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Structural and luminescence studies on Dy^{3+} doped lead boro–telluro-phosphate glasses

S. Selvi [a], G. Venkataiah [b], S. Arunkumar [a], G. Muralidharan [a], K. Marimuthu [a,*]

[a] Department of Physics, Gandhigram Rural University, Gandhigram 624302, India
[b] Department of Physics, Sri Venkateswara University, Tirupati 517502, India

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ABSTRACT

This paper reports results obtained on the structural and luminescence properties of Dy^{3+} doped lead boro–telluro-phosphate glasses prepared following the melt quenching technique. FTIR spectra exhibit the presence of B–O vibrations, P–O–P symmetric vibrations and Te–O stretching modes of TeO_3 and TeO_6 units. The metal–ligand bond was identified through UV–vis–NIR absorption spectra and to determine the band tailing parameter, direct and indirect band gap energy of the prepared glasses. The Judd–Ofelt (JO) intensity parameters (Ω_2, Ω_4 and Ω_6), experimental and theoretical oscillator strengths were also determined and reported. Luminescence measurements were made to determine the transition probability (A), stimulated emission cross-section (σ_P^E) and branching ratio (β_R) for the transitions that include $^4F_{9/2} \rightarrow {}^6H_{11/2}$, $^6H_{13/2}$ and $^6H_{15/2}$ bands. The effect of Dy^{3+} ion concentration on the intensity ratio of yellow to blue emission bands has also been studied and reported. The lifetime corresponding to the $^4F_{9/2}$ level of the title glasses has been found to decrease with the increase in Dy^{3+} ion concentration. The chromaticity coordinates (x,y) have been estimated from the luminescence spectra and the suitability of title glasses for white light applications has been analyzed using CIE chromaticity diagram. The variation of optical properties with the concentration of dysprosium oxide content in the glasses have been studied and reported.

1. Introduction

Over the past few decades, spectroscopic properties of rare earth (RE) ion doped glasses have been widely studied due to their potential applications in the formulation of new optical devices such as optical communication fibers, solid state lasers, light converters and sensors etc., Optical studies reveal the fact that the radiative properties of RE ions in glasses strongly depend on the host matrix and can be modified by proper choice of network forming and network modifying ions [1]. Nowadays Dy^{3+} ion doped glasses such as, boro–tellurite [2], fluorophosphate [3], oxyfluoroborate [4], lead tellurofluoroborate [5], lead silicate [6] and zinc alumino bismuth borate [7] glasses are receiving more attention. Among these oxide glasses, lead boro–telluro-phosphate glasses are known to be a good choice because of possible use in a wide range of applications such as laser hosts, glass to metal seals, solid state ionic conductors and bio compatible materials [8,9]. The borate based glasses provide interesting structural and optical properties. The borate glass structure is not a random distribution of BO_3 triangles and BO_4 tetrahedrals, but all these units form a clear and stable borate groups like diborates, triborates and tetraborates that forms a three-dimensional random glass network [10]. These structural changes usually occur due to the chosen chemical composition, involvement of various types of modifiers and conditions applied during glass preparation.

Borates assorted with tellurite and phosphate networks are expected to enhance the glass quality with an improvement in transparency, refractive index, density, thermal stability, moisture resistance, high gain coefficient, wide bandwidth capability and IR transmission. Low phonon energy of the telluro-phosphate glasses yields low non-radiative decay and high radiative emission rates of the RE ions which in turn lead to higher quantum efficiency. In addition to this, tellurium oxide easily forms a glass compared to other modifiers like alkali, alkaline earth and transition metal oxides. During the glass formation, the binary tellurite glass is trigonal bipyramid with lone pair of electrons and it changes the Te–O–Te bond [11,12]. The phosphate network might provide many sites for rare earth dopants allowing relatively higher RE ion solubility. Addition of PbO is necessary to improve the moisture resistance of these glasses. The strong interaction of easily polarizable valence shells of Pb^{2+} ions with highly polarizable O^{2-} ions present in the lead oxide may also be of particular interest for nonlinear optical materials. Due to these reasons, lead boro–telluro-phosphate glass has been

* Corresponding author. Tel.: +91 451 2452371; fax: +91 451 2454466.
E-mail address: mari_ram2000@yahoo.com (K. Marimuthu).

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chosen as the host matrix for rare earth (RE) ion doping to achieve higher luminescence quantum efficiency [13–16].

The Dy^{3+} ion exhibits $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (red) transitions in the visible region and the same is used to produce solid state lasers, up converters and optical amplifiers [17,18]. The yellow to blue intensity ratio of these transitions suggest that the Dy^{3+} ions doped materials are capable of generating white light and are useful in potential applications such as solid state lighting. The Dy^{3+} ions exhibit laser transitions in the NIR region at 3.02 μm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and 1.34 μm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) [19] and also in the visible region. These NIR and visible emissions have great technological applications in commercial display devices [20]. Saleem et al. [5] have studied and reported the luminescence behavior of Dy^{3+} ions in alkali lead tellurofluoroborate glasses. Jamalaiah et al. [21] explored the optical properties of Dy^{3+} ions in $PbO-H_3BO_3-TiO_2-Al_2F_3$ glasses by varying the lead oxide content and found that the CIE color coordinates fall well within the yellow light region. Vijayakumar et al. [22] studied the absorption and fluorescence behavior of Dy^{3+} ions in lead telluroborate glasses and reported that the high optical gain value is suitable for optical amplifiers. Mohan Babu et al. [23] and Babu et al. [24] explored the luminescence properties of Dy^{3+} ions in heavy metal glasses and glass ceramics and found that, addition of BaF_2 in the phosphate glasses decreases the non-radiative decay and in turn increases the quantum efficiency. Sasikumar et al. [25] discussed the optical absorption and photoluminescence properties of Dy^{3+} doped heavy metal borate glasses by varying the Li, Na and K modifier content and reported that the prepared glasses exhibit white light emission.

