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Investigations on spectroscopic properties of Dy^{3+} doped zinc telluro-fluoroborate glasses for laser and white LED applications

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ABSTRACT

A new series of Zinc telluro-fluoroborate glasses (ZTFB) doped with Dy^{3+} ions with the chemical composition (30−x) B_2O_3 + 30TeO_2 + 16ZnO + 10ZnF_2 + 7CaF_2 + 7BaF_2 + xDy_2O_3 (where x = 0.05, 0.1, 0.25, 0.5, 1 and 2 in wt%) have been synthesized by the conventional melt quenching technique and the prepared glass samples were characterized through XRD, FTIR, UV-Vis-NIR optical absorption, photo-luminescence and decay spectral measurements. The XRD patterns have been recorded to confirm the amorphous nature. The FTIR spectral measurements were carried out to identify the functional groups present in the title glasses. From the energy band positions of the absorption spectra, bonding parameters ($\bar{\beta}$ and δ) have been calculated to identify the covalent/ionic nature of the metal-ligand bond present in the prepared glasses. The Judd-Ofelt (JO) intensity parameters Ω_λ (λ = 2, 4 and 6) have been calculated from the oscillator strengths of the different absorption bands to understand the nature of the ligand environment around the Dy^{3+} ions. The radiative parameters such as transition probability (A), stimulated emission cross-section (σ_P^E), radiative lifetime (τ_R) and branching ratios (β_R) corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ emission transitions have been determined using JO parameters and the refractive index values. The CIE chromaticity coordinates were calculated from the luminescence spectra to explore the dominant emission colour of the title glasses and the obtained results were discussed in detail and reported.

1. Introduction

Recently many researchers paid much attention towards exploring the luminescence properties of rare earth ions (RE) doped crystalline as well as amorphous materials due to their usage in optoelectronics devices such as lasers, light emitting diodes, optical fiber amplifiers, color displays and sensors etc [1–5]. Now a day's amorphous materials particularly glasses have been widely chosen as the host matrix for RE ion doping since it exhibits tremendous advantages over crystalline materials like transparency, excellent recycling capability, flexibility of choosing various glass composition, less fabrication time, ability to accommodate large number of RE ions and the possibility of constructing larger laser gain media with good optical quality in different shapes (rod, disc) etc., Further, RE ions doped glasses are the favorable materials for the above mentioned applications because they hold advantages like fluorescence over UV-Vis-IR spectral regions, longer lifetimes and higher quantum efficiency [6–9]. It is essential to find suitable host matrix for RE ion doping due to its prominent role in the development of optoelectronic devices because the optical properties and quantum efficiency of the RE ions exhibit much dependency on the nature of the ligand environment around the RE ion site and the phonon energy of the host matrix. Among the several hosts, borate (B_2O_3) based glasses are considered to be promising candidates for RE ion doping due to their peculiar properties like high thermal stability, low melting point and good RE ion solubility etc., [1,8,10]. However, it possesses drawbacks like higher phonon energy (~1300–1500 cm^{-1}) which leads to non-radiative transitions and restricts their usefulness in several applications. In order to conquer this problem, low phonon energy fluoride compounds such as BaF_2, CaF_2 and ZnF_2 can be added to the borate matrix which inturn improve the radiative transition rate and quantum efficiency [5,10,11]. Tellurite (TeO_2) is identified to be a conditional glass former which has been widely investigated over the years due to its practical advantages like high refractive index, low phonon energy and high transparency in the mid-IR region [9,12].

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In the present study borate, tellurite and fluorides have been combined to form telluro-fluoroborate glasses to avail the advantages of all the three network formers. The addition of ZnO into the telluro-fluoroborate network provides merits like non-hygroscopic nature, non-toxicity and wide band gap which in turn claim them as potential candidates for optoelectronic applications. The promising results exhibited by the Er^{3+} [13] and Er^{3+}/Yb^{3+} [14] doped B_2O_3–TeO_2–ZnO–ZnF_2–CaF_2–BaF_2 glasses motivated the authors to choose the same matrix with Dy^{3+} ion as a new dopant and to explore its suitability for white light applications.

White light emitting diodes (W-LEDs) play a crucial role in solid state lighting technology because of their significant properties like low electrical power consumption, longer lifetime, high efficiency, environmental friendliness, high brightness etc., over the conventional light sources [15–17]. Among the several RE ions, Dy^{3+} ions doped glasses are found to be the suitable candidate for white light applications because they exhibit two intense emission in the blue and yellow regions due to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) transitions respectively. The appropriate combination of these yellow and blue emission bands produce white light and this Y/B (yellow to blue) intensity ratio can be adjusted by varying the chemical composition, pumping wavelengths and Dy^{3+} ion concentration. It is a well known fact that $^4F_{9/2} \rightarrow {}^6H_{13/2}$ electric-dipole transition is hypersensitive in nature and its intensity exhibits considerable dependency on the nature of the ligand field environment around the Dy^{3+} ions whereas the intensity of the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ magnetic-dipole transition exhibits less dependency on the host matrix [18,19]. Further, Dy^{3+} doped glasses also exhibit numerous applications in the development of solid state visible lasers, color displays and telecommunication systems since they exhibit intense emission in the visible yellow and NIR (1.35 and 2.9 μm) regions [20–22].

