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Spectrochimica Acta Part A 66 (2007) 1307–1311
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Upconversion in Er^{3+}-doped Bi_2O_3–Li_2O–BaO–PbO tertiary glass

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Received 3 May 2006; accepted 12 June 2006

Abstract

Radiative properties of Er^{3+}-doped tertiary bismuth glass has been analyzed by the Judd–Ofelt theory. NIR to visible upconversion in the Er^{3+}-doped glass has been reported. The mechanism for the upconversion is explained on the basis of quadratic dependence on excitation power and on the energy-matching scheme. Energy transfer is noted as the dominant process including the long-lived $^4I_{11/2}$ level as the intermediate state for the green and red upconversion emissions. The effect of temperature on the fluorescence intensity of the two bands due to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions as well as on the transitions due to Stark components of the $^4S_{3/2}$ level have been monitored and it is concluded that their intensity ratio may serve as better temperature sensing device.

PACS: 42.70Ce; 42.70.Hj

Keywords: Tertiary glass; Upconversion; Energy transfer; FIR; Sensors; Stark sub-levels

1. Introduction

Glass materials doped with rare earth ions are capable of high peak power generation due to their high saturation frequencies, broad emission band width, and long upper state lifetime. Currently, attention has been devoted to the upconversion of near infrared into visible light because of its many applications in, color display, optical data storage, biomedical diagnostics, sensors, optical fiber and under sea optical communications [1–3].

Many trivalent rare earth ions like Pr^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+} are among the most studied triply ionized rare earth ions and the upconversion process in these ions in various kinds of crystals and glasses have been studied [4–15].

The oxide glasses have small absorption coefficient within the wavelength range of interest and ultrafast response time. They also have compatibility with waveguide fabrication process; their optical damage threshold is quite high. They also have high chemical and thermal durability, and are thus suitable material for technological applications. However, the high phonon energy corresponding to the stretching vibrations of the oxide glass network modifier creates difficulty in the generation of upconversions. Bismuth oxide glass is a high refractive index and low phonon energy system which enhances the radiative transitions of the rare earth ions and is expected to have high fluorescence quantum efficiency. The upconversion luminescence has been earlier studied in Er^{3+}-doped Bi_2O_3–K_2O–Ga_2O_3 [16]. NIR to visible upconversion in Er^{3+}-doped fluoride glass like ZBLAN and ZBS glass has also been observed. However, due to their hygroscopic nature their applications are limited [17,18].

The present paper deals with the radiative properties as well as the upconversion mechanisms involved in Er^{3+}-doped tertiary glass with $^4I_{11/2}$ level of Er^{3+} serving as the intermediate state. The effect of temperature on the upconversion luminescence intensity of the two bands (coming from the two close lying levels $^2H_{11/2}$ and $^4S_{3/2}$ to a common lower level $^4I_{15/2}$) as well as on the Stark components ($^4S_{3/2}(1) \rightarrow {}^4I_{15/2}$ and $^4S_{3/2}(2) \rightarrow {}^4I_{15/2}$) of $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition have been monitored and it is noted that the two Stark components of a particular transition may be used as a better temperature sensing device.

2. Experimental details

The doped glass utilized in the present work was synthesized by quenching method. The molar composition of the glass was as follows:

$$(60 - x)Bi_2O_3 + 20Li_2CO_3 + 10BaCO_3 + 10PbO + xEr_2O_3$$

where $x = 0.5$, 1.0, 1.5 and 2.0 mol%.

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doi:10.1016/j.saa.2006.06.024

The well-mixed material (5 g) was melted at 950 °C for 30 min in a platinum crucible. The molten mass was then poured into a stainless steel plate. The obtained glass was annealed to room temperature to minimize the strain and then polished carefully in order to meet the essential requirements. The density and the refractive index of the sample was measured using Archimedes principle and Brewster angle polarization method. The value of density and refractive index for the present glass with 1.0 mol% of Er^{3+} are 7.61 and 2.25 g/cm^3, respectively. The upconversion fluorescence was recorded using a Ti-sapphire laser pumped by 532 nm line of Nd:YVO_4 laser. The fluorescence emitted by the doped glasses were dispersed by the monochromator and then fed into a PMT. Finally, the signal is recorded on a chart recorder in the form of wavelength versus signal intensity.

For the temperature measurement the doped glass was placed in a small furnace with holes in two perpendicular directions for entrance/emergence of NIR laser and fluorescence.

