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Effect of Pr^{3+} ions concentration on the spectroscopic properties of Zinc telluro-fluoroborate glasses for laser and optical amplifier applications

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ABSTRACT

A new series of Pr^{3+} ions doped Zinc telluro-fluoroborate (PrZTFB) glasses have been prepared by adding up to 2 wt% Pr_2O_3. Spectroscopic properties were explored through X-ray diffraction, Raman, optical absorption, photoluminescence and decay measurements. The Raman spectra reveal the presence of different vibrational bonds of the borate and tellurite network(s). The bonding parameters have shown the ionic nature of the bonding Pr–X (X=O,F). The optical band gap energy and Urbach energy have been determined to understand the electronic band structure. The Judd-Ofelt parameters Ω_λ (λ=2, 4 and 6) have been calculated to explore the bonding environment around the Pr^{3+} ions. The luminescence spectra exhibit emission bands in the visible region attributed to the $^3P_0\rightarrow{}^3H_4$, $^3F_2$, $^3F_3$, $^3F_4$ and $^3P_1\rightarrow{}^3H_5$ and $^1D_2\rightarrow{}^3H_4$, $^3H_5$ transitions and a broad near infrared emission band at around 1330 nm corresponding to the $^1G_4\rightarrow{}^3H_5$ transition with a FWHM $\approx$ 70 nm. The glasses lying in the reddish orange region of CIE 1931 chromaticity diagram have been found suitable for light emitting diode applications. The decay curves of $^3P_0$ and $^1D_2$ levels of Pr^{3+} exhibit non exponential behavior for all the glasses and experimental lifetime value is found to decrease while increasing the Pr^{3+} ions due to cross-relaxation mechanisms. The radiative parameters corresponding to the prominent $^3P_0\rightarrow{}^3H_4$, $^1D_2\rightarrow{}^3H_4$ and $^1G_4\rightarrow{}^3H_5$ emission transitions have been determined to elucidate the suitability of the studied glasses for the fabrication of photonic devices that includes laser materials and broad band optical amplifiers.

1. Introduction

Nowadays, rare earth (RE) ions doped crystals as well as glass materials play a vital role in many scientific and technological applications such as solid state lasers, optical amplifiers, bar-code reading, sensors, display devices and telecommunications etc., since they exhibit sharp excitation and emission bands due to the shielding effect of 4f electrons by $5s^2$ and $5p^6$ shells. This shielding effect makes the RE ions to retain their emission properties though they are doped into different host matrices due to the less dependency of RE ions on the ligand field environment [1–5]. Glasses are the most favorable one for RE doping because of the fact that they exhibit broad emission and absorption spectral bands compared to the crystalline host materials and further it possess remarkable advantages like flexibility in choosing different chemical composition and ease of fabrication. Among the RE ions, number of investigations have been carried out on Pr^{3+} doped glass matrices towards the development of solid state lasers, up-converters, optical temperature sensors [6–9] and other opto-electronic devices. Furthermore, energy levels of Pr^{3+} ions demonstrate several meta-stable states and many of the researchers focus on the $^3P_0\rightarrow{}^3H_4$ (blue) and $^1D_2\rightarrow{}^3H_4$ (orange) laser transitions which offer emission in the visible region [7,10,11].

Among the several glass forming oxides, there is extensive amount of interest in the selection of borate based glass as the host matrix for RE ion doping because of their remarkable physical, mechanical, structural and optical properties [12] like transparency, lower melting temperature, higher dielectric constant and good RE ion solubility despite the fact that they possess larger phonon energy. In addition to that, research community shows enormous interest towards tellurite (TeO_2) based glasses due to their advantages which includes high density, high transparency in the mid infrared region, moderate phonon energy, good mechanical and chemical stability, large thermal expansion, good corrosion resistance and importantly high refractive index which

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make them potential candidate for the fabrication of optoelectronic devices such as optical amplifiers, planar waveguides, single mode fiber lasers and optical switching etc., [1,13]. Since borate (B_2O_3) possess larger phonon energy, addition of fluoride compounds such as ZnF_2, CaF_2 and BaF_2 with their lesser phonon energy as network modifiers would result in the phonon energy of the borates ($\approx$1300–1500 cm^{-1}) to a relatively lower value ($\approx$600–800 cm^{-1}) thus improves the excited state lifetime and luminescence efficiency of the RE ions by reducing the non-radiative (NR) losses. Furthermore, addition of fluoride compounds into the chosen glass matrix strongly decreases the OH absorption which inturn increases the transparency, mechanical and thermal stability [2,14]. Moreover, presence of Zinc oxide in the chosen glass matrix improves the mechanical strength, chemical stability and lower thermal expansion, hygroscopic nature further enhances the glass forming nature [15]. The suitability of the Zinc telluro-fluoroborate (B_2O_3–TeO_2–ZnO–ZnF_2–CaF_2–BaF_2) host matrix for laser applications have been reported [16–18] by the same authors and the proven results invokes interest to explore the lasing action as well as optical amplification of Pr^{3+} ions in the same host matrix.

