^{3+} doped Lithium Zinc borate glasses following the melt quenching technique with varying Er^{3+} ion concentrations; (ii) to identify the different vibrational bands of the borate network in the prepared glasses; (iii) to evaluate the predominant covalent/ionic nature and to determine the direct and indirect band gaps from the absorption spectra; (iv) to calculate the oscillator strengths and Judd-Ofelt parameters (Ω_2, Ω_4, Ω_6) from the absorption energy levels and refractive index of the prepared glasses; (v) to study the luminescence characteristics of the thermally coupled energy level transition $^2H_{11/2} + {}^4S_{3/2} \rightarrow {}^4I_{15/2}$ in the visible region and the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in the NIR region; (vi) to calculate the radiative parameters of the desired transitions; (vii) to determine the stimulated emission cross-section of the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions for the suitability of green and NIR laser applications and finally (viii) to determine the optical gain bandwidth and Figure of Merit of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition for optical amplifier applications.

2. Experimental

Er^{3+} doped Lithium Zinc borate glasses with the chemical composition $(55–x)H_3BO_3 + 20Li_2CO_3 + 20ZnO + 5LiF + xEr_2O_3$ (where x = 0.01, 0.05, 0.1, 0.5, 1.0 and 2.0 in mol%) have been prepared following the procedure reported in literature [1] and labeled with the codes LZB0.01E, LZB0.05E, LZB0.1E, LZB0.5E, LZB1.0E and LZB2.0E respectively. All the precursors used for the preparation of glasses are of high purity analytical grade (99.99%) from Sigma Aldrich. The infrared transmittance spectra of the prepared glasses were recorded using JASCO FTIR 460 plus in the mid-IR region (400–4000 cm^{-1}) with a spectral resolution of ± 1.0 cm^{-1} and 16 scans per sample. The background correction and baseline correction were carried out with the help of spectra manager software. The pellet was prepared following the KBr pellet technique. In this technique, the sample was powdered and added with 0.3 g of KBr in the ratio 2:100 and is kept in a die set of diameter 45 mm. After that about 7–10 tonnes of pressure was applied in an evacuated chamber to obtain transparent pellet of 0.5 mm thickness. The Raman spectra were recorded using Micro Raman spectrometer (Renishaw, UK model inVia) with 514 laser excitation. The absorption spectral measurements were made employing PerkinElmer Lambda 950 UV–vis-NIR spectrophotometer in the wavelength range 350–1800 nm. The luminescence spectra were recorded in the wavelength range 500–600 nm with Jobin YVon Fluorolog-3 spectrofluorometer using xenon lamp (450 W) as an excitation source. Luminescence spectra in the wavelength region 1400–1700 nm were recorded using EG&G Princeton Applied Research model 5210 with a spectral resolution of ± 0.5 nm. The physical properties such as density, polaron radius, and field strength providing an insight into the atomic arrangements in a glass network were determined using the expressions given below and were listed in Table 1. The densities of the prepared glasses were determined employing Archimedes principle in which glass was weighed in air and then in xylene liquid at room temperature using a monopane balance. The density (ρ) was calculated using the formula,

$$\rho = \frac{W}{W - W_1} \times 0.865 \quad (1)$$

where

W	weight of the prepared glass sample in air
W_1	weight of the prepared glass sample in xylene
0.865	density of xylene at room temperature.

The refractive indices have been measured at 589.3 nm using Abbe refractometer with monobromonapthalene as the contact liquid between sample and the prism of the refractometer using sodium vapour lamp as the source. Using the parameters like average molecular weight, glass density and mole percent of the rare earth oxide, rare earth ion concentration in the prepared glass has been calculated. Average molecular weight of the glass sample has been calculated by summing the molecular weights of the constituents of the glass samples taken in the required proportions.

Rare earth ion concentration indicates the concentration of rare earth ions in the prepared glass samples. In the present work, concentration of the Er^{3+} ions in the Lithium borate glasses was calculated using the formula:

$$N = \frac{\text{Mole \% of rare earth} \times \text{Glass density} \times \text{Avagadro number} \times 2}{\text{Glass average molecular weight} \times \text{Molecular Weight of RE ion}}. \quad (2)$$

Polaron radius is calculated using the expression:

$$r_p = {}^1/_2\left({}^\pi/_{6N}\right)^{1/3} \quad (3)$$

where N is the concentration of the RE ion. The interionic distance is the distance of separation between the two ions and is calculated using the

Table 1
Physical properties of the Er^{3+} doped Lithium Zinc borate glasses.

Physical properties	LZB0.01E	LZB0.05E	LZB0.1E	LZB0.5E	LZB1.0E	LZB2.0E
Density ρ (g/cm^3)	2.89	2.91	2.94	2.98	2.99	3.12
Refractive index n_d (589.3 nm)	1.612	1.623	1.633	1.642	1.651	1.659
Er^{3+} ion concentration N_E (10^{20} ions/cm^3)	0.05	0.26	0.53	2.64	5.18	10.33
Polaron radius r_p (Å)	23.3	13.5	10.7	6.28	5.02	3.99
Inter ionic distance r_i (Å)	57.7	33.58	26.6	15.58	12.45	9.89
Field strength F (10^{14} cm^{-2})	0.09	0.27	0.42	1.23	1.93	3.07
Molar refractivity R_m (cm^3)	7.99	8.06	8.10	8.24	8.50	8.60
Dielectric constant (ε)	2.60	2.63	2.67	2.70	2.73	2.75
Reflection losses R (%)	5.49	5.64	5.78	5.90	6.03	6.14
Molar volume V_m (cm^3/mol)	22.97	22.86	22.68	22.81	23.27	23.32
Electronic polarizability α_e (10^{-22} cm^3)	159.6	31.9	16.06	3.27	1.68	0.85