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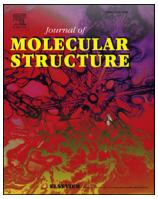

Red light generation through the lead boro–telluro–phosphate glasses activated by Eu^{3+} ions

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ABSTRACT

Lead boro–telluro–phosphate glasses containing 0.05 to 2.0 wt% of Eu^{3+} ions were prepared through melt quenching technique. Structural characteristics of title glasses were identified through XRD, FTIR and Raman studies. The optical properties of the prepared glasses were studied using UV–Vis–NIR absorption and photoluminescence spectra. From the resultant spectra, we have obtained the bonding parameters (δ), nephelauxetic ratio (β), direct and indirect band gaps and Urbach energy (ΔE) values. A deep red luminescence due to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions could be observed for the title glasses. The local site symmetry around the Eu^{3+} ions and the degree of Eu^{3+}–O^{2-} covalence were assessed from the luminescence intensity ratio of $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ transitions. Judd–Ofelt intensity parameters, calculated from the luminescence spectra, were used to estimate the radiative parameters like transition probability (A), branching ratio (β_{exp}, β_{cal}) and stimulated emission cross-section (σ_P^E) concerning the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 and 4) transitions. The important laser parameters, gain bandwidth and optical gain are also estimated. The decay curves associated with the transition from $^5D_0$ state was found to be single-exponential at all Eu^{3+} ion concentrations. CIE colour coordinates and colour purity of the prepared glasses were estimated from the CIE chromaticity diagram.

1. Introduction

The quest for efficient lamp phosphors, white LED phosphors and laser materials lead to a larger interest in Ln^{3+} ion incorporated materials. Among the Ln^{3+} ions, triply ionized europium (Eu^{3+}) ion is one of the efficient activators for photonic applications. Europium is also the most suitable material for red emitting phosphors in field–emission technology due to the $^5D_0 \rightarrow {}^7F_2$ emission transition yielding photons at 615 nm [1]. The Eu^{3+} ions give a narrow band monochromatic light owing to the long life time of the optically active state [2]. The non-degenerate ground state $^7F_0$ and excited state $^5D_0$ of the Eu^{3+} ions are highly suitable for studying the symmetry and inhomogeneity in the host matrix which mainly depends on the Stark splitting of emission bands from $^5D_0 \rightarrow {}^7F_{1,2}$ transition [3]. The probability of electronic transitions from $^5D_0$ to the multiplicity of $^7F_{0-6}$ states of Eu^{3+} ions depends on the site symmetry. At a site without inversion symmetry, Eu^{3+} ion exhibits the hypersensitive forced electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) with emission wavelengths at 615 nm while for a site with inversion symmetry, the allowed magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition is observed at 592 nm [4]. The local structure around the Eu^{3+} ions can be obtained from the f–f transition spectra. The selection of suitable network former and network modifier is important for tailoring the glass matrix and to enhance the performance of the material. The required properties of host material are low phonon energy, high quantum efficiency, easy incorporation of RE^{3+} ion and reduced multiphonon de-excitation between RE^{3+} ions [5]. In the recent years, the Eu^{3+} ions have been doped into various host matrices, such as oxides [6], fluoroborate [7], boro-tellurite [8] and silicates [9]. Among all these host matrices, the boro-tellurite is the suitable network former due to high transparency in the mid–infrared region, low melting point, high thermal stability, low phonon energies (700–800 cm^{-1}) and high solubility for the RE^{3+} ions [10]. The addition of oxides like ZnO, PbO and P_2O_5 to the boro-tellurite glass network enhances the mechanical strength, increases the fluorescence efficiency, chemical durability and reduces the non-radiative losses by reducing the number of hydroxyl (OH^-) groups in the glass network [11].

Several authors have reported the luminescence of Eu^{3+} doped

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glasses with different chemical compositions. Kassab et al. [12] studied piezo-optical effects of tellurite glasses doped with europium and gold. These glasses are used as nonlinear optical materials. Linganna and Jayasankar [5] analyzed the Eu^{3+} ions in phosphate glasses and they found the concentration quenching effect to be limited by the addition of Al_2O_3. Trivalent europium doped fluorometaphosphate glasses, which are useful in simultaneous high energy and high peak power laser applications (multi-kilo Joule and multi terawatt) have been examined by Babu et al. [13]. Annapurna et al. [9] investigated the $ZnO-B_2O_3-SiO_2$ glasses doped with europium were found to be suitable for CRT screens and X-ray intensifiers. Colour-tunable luminescence of Eu^{3+} in the PbF_2 embedded in oxyfluoroborate glass and nanocrystals was studied by Zhou et al. [14]. This nanocomposite glass was used to produce white-light. Enhanced fluorescence Eu^{3+}doped fluoroborate glasses containing silver particles was reported by De Sa et al. [7]. The influence of tungsten on the Nd^{3+}, Sm^{3+} and Eu^{3+} ions in $ZnF_2-WO_3-TeO_2$ glasses was examined by Gandhi et al. [15]. They found these glasses to exhibit photochromic and electrochromic properties.

In the present work, lead boro-telluro-phosphate glasses were prepared by varying the Eu^{3+} concentration to study and enhance the optical and luminescence properties with the aim to ascertain their usefulness for solid state lasers devices for red light generation.

