



## Spectroscopic study of Er:Sm doped barium fluorotellurite glass

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## ARTICLE INFO

## Article history:

Received 12 January 2010

Received in revised form 25 April 2010

Accepted 28 April 2010

## PACS:

42.07e

42.70.Hj

42.81.Bm

## Keywords:

Energy transfer

Barium fluorotellurite glass

Er<sup>3+</sup> ionSm<sup>3+</sup> ion

Upconversion

## ABSTRACT

In this paper, we report the physical and spectroscopic properties of Er<sup>3+</sup>, Sm<sup>3+</sup> and Er<sup>3+</sup>:Sm<sup>3+</sup> ions codoped barium fluorotellurite (BFT) glasses. Different Stokes and anti-Stokes emissions were observed under 532 nm and 976 nm laser excitations. Energy transfer from Er<sup>3+</sup> ion to Sm<sup>3+</sup> ion was confirmed on the basis of luminescence intensity variation and decay curve analysis in both the cases. Under green (532 nm) excitation emission intensity of Sm<sup>3+</sup> ion bands improves whereas on NIR (976 nm) excitation new emission bands of Sm<sup>3+</sup> ions were observed in Er:Sm codoped samples. Ion interactions and the different energy transfer parameters were also calculated.

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## 1. Introduction

Heavy metal oxide glasses are reported as promising hosts for the rare earth ions as the maximum phonon frequency of these hosts are comparably lower than those in borate, phosphate, silicate and germanate glasses [1,2]. Among them, tellurite glass shows interesting properties viz. improved chemical durability, lower melting temperature and excellent transmittance in the visible and near infrared spectral regions. High refractive index and optical non-linearity of this host facilitate the development of lasers and amplifiers at longer wavelengths. In presence of suitable modifiers like alkali, alkaline earths, transition metal oxides, etc., tellurium oxide easily forms glass. The basic structural unit of binary tellurite glass is trigonal bipyramid, with lone pair of electrons, and it forms the Te–O–Te bond while forming the glass. Introducing BaF<sub>2</sub> modifier in this glass, it reduces the phonon energy markedly as its maximum phonon energy (~346 cm<sup>-1</sup>) is much less than the phonon energy of the tellurite oxides (Te–O ~ 800 cm<sup>-1</sup>) [1].

Rare earth spectroscopy plays a vital role in progress of display devices, optical detectors, lasers, in the telecommunication fields, etc. Particularly, research on Sm<sup>3+</sup> rare earth ions is significant due to its increasing demand in various fluorescent devices, high-density optical storage, under sea communication, colour displays and visible solid-state lasers due to its bright emission in

orange/red regions [3,4]. The <sup>4</sup>G<sub>5/2</sub> level of Sm<sup>3+</sup> exhibits relatively high quantum efficiency and shows various populating and quenching emission channels resulting interesting fluorescence properties [5]. Temperature sensing behavior of Sm<sup>3+</sup> ions has also well reported [6,7]. Studies on pairs of rare earth ions, e.g. Sm–Ce, Sm–Eu and Er–Sm doped in different host matrices have been reported earlier in literature [8–10]. In recent years, NIR lasers are being used to get intense visible emission through upconversion process. Unfortunately in case of Sm<sup>3+</sup> ion, extinction corresponding to 976 nm wavelength is weak and hence upconversion emissions are rarely observed [3]. One solution of this problem is the effective sensitization of Sm<sup>3+</sup> ions by other rare earth ion which shows intense upconversion emission on NIR excitations and the emission band overlap with the absorption of Sm<sup>3+</sup> levels.

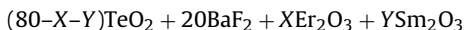
Upconversion luminescence in Er<sup>3+</sup> ion has been investigated extensively in various host materials. Visible upconversion lasers have also been developed in green and red regions of spectrum in several Er<sup>3+</sup> doped host materials [11]. Er<sup>3+</sup> ions have also been used to tune white light emission in combination with other rare earth ions [12]. Moreover among rare earth ions, Er<sup>3+</sup> ion shows best green upconversion emissions on 976 nm which is in resonance with the absorption of Sm<sup>3+</sup> ions. Er<sup>3+</sup> ion can be efficiently pumped by NIR semiconductor lasers due to its favorable energy level at 10,204 cm<sup>-1</sup> (<sup>4</sup>I<sub>11/2</sub>). The excited Er<sup>3+</sup> ions in metastable excited levels can excite the levels of other rare earth ions through energy transfer. As the energy gap between the Er<sup>3+</sup>:<sup>4</sup>S<sub>3/2</sub> level and Sm<sup>3+</sup>:<sup>4</sup>G<sub>5/2</sub> level is only ~388 cm<sup>-1</sup>, an energy transfer from Er<sup>3+</sup> ion to Sm<sup>3+</sup> ion may be anticipated.

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In the present paper we have studied the physical and spectroscopic properties of  $\text{Sm}^{3+}$  ion,  $\text{Er}^{3+}$  ion and  $\text{Er}:\text{Sm}$  ions codoped barium fluorotellurite (BFT) glass. We have observed the energy transfer frequency upconversion emission in red region corresponding to  $\text{Sm}^{3+}$  ions in the presence of  $\text{Er}^{3+}$  ions on 976 nm excitation. The energy transfer mechanism and the photo-physics involved have been explained in detail using luminescence emission and decay curve analysis.

## 2. Material synthesis and measurements

The rare earth ions doped BFT glasses have been prepared following the protocol of melt quench method [1]. The following molar composition used:



where  $X = 0.01, 0.02, 0.03, 0.04$  mol%,  $Y = 0, 0.15, 0.3, 0.4$  mol%.

