Journal of Luminescence 171 (2016) 19–26

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full length article

Influence of Er^{3+} ion concentration on spectroscopic properties and luminescence behavior in Er^{3+} doped Strontium telluroborate glasses

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ARTICLE INFO

Article history:
Received 11 May 2015
Received in revised form
14 September 2015
Accepted 29 October 2015
Available online 6 November 2015

Keywords:
Raman spectra
Upconversion luminescence
Judd–Ofelt parameters
Glasses.

ABSTRACT

Er^{3+} doped Strontium telluroborate glasses were prepared following melt quenching technique by varying the concentration of Er^{3+} ion with respect to Borate content as 0.01, 0.05, 0.1, 0.5, 1.0 and 2.0 mol%. The presence of different vibrational groups was identified through FTIR and Raman spectral measurements. The variation in JO parameters with the increase in Er^{3+} ions concentration was discussed with respect to the covalency of the prepared glasses. The direct and indirect band gap values were found to decrease with the increase in Er^{3+} ion content and are discussed in terms of metallization factor and non-bridging oxygens. The green luminescence corresponding to the thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ states under 379 nm and 980 nm excitations was discussed. The luminescence intensity quenches beyond 0.5 mol% of Er^{3+} ion concentration in both the excitations due to the energy transfer process which takes place between Er^{3+} and Er^{3+} ions. The different possible mechanisms (ESA, ETU) responsible for the upconversion luminescence were also discussed with partial energy level diagram. The radiative parameters such as A, β and τ were determined for the $^4S_{3/2}$ excited level which in turn helps one to calculate the stimulated emission cross-section (σ_p^E). Among the studied glasses, STB0.5E glass exhibits higher A, σ_p^E and β_R values and these in turn specify its suitability for laser applications.

1. Introduction

Due to high stability, large stokes and anti-stokes shift, and long lifetime, trivalent lanthanide ions find applications in various fields such as lasers, optical amplifiers, temperature sensors, etc. [1–3]. Among the lanthanide ions, Er^{3+} ions exhibit dominant emission from $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition at around 18,300 cm^{-1} and is more preferable for green upconversion lasers. While exciting at 980 nm, the Er^{3+} ions exhibit an optically transparent window in the NIR region (1400–1600 nm) which is advantageous due to low auto-fluorescence background, high signal to noise ratio, high detector sensitivity and high penetration depth in biological tissues. For highly efficient luminescence, better tunability between host matrices and dopant ion is required i.e., lattice of the host material should match with the dopant ions and possess low phonon energy [4].

Glass matrix is more preferable than crystalline matrix for the doping of Lanthanide ions because of the fact that these systems can easily be prepared in different shapes and sizes with uniform distribution of RE ion concentration and is suitable for developing low loss, high strength and low cost optical fibers. Good thermal and elastic matrix allow for the solubility of large concentration of RE ions. Due to weak absorption which occurs as a result of disorderness in the structure and low reflection losses, glasses exhibit a large optical transparent window covering UV, visible and IR regions. Generally oxyfluoride glasses are preferred since they exhibit both the features of oxide and fluoride matrices like ease of preparation, thermal stability and moisture resistance. They have low phonon energy characteristics to permit fluorescence of a rare earth ion over a wide spectral region. The incorporation of boron ion as a glass former into the host matrix increases the thermal stability, chemical durability and ease of fabrication. Also, it can exist in two coordination states such as trigonal and tetrahedron states when alkaline earth metals such as $Ba^{2+}$and Sr^{3+} are added into the network thus creating more non-bridging oxygens which favors the formation of glasses. The addition of tellurium dioxide into the network increases RE ion solubility, increases its

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http://dx.doi.org/10.1016/j.jlumin.2015.10.071

Table 1
Physical properties of Er^{3+} doped Strontium telluroborate glasses.

Physical properties	STB0.01E	STB0.05E	STB0.1E	STB0.5E	STB1.0E	STB2.0E
Density ρ (g/cm^3)	4.16	4.26	4.29	4.38	4.38	4.44
Refractive index n_d (589.3 nm)	1.63	1.65	1.68	1.7	1.71	1.72
Er^{3+} ion concentration N_E (10^{20} $ions/cm^3$)	0.04	0.21	0.43	2.16	4.26	8.41
Polaron radius r_p (A°)	25.10	14.60	11.50	6.72	5.36	4.27
Inter ionic distance r_i (A°)	62.17	36.13	28.61	16.67	13.29	10.59
Field strength F (10^{14} cm^{-2})	0.08	0.23	0.37	1.07	1.69	2.67
Molar refractivity R_m (cm^3)	10.32	10.36	10.66	10.80	11.04	11.32
Dielectric constant (ε)	2.66	2.72	2.82	2.89	2.92	2.96
Reflection losses R (%)	5.74	6.02	6.44	6.72	6.86	7.01
Molar volume V_m (cm^3/mol)	29.02	28.39	28.20	27.93	28.26	28.65
Electronic polarizability α_e (10^{-22} cm^3)	204	41.09	21.11	4.27	2.19	1.12
Metalization factor (M)	0.64	0.64	0.62	0.61	0.61	0.61
Average boron–boron separation d_{B-B} (nm)	0.342	0.339	0.338	0.336	0.335	0.341

transmittance and refractive index which in turn increases the stimulated emission cross-section, decreases the phonon energy thus reducing the deleterious non-radiative emission and enhances the upconversion emission in the prepared glasses. The addition of alkaline earth metals such as Ba^{2+}, Sr^{3+} modifies the glass network due to the fact that they exhibit ionic radii close to the lanthanide ions. Thus strontium telluroborate glasses have been selected as a host matrix with Er^{3+} ion as a dopant for the fabrication of a better lasing material.