2. Experimental

2.1. XLBTPE glass preparation

10 g batches of Eu^{3+} doped lead boro–telluro–phosphate glasses with the composition $30B_2O_3 + (20-x) PbO + 15TeO_2 + 10P_2O_5 + 10ZnO + 15BaO + xEu_2O_3$ (where x = 0.05, 0.1, 0.25, 0.5, 1 and 2 in wt%) were prepared by melt quenching technique. The numbers here indicate the weight percentage of the components used. These chemical compositions were thoroughly mixed using an agate mortar. The fine homogeneous mixture was heated in a porcelain crucible at 1100 °C for 30 min. The melt was quickly quenched by pouring it into a preheated brass mold held at 350 °C. The glass samples were annealed at 350 °C for 8 h in order to remove the internal stress and thermal strain, These glasses are labelled as 0.05LBTPE, 0.1LBTPE, 0.25LBTPE, 0.5LBTPE, 1.0LBTPE, 2.0LBTPE respectively and the numbers indicate the wt% of Eu_2O_3 added to the glass.

The XRD spectra were recorded using PANalytical XPERT- PRO X-Ray diffractometer using CuKα radiation. The FTIR spectra of the prepared glasses were recorded in the range 4000–400 cm^{-1} using Perkin–Elmer BX-II spectrometer. Imaging Spectrograph STR 500 SEKI Laser Raman Spectrometer with a resolution of 1/0.6 cm^{-1}/pixel (SEK, Japan) was used to record the Raman spectra. The UV–Vis absorption measurements were made using Perkin- Elemer Lambda 35 in the wavelength range of 200–1100 nm with a resolution of 0.5 nm. The NIR absorption measurements were made using Jasco V- 670 spectrophotometer in the wavelength range 1100–2700 nm with a resolution of 0.5 nm. The luminescence spectra were recorded in the wavelength range between 325 and 725 nm using Perkin Elmer LS55 spectrophotometer with a spectral resolution of 1.0 nm. The decay measurements were carried out through a digital storage oscilloscope (Tektronix TDS 1001B) coupled with personal computer. All these measurements were carried out at room temperature.

The densities of the prepared XLBTPE glasses have been measured using Archimedes principle with xylene as the immersion liquid. Refractive index of the title glasses was obtained with an Abbe refractometer at sodium wavelength (5893 Å) using the monobromonapthalene as the contact liquid. The physical properties of the XLBTPE glasses have been estimated and presented in Table 1.

3. Results and discussion

3.1. Structural analysis

XRD patterns corresponding to all the title glasses did not reveal any diffraction peaks. As a representative case, the XRD pattern of 1.0LBTPE glass is shown in Fig. 1. The absence of any discrete diffraction peak confirms the glassy nature of the XLBTPE glasses.

3.1.1. FTIR spectral analysis

Fig. 2 shows the FTIR spectra for the Eu^{3+} doped lead boro–telluro–phosphate glasses. The infrared absorption bands (in wavenumber) and their assignment are presented in Table 2. The band at 461 cm^{-1} is attributed to the bending mode of Te–O–Te (or) O–Te–O linkages [9]. The band at 552 cm^{-1} is ascribed to the vibration of metal cations [16]. The band centered around 679 cm^{-1} is attributed to the combined vibrations of BO_4 and PbO_4 [17]. The PbO enters in the XLBTPE glass network by breaking the Te–O–Te and B–O–B bonds and introduce coordinate defects is known as dangling bonds along with non-bridging oxygen ions by forming the TeO_3 and BO_4 units. The oxygen of PbO breaks the local symmetry around the Te–O–Te and B–O–B bonds while the Pb^{2+} ions occupy interstitial positions [18]. Due to the boron anomaly, the B_2O_3 based glasses have interesting structural peculiarities [19]. The presence of symmetric (BO_3) triangles, (BO_4) tetrahedral and asymmetric $(BO_3)^{3-}$ units (non-bridging oxygen) could be observed in each of the XLBTPE glass samples. The band around 1227 cm^{-1} is attributed to the B–O asymmetric stretching of the tetrahedral BO_4 and orthoborate groups [20]. The absorption band due to the stretching vibrations of B–O bond in trigonal BO_3 units is observed at 1347–1382 cm^{-1} [21]. The broad composite bands extending from 2928 to 2858 cm^{-1} are attributed to the hydrogen bonding [8]. The absorption around 3420 cm^{-1} corresponds to the hydroxyl or water groups [19] that have been included into the glasses during the melt quenching process.

3.1.2. Raman spectral analysis

The Raman spectrum for 1.0LBTPE glass is shown in Fig. 3. This is given as a representative spectrum as the spectra were qualitatively the same. The Raman band positions (cm^{-1}) and corresponding band assignments are presented in Table 3. The Raman band around 436 cm^{-1} is assigned to the symmetric Te–O–Te stretching mode [22]. The shoulder around 691 cm^{-1} is an indication of the presence of $B-O^-$ stretching in meta borate groups [23]. The band at 753 cm^{-1} in the title glasses is attributed to the symmetric stretching of P–O–P vibrations of borate linkages [24] and the same is assigned to the TeO_4 bi-pyramid arrangement, TeO_{3+1} (or distorted TeO_4) and TeO_3 pyramids structural units [17]. The strong band at 1030 cm^{-1} is related to the asymmetric stretching of the PO_3 units [24]. The prominent band centered at 1106 cm^{-1} is due to the vibrations of the BO_3 groups [25]. The absorptions due to chain and ring type metaborate groups could be observed at 1234 cm^{-1} [26]. The Raman band at 1341 cm^{-1} is due to the asymmetric stretching vibrations of PO_2 groups [13]. The weak band at high frequency region 1687 cm^{-1} is assigned to the $B-O^-$ stretching vibration involving non bridging oxygen in various borate groups [27].

3.2. Optical absorption and bonding parameters

The optical absorption spectra of XLBTPE glasses are similar;