The purity of the compounds used was better than 99.9%. Good optical quality glasses of dimensions  $1.0 \text{ cm} \times 1.0 \text{ cm} \times 0.3 \text{ cm}$  were prepared. They were cleaned, polished and then used for further optical measurements.

The density of the glass samples was measured by the Archimedes principle using hexane as an immersion liquid (density =  $0.655 \text{ g/cm}^3$  at room temperature) while refractive index of the glasses were calculated using Dimitrov and Sakka method [13]. Differential Thermal Analysis (DTA) was carried out to confirm the glassy nature of the 'as prepared' glass. The glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) were also estimated from the DTA measurements using Pyris Diamond Thermal analyzer at a fixed heating rate of  $10^\circ\text{C/min}$ , under  $\text{N}_2$ -gas atmosphere. The absorption spectra of samples were measured using JASCO V-670 double beam spectrophotometer in the range of 200–2300 nm. The fluorescence measurements were carried out using the second harmonic (532 nm) of Nd:YAG laser (Spotlight, Germany) and NIR diode laser (500 mW) emitting at 976 nm as the excitation source. An iHR320 computer controlled trix monochromator equipped with grating blazed at 500 nm and PMT (model-1424M) was used as detector to detect the dispersed luminescence. Photoluminescence decay curves have been recorded using 532 nm pulsed radiation (repetition rate  $\sim 10 \text{ Hz}$ , pulse width  $\sim 7 \text{ ns}$ ) of Nd:YAG laser. The collected signal was fed to 150 MHz digital oscilloscope (model no. HM 1507, Hameg Instruments) and the decay curves were obtained for further analysis. Lifetimes of the radiative levels were estimated by fitting as exponential function to the recorded curves. The detector offset was removed before fitting and the data were normalized to the initial voltage.

## 3. Results and discussions

### 3.1. Physical properties

Physical properties like density, refractive index, energy band gap, etc. of the undoped and doped BFT glasses have been calculated and are shown in Table 1. The optical absorption spectra of all the samples have been recorded (Fig. 1). It was observed that the UV cutoff of the BFT glass slightly red shifted as the rare earth ions were introduced in the glass. It is well known that the UV cutoff limit of the glass depends to the chemical composition of the glass and is directly related to the electron donating power, i.e. optical basicity of the oxygen atom in the host, which is influenced by the constituents of the glass and the electronegativity of the cations (e.g.  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{RE}^{3+}$ ,  $\text{RE}^{4+}$ , etc.) in the glass [14]. Change in optical basicity of oxygen changes the bonding in glass forming network. Modifications in oxygen bonding in glassy network such as forma-

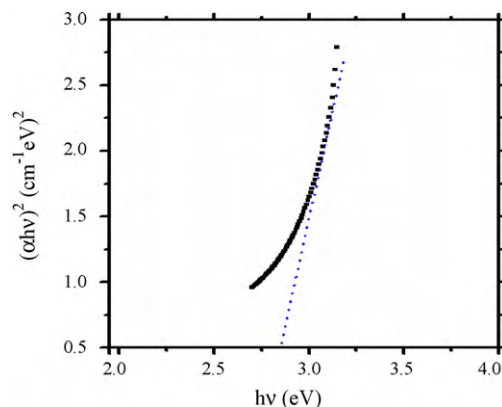


Fig. 1. Tauc's plots of Er:Sm doped BFT glass.

tion of non-bridging oxygen influence the density, refractive index and molar volume which ultimately affect the absorption characteristics of the glass samples. To monitor the effect of RE ions in the glassy network we have calculated different physical parameters of the samples and values thus obtained are tabulated in Table 1.

The optical band gap calculations have been performed using the relationship between the absorption coefficient and frequency around the absorption edge given by Mott and Davis for amorphous materials [15]:

$$\alpha h\nu = B(h\nu - E_g)^n$$

where  $B$  is band tailing parameter,  $E_g$  is optical band gap,  $n = 2, 3, 1/2$  and  $1/3$  corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively and  $h\nu$  is the incident photon energy. Band gap can be calculated from the linear region of the curve by extrapolating them to meet the  $h\nu$  axis at  $(\alpha h\nu)^n = 0$ . Calculations reveal a slight reduction in the band gap of BFT glass with the introduction of rare earth ions, as the band gap for BFT glass is 2.91 eV while for BFTSm, BFTEr, and BFTSmEr band gaps are 2.82 eV, 2.87 eV, and 2.81 eV, respectively. The densities and the molar volumes of the samples also changed in a similar way. The density of the sample is an effective probe to measure the any alteration in the geometrical configuration and the variation in the dimensions of the interstitial holes.

A comparison of different physical parameters of undoped and doped BFT glass samples indicates that the introduction of the rare earth ions causes a change in the glass structure. Nelson et al. [16] reported the formation of a high number of non-bridging oxygen atom with the rare earth ions in the lattice which consequently leads a decrease in the density and the molar volume of the sample. The oxygen bonding strength is directly related with the absorption edge which changes with the formation of non-bridging oxygen consequently optical band gap reduced [17]. The gradual changes near the absorption edge are expressed by the following Urbach rule [18] as:

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{h\omega}{E_c}\right)$$

where  $\alpha(\omega)$  is absorption coefficient,  $\alpha_0$  is a constant and  $E_c$  is the Urbach energy, describing the optical transitions between localized tail states adjacent to the valence band and the extended states in the conduction band above the mobility edge, i.e. the width of the band tails of the localized states in the normally forbidden band gap [18]. The extent of this band tailing is a measure of the disorder in the material. The lower Urbach energies observed for the prepared glasses indicate the minimum defects in these glasses [19], i.e. the glasses are highly homogeneous and stable.

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