Many works have been carried out and reported based on Er^{3+} doped glasses for the fabrication of frequency upconvertors. Babu et al. studied the luminescence behavior under direct excitation and NIR excitation in Er^{3+} doped metaphosphate glasses and reported the various mechanisms responsible for upconversion and quenching of luminescence [5]. Zahra Asur Said Mahraz et al. have studied the concentration dependent luminescence quenching of Er^{3+} doped Zinc borotellurite glass [6]. Kesavalu et al. have discussed the structural, thermal and spectroscopic properties of Er^{3+} in oxyfluoride glasses for photonic application [7].

Assadi et al. have discussed the spectroscopic and luminescence characteristics of erbium doped TNZL glass for lasing materials [1].

The aim of the present work is to (i) prepare strontium telluroborate glasses by varying Er^{3+} ion concentration, (ii) identify the presence of different vibrational modes through Raman and FTIR spectra, (iii) study the effect of Er–O bond with increasing concentration of Er^{3+} ion in terms of Nephelauxetic effect, (iv) determine the oscillator strengths of different transitions from the absorption spectra and hence derive the Judd–Ofelt parameters (Ω_2, Ω_4, Ω_6), (v) determine the direct and indirect band gap using Davis and Mott theory, (vi) study the effect of Er^{3+} ion concentration on green luminescence observed from $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions monitoring an excitation at 379 nm and 980 nm and to discuss the different possible mechanisms for green upconversion luminescence, and finally (vii) to determine the radiative parameters for the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ level of Er^{3+} ions in the glass composition with an excitation wavelength at 379 nm for the fabrication of lasing materials.

2. Experimental

Er^{3+} doped Strontium telluroborate glasses were prepared following melt quenching technique [5] with the chemical composition $(40-x)H_3BO_3+15TeO_2+15SrCO_3+10SrF_2+10BaCO_3+10BaF_2+xEr_2O_3$ (where $x=0.01$, 0.05, 0.1, 0.5, 1.0 and 2.0 in mol%) and labeled as STB0.01E, STB0.05E, STB0.1E, STB0.5E, STB1.0E and STB2.0E respectively. All the precursors used for the preparation of glasses are of high purity analytical grade (99.99%) from Sigma Aldrich.

The FTIR spectra of the prepared glasses were recorded with Perkin Elmer paragon FTIR spectrum BX spectrophotometer with a spectral resolution 2.0 cm^{-1}. The Raman spectra were recorded using Micro Raman spectrometer (Reinshaw, UK model in Via) with 514 laser excitation. The absorption spectral measurements were made employing Perkin Elmer Lambda 950 UV–vis–NIR spectrophotometer in the wavelength range 340–1800 nm. The luminescence spectra were recorded in the wavelength range 500–700 nm with Jobin YVon Fluorolog-3 spectrofluorimeter using xenon lamp (450 W) as an excitation source. The upconversion luminescence spectra have been measured using Varian Cary Eclipse fluorescence Spectrometer (Varian Scientific Instruments, Mulgrave, Australia) with a standard R928 red sensitive photomultiplier (Hamamatsu Photonics, Shizuoka, Japan) equipped with IR laser diode module C2021-F1 (Roithner Lasertchnik, Vienna, Austria).

The density was measured by following Archimedes principle employing xylene as an immersion liquid and the values are found to increase from 4.16 to 4.44 g/cm^3 due to the decrease in the average boron–boron separation in the prepared glasses. The refractive indices were measured through Abbe Refractometer using mono bromonaphthalene as a contact liquid at sodium wavelength and it increases with the increase in RE ion concentration. The Metallization factor (M) or covalency parameter was found to decrease from 0.64 to 0.61 which confirms the fall in ionic nature in the prepared glasses. The concentration of the Er^{3+} ions in the prepared glasses was calculated using the formula $N=$ [(mol% of the dopant ions $\times \rho \times N_A$)/average molecular weight of the glass] where 'ρ' is the density of the material ($g\,cm^{-3}$), 'N_A' is the Avagadro number and is shown in Table 1 along with the other physical properties.

3. Results and discussion

3.1. Structural studies

3.1.1. Raman spectra

The study of different vibrational bonds involved in the title glasses was made with Raman spectra in the range between 0 and 2000 cm^{-1} and Raman spectrum for the STB0.01E glass is shown in Fig. 1 as a representative case along with their assignments in Table 2. The spectrum exhibits nine peaks positioned at 75, 361, 503, 764, 1066, 1121, 1337, 1423 and 1654 cm^{-1} among which the peaks found at 764, 1121, and 1423 cm^{-1} were more intense. The two primary network formers involved in the prepared glasses were TeO_2 (O=Te=O) and B_2O_3 (O=B–O–B=O). These network formers exist in different forms such as TeO_4, TeO_3, TeO_{3+1},