3. Results and discussion

The absorption spectrum of 1.0 mol% doped Bi_2O_3–Li_2O–BaO–PbO tertiary glass in the 400–2000 nm region is shown in Fig. 1. From this figure its clear that there are seven bands observed at 1532, 976, 800, 653, 547, 521, and 488 nm corresponding to the absorptions from the ground state $^4I_{15/2}$ to the excited states $^4I_{13/2}$, $^4I_{11/2}$ $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{7/2}$, respectively. The energies of different bands along with their assignments are given in Table 1. On the basis of these observed absorption bands Judd–Ofelt intensity parameters have been calculated and these were used to determine the various optical properties such as electric dipole line strength, transition probability, radiative lifetime, branching ratio, etc. (Table 2) using the standard relations [5]. A comparison of the intensity parameters for Er^{3+}-doped in different host matrices are given in Table 3. The upconverted luminescence spectrum of 1.0 mol% Er^{3+}-doped tertiary glass under excitation with 800 nm NIR radiation is shown in Fig. 2. Intense green emission bands around 513–538 and 538–547 nm are observed. These bands are due to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions while the weak band at 654 nm is due to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. Blue emission peak was not detected in this case due to the absorption of lattice of the glass in this region. Each of the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions is found to consist of two components at 526, 535 nm and at 547, 556 nm, respectively. The green emission is bright enough and can be seen even by the naked eye at excitation power as low as 50 mW for this glass composition.

Table 1
The absorption energies of different bands along with their assignment for 1 mol% Er-doped BiLiBaPb glass

Assignment	Wavelength of the bands (nm)	Energies of the bands (cm^{-1})
$^4I_{15/2} \rightarrow {}^4I_{13/2}$	1532	6527
$^4I_{15/2} \rightarrow {}^4I_{11/2}$	976	10243
$^4I_{15/2} \rightarrow {}^4I_{9/2}$	800	12500
$^4I_{15/2} \rightarrow {}^4F_{9/2}$	653	15312
$^4I_{15/2} \rightarrow {}^4S_{3/2}$	547	18282
$^4I_{15/2} \rightarrow {}^2H_{11/2}$	521	19194
$^4I_{15/2} \rightarrow {}^4F_{7/2}$	488	20490

In an upconversion mechanism the upconversion intensity I_{up} is proportional to the nth power of the NIR excitation intensity (I_{NIR}), i.e. $I_{up} \propto (I_{NIR})^n$, where n is the number of NIR photons required to be absorbed for emitting the visible photon. A plot of $\log I_{up}$ versus $\log I_{NIR}$ yields a straight line with slope $\sim n$. Fig. 3 shows such a plot for $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions and the slopes corresponding to different transitions are 1.91, 1.80 and 1.63, respectively. This indicates that two photons are involved to populate the $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ levels.

Generally, three excitation processes are supposed to play a vital role in populating the various excited states, viz., multiphoton absorption, excited state absorption (ESA) and energy transfer (ET).

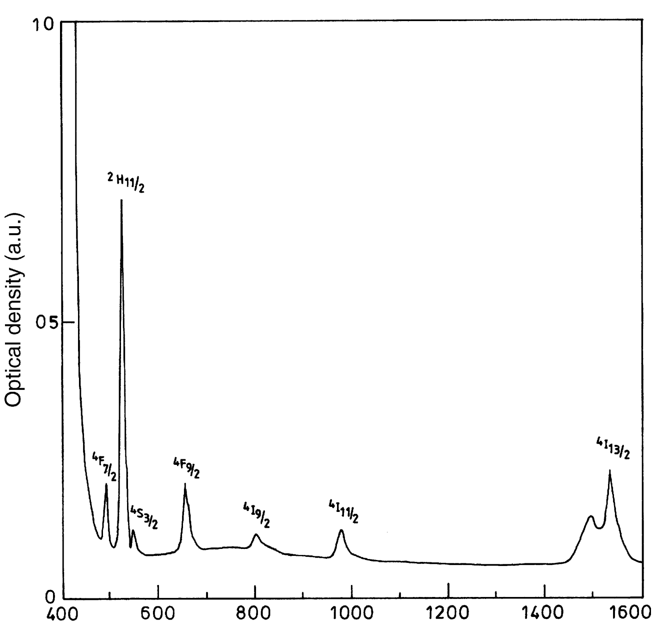

Fig. 1. Absorption Spectra of 1 mol% Er-doped BiLiBaPb tertiary glass.

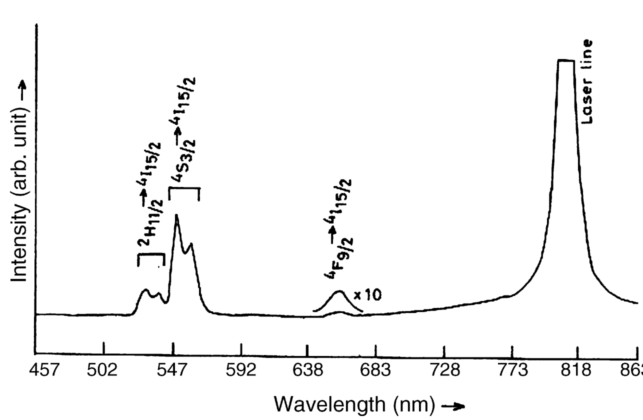

Fig. 2. Upconversion fluorescence spectrum of 1 mol% Er-doped BiLiBaPb tertiary glass under 800 nm excitation.