Hence, special attentions have been paid by many researches on Dy^{3+} doped glass systems towards the fabrication of laser materials as well as light emitting sources. The effect of replacing borate (B_2O_3) by dysprosium (Dy_2O_3) content on the optical properties of Dy^{3+} doped borate glasses have been investigated recently by Venkata Rao et al. [23]. Subsequently, lasing ability and the white light generation capability of Dy^{3+} doped oxy-fluoroborate glasses have been studied and reported by Mahamuda et al. [24]. Ravi et al. [25] have examined the Judd-Ofelt analysis of Dy^{3+} ions doped borate-tellurium-calcium-zinc-niobium glasses for the laser applications. The white light generation from Dy^{3+} doped tellurite based glasses exciting at blue wavelength has been studied and reported by Damak et al. [26]. The present work reports the effect of Dy^{3+} ion concentration on the spectroscopic properties of Dy^{3+} doped Zinc telluro-fluoroborate glasses for lasers and white light applications.

2. Experimental

By employing the conventional melt quenching technique, Dy^{3+} doped Zinc telluro-fluoroborate glasses with the composition $(30-x)B_2O_3 + 30TeO_2 + 16ZnO + 10ZnF_2 + 7CaF_2 + 7BaF_2 + xDy_2O_3$ (where x = 0.05, 0.1, 0.25, 0.5, 1 and 2 in wt%) were prepared following the experimental procedure reported in literature [14] using high purity analytical grade (99.99% purity) chemicals such as H_3BO_3, TeO_2, ZnO, ZnF_2, CaF_2, BaF_2 and Dy_2O_3. The obtained glass samples were labeled as 0.05DZTFB, 0.1DZTFB, 0.25DZTFB, 0.5DZTFB, 1DZTFB and 2DZTFB based on the Dy^{3+} ion concentration.

The densities of the glass samples were measured based on the Archimedes principle using xylene as an immersion liquid and the refractive index measurements were carried out at sodium wavelength (5893 A°) employing Abbe refractometer using monobromonapthaline as a contact liquid. The physical properties of the Dy^{3+} doped title glasses have been calculated and presented in Table 1. The X-ray diffraction analysis was made using JEOL 8530 X-ray diffractometer employing CuK radiation. FTIR spectral measurements were made in the wave number range 400–4000 cm^{-1} using Perkin-Elmer paragon 500 FTIR spectrophotometer following the KBr Pellet technique. The absorption spectral measurements were made using Perkin Elmer Lambda-950 UV-Vis-NIR spectrophotometer in the wavelength region 420–1800 nm with a spectral resolution of ±0.1 nm. The emission and decay spectral measurements were carried out employing Jobin Yvon Fluorolog-3 Spectrofluorimeter with xenon lamp (450 W) as an excitation source. All these measurements were carried out at room temperature (RT) only.

3. Results and discussion

3.1. X-ray diffraction and FTIR spectral analysis

Fig. 1 shows the X-ray diffraction pattern of the 1DZTFB glass recorded in the range $5^\circ \leq \theta \leq 80^\circ$. The XRD pattern exhibits broad diffused scattering at lower angles instead of any sharp crystalline diffraction peaks thus confirms the amorphous nature [6] of the title glasses.

In order to explore the presence of different functional groups in the Dy^{3+} doped Zinc telluro-fluoroborate glasses, FTIR spectra have been recorded in the wave number range 400–4000 cm^{-1} and the same is shown in Fig. 2. The observed band positions and the corresponding band assignments are given in Table 2. The IR transmission band at around 3448 cm^{-1} is due to the fundamental stretching vibrations of OH group. The two weak bands observed around 2926 cm^{-1} and 2857 cm^{-1} are analogous to the hydrogen bond present in the title glasses [15]. The band at 1656 cm^{-1}

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

Physical properties	0.05DZTFB	0.1DZTFB	0.25DZTFB	0.5DZTFB	1DZTFB	2DZTFB
Density ρ (g/cm^3)	4.244	4.362	4.452	4.467	4.633	4.868
Refractive index n_d	1.529	1.531	1.534	1.537	1.539	1.542
Average molecular weight	107.68	107.84	108.31	109.08	110.64	113.75
RE ion concentration N (10^{20} ions/cm^3)	0.237	0.487	1.238	2.467	5.044	10.309
Polaron radius r_p (A°)	14.028	11.034	8.085	6.425	5.062	3.989
Inter ionic distance r_i (A°)	34.814	27.384	20.064	15.974	12.562	9.899
Field strength F (10^{14} cm^{-2})	0.248	0.400	0.745	1.180	1.901	3.061
Electronic polarizability α_e (10^{-22} cm^3)	31.082	15.174	5.997	3.024	1.483	0.729
Molar refractivity R_m (cm^3)	0.950	1.064	1.044	1.052	1.107	1.019
Dielectric constant (ε)	2.338	2.344	2.353	2.362	2.369	2.378
Reflection losses R (%)	20.917	20.980	21.073	21.167	21.229	21.322
Optical dielectric constant ($P\frac{\partial t}{\partial P}$)	1.338	1.344	1.353	1.362	1.369	1.378