In recent times many researchers pay much attention on Pr^{3+} doped glasses due to their versatile photonic and optoelectronic applications since they exhibit an important feature of rich emission that nearly covers the whole visible and NIR spectral region. Kumar et al. [19] reported the fluorescence properties of Pr^{3+} doped lead telluroborate (PTBPr) glasses for efficient visible laser applications. Naresh et al. [20] examined the visible and NIR emission characteristics of Pr^{3+} doped borosilicate glasses and reported on multiphonon and cross-relaxation (CR) channels for the different emission levels of Pr^{3+} ions. Brahmachary et al. [21] studied and reported the concentration effect of Pr^{3+} ions on the spectroscopic properties of ZANP glasses. Multichannel emission from Pr^{3+} doped borate based heavy-metal oxide glasses have been investigated and reported by Herrera et al. [9]. The aim of the present study is to (i) synthesize Pr^{3+} doped Zinc telluro-fluoroborate glasses by varying the Pr^{3+} ions concentration (ii) explore the presence of various functional groups in the prepared glasses (iii) investigate the spectroscopic properties employing the Judd-Ofelt (JO) theory [22,23] and finally (iv) determine the important radiative properties like transition probability (A), stimulated emission cross-section (σ_P^E) and branching ratios (β_R) for the different emission transitions of Pr^{3+} ions and to compare the results with the reported Pr^{3+} doped glasses.

2. Experimental

Pr^{3+} doped Zinc telluro-fluoroborate (xPrZTFB) glasses with the chemical composition $(30-x)B_2O_3+30TeO_2+16ZnO+10ZnF_2+7CaF_2+7BaF_2+xPr_2O_3$ (xPrZTFB; where x= 0.05, 0.1, 0.25, 0.5, 0.75, 1 and 2 in wt%) have been synthesized by melt quenching technique by taking the high purity (99.99%) analytical grade chemicals such as H_3BO_3, TeO_2, ZnO, ZnF_2, CaF_2, BaF_2 and Pr_2O_3 as starting materials purchased from Sigma Aldrich following the procedure reported in literature [17]. About 15 g batches were put into a porcelain crucible and melted in an electric furnace at 1050 °C for 45 min. The obtained glass melt was poured on to a preheated brass mold and subsequently annealed at 350 °C for 12 h to remove the thermal strain.

The refractive indices of the title glasses were measured using Abbe refractometer at sodium wavelength (5893 Å) having 1-bromonapthaline as a contact liquid. Subsequently, the densities were determined employing Archimedes's principle with xylene as an immersion liquid. In order to ensure the amorphous nature, X-ray diffraction measurements were performed using JEOL 8030 X-ray diffractometer employing CuK_α radiation. The Raman spectral analysis was carried out using SJ-301 Mitutoyo surface Profilometer with Imaging Spectrograph STR 500 mm focal length Laser Raman spectrometer. The optical absorption measurements were made using Perkin Elmer Lambda-950 UV–Vis–NIR spectrophotometer in the wavelength range 400–2500 nm. Visible luminescence spectra have been recorded in the wavelength region 470–760 nm using Jobin Yvon Fluorolog-3 Spectrofluorimeter exciting with xenon lamp (450 W) and the NIR luminescence spectra in the wavelength region 1250–1450 nm were recorded using EG&G Princeton Applied Research model 5210 with a spectral resolution of $\pm$0.5 nm.

3. Results and discussion

3.1. Physical properties

The physical properties which exhibit great influence on the optical properties have been studied for the Pr^{3+} doped Zinc telluro-fluoroborate glasses. The densities of the prepared glasses were found to increase due to the replacement of B_2O_3 by higher molecular weight Pr_2O_3 content. Refractive index (n_D) is one among the most significant properties which decides the suitability of the materials for optical applications and play an important role in calculating the JO intensity parameters and laser parameters. The obtained n_D values of the present glasses are given in Table 1 and it is observed that the n_D values increases with the increasing concentration of Pr_2O_3. The direct replacement of B_2O_3 by Pr_2O_3 in the present study modifies the boron to oxygen ratio which converts BO_3 units into BO_4 tetrahedral units thus enhances the formation of number of non-bridging oxygen's

Table 1
Physical properties of the Pr^{3+} doped Zinc telluro-fluoroborate glasses.

Physical properties	0.05PrZTFB	0.1PrZTFB	0.25PrZTFB	0.5PrZTFB	0.75PrZTFB	1PrZTFB	2PrZTFB
Density ρ (g/cm^3)	4.446	4.462	4.482	4.569	4.583	4.688	4.951
Refractive index n_D	1.612	1.614	1.617	1.619	1.622	1.624	1.627
Average molecular weight M_T (g)	107.66	107.80	108.20	108.87	109.54	110.21	112.89
Molar volume V_M (cm^3)	24.215	24.157	24.138	23.826	23.899	23.507	22.802
Rare earth ion concentration N (10^{20} ions/cm^3)	0.25	0.50	1.25	2.53	3.78	5.12	10.57
Polaron radius r_p (Å)	13.79	10.94	8.06	6.37	5.57	5.04	3.96
Inter ionic distance r_i (Å)	34.25	27.16	20.01	15.81	13.83	12.49	9.82
Field strength F (10^{14} cm^{-2})	0.256	0.407	0.749	1.199	1.568	1.921	3.112
Electronic polarizability α_e (10^{-22} cm^3)	33.345	16.683	6.697	3.315	2.225	1.646	0.801
Molar refractivity R_m (cm^3/mol)	1.173	1.172	1.171	1.152	1.153	1.130	1.074
Dielectric constant (ε)	2.599	2.605	2.615	2.621	2.631	2.637	2.647
Reflection losses R (%)	5.49	5.52	5.56	5.59	5.63	5.66	5.70
Optical dielectric constant (P $\frac{\partial t}{\partial P}$)	1.599	1.605	1.615	1.621	1.631	1.637	1.647