The present work reports studies made on Dy^{3+} doped lead boro–telluro-phosphate glasses prepared via melt quenching technique and the results obtained on their structural and luminescence properties. The aim of the present study is to (i) identify the local structural groups through FTIR spectra; (ii) calculate the bonding ($\overline{\beta}$ and δ) parameters; (iii) calculate the optical band gap and Urbach's energy values; (iv) analyze the oscillator strengths and JO parameters; (v) determine the radiative properties for the significant excited energy levels; (vi) determine the experimental lifetime of the $^4F_{9/2}$ level through decay curves and to compare the results with the calculated lifetime values; and (vii) finally to explore the suitability of these glasses towards white light applications through CIE chromaticity diagram.

2. Experimental

Dy^{3+} doped lead boro–telluro-phosphate glasses with the chemical composition $30B_2O_3+(20–x)PbO+15TeO_2+10P_2O_5+10ZnO+15BaO+xDy_2O_3$ (where $x=0.05$, 0.1, 0.25, 0.5, 1 and 2 in wt%) labeled as 0.05LBTPD, 0.1LBTPD, 0.25LBTPD, 0.5LBTPD, 1.0LBTPD, 2.0LBTPD were prepared by melt quenching technique following the procedure reported in the literature [2]. Infrared spectra of the glass samples were recorded using Perkin-Elmer paragon 500 FTIR spectrometer with a spectral resolution of 4 cm^{-1} in the wavenumber region 400–4000 cm^{-1}. CARY 500 spectrometer was employed to record the optical absorption spectra at a resolution of 0.1 nm in the wavelength range 400–1800 nm. The Photoluminescence measurements were made in the region 400–750 nm with a spectral resolution of 1.0 nm using Perkin-Elemer LS55 spectrometer. Lifetime measurements were made using digital storage oscilloscope (Tektronix TDS 1001B) interfaced to a personal computer that records and averages the signal monitoring the emission due to excitation at 375 nm. All these measurements were carried out at room temperature (RT) only.

The density of present glasses was measured employing Archimedes principle using xylene as an immersion liquid. The refractive indices were measured at 589.3 nm using Abbe refractometer with monobromonaphthalene as the contact liquid. The physical properties such as density, refractive index, dielectric constant, reflection losses, polaron radius and inter-ionic distance have been calculated and presented in Table 1.

3. Results and discussion

3.1. Structural analysis

In order to explore the presence of functional groups and local structural units in the prepared glasses FTIR spectral measurements have been made and the same is presented in Fig. 1. The transmission band positions along with their assignment are presented in Table 2. The FTIR spectra of the Dy^{3+} doped lead boro–telluro-phosphate glasses contain several bands specifying the local structure in them with broad or moderate bandwidth. Existence of high degeneracy of vibrational states, thermal broadening and photon scattering from the samples are the influencing factors for the presence of broad bands in the spectra [26]. The band around 3441 cm^{-1} is attributed to the fundamental stretching vibrations of the hydroxyl groups [27,28]. The IR absorption at around 2858 and 2922 cm^{-1} are due to the presence of hydrogen bonding [29–31]. The band at 1656 cm^{-1} in the IR spectrum evidences the presence of B–O$^-$stretching vibrations of BO_3 units [32]. The band observed at 1368 cm^{-1} is due to the B–O stretching vibration of BO_3 units of meta, ortho and pyroborate groups [33,34]. The band at 1024 cm^{-1} is related to the symmetrical stretching vibration of PO_4 groups [35,36]. The band observed around 672 cm^{-1} is attributed to the combined vibrations of BO_4 and PbO_4 units [6]. A broad absorption at 552 cm^{-1} is an indicative of the bending vibrations of basic structural units of phosphate glasses [37]. The Te–O–Te linkage bending vibrations of the TeO_3 and TeO_6 units are observed around 452 cm^{-1} [38,39]. The observed IR bands in the prepared glasses are in good

Table 1
Physical properties of the Dy^{3+} doped lead boro–telluro-phosphate glasses.

Sl. no	Physical properties	0.05LBTPD	0.1LBTPD	0.25LBTPD	0.5LBTPD	1.0LBTPD	2.0LBTPD
1	Density ρ (g/cm^3)	3.472	3.286	3.739	3.815	4.107	4.022
2	Refractive index n_d (589.3 nm)	1.768	1.771	1.772	1.774	1.779	1.784
3	Rare earth ion concentration N (10^{20} ions/cm^3)	0.159	0.301	0.856	1.741	3.728	7.220
4	Polaron radius r_p (A°)	16.01	12.95	9.14	7.21	5.59	4.49
5	Inter ionic distance r_i (A°)	39.74	32.14	22.69	17.91	13.89	11.15
6	Field strength F (10^{14} cm^{-2})	0.189	0.291	0.583	0.935	1.554	2.415
7	Electronic polarizability α_e (10^{-22} cm^3)	0.622	0.624	0.116	5.723	2.685	1.393
8	Molar refractivity R_m (cm^3)	1.197	1.269	1.114	1.097	1.026	1.044
9	Dielectric constant (ε)	3.126	3.136	3.139	3.147	3.165	3.183
10	Reflection losses R (%)	7.698	7.742	7.756	7.785	7.858	7.930