

Enhancement of luminescence properties in Er^{3+} doped $\text{TeO}_2\text{--Na}_2\text{O--PbX}$ ($\text{X} = \text{O}$ and F) ternary glasses

Kaushal Kumar, S.B. Rai*, D.K. Rai

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221005, India

Received 3 April 2006; accepted 26 April 2006

Abstract

An enhancement of luminescence properties in Er^{3+} doped ternary glasses is observed on the addition of PbO/PbF_2 . The infrared to visible upconversion emission bands are observed at 410, 525, 550 and 658 nm, due to the $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$, $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions respectively, on excitation with 797 nm laser line. A detailed study reveals that the $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition arises due to three step upconversion process while other transitions arise due to two step absorption. On excitation with 532 nm radiation, ultraviolet and violet upconversion bands centered at 380, 404, 410 and 475 nm wavelengths are observed along with one photon luminescence bands at 525, 550, 658 and 843 nm wavelengths. These bands are found due to the $^4\text{G}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^2\text{P}_{3/2} \rightarrow ^4\text{I}_{13/2}$, $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$, $^2\text{P}_{3/2} \rightarrow ^4\text{I}_{11/2}$, $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ transitions, respectively. Though incorporation of PbO and PbF_2 both enhances fluorescence intensities however, PbF_2 content has an important influence on upconversion luminescence emission. The incorporation of PbF_2 enhances the red emission (658 nm) intensity by 1.5 times and the violet emission (410 nm) intensity by 2.0 times. A concentration dependence study of fluorescence reveals the rapid increase in the red ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) emission intensity relative to the green ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) emission with increase in the Er^{3+} ion concentration. This behaviour has been explained in terms of an energy transfer by relaxation between excited ions.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Upconversion; Excited state absorption; Energy transfer; Glass modifier

1. Introduction

With the development of efficient semiconductor lasers emitting in the near infrared regions, the frequency upconversion of infrared-to-visible and UV radiation in rare earth doped materials have been given much attention now a days. There are also several other important applications of these in areas like optical data transmission, display devices, sensors [1–5]. The rare earth doped glasses probably have greater impact than those of crystals because of its several superior properties over crystals such as easy preparation, large RE^{3+} doping, large inhomogeneous line broadening etc [1–25]. The tellurite glass have extensively been investigated due to its advantages such as good transparency in mid infra-red region, relatively lower phonon frequency amongst oxide glasses, high refractive index and good rare-earth solubility [6,7].

The host materials used for rare-earth doping play important role for obtaining highly efficient upconversions. This is

because host materials with low phonon energy can reduce the non-radiative loss due to the multiphonon relaxations and thus achieves strong upconversion luminescence. Efforts have been made on heavy modified glasses (HMO) owing to their lower phonon energies. Another way to achieve this may be by addition of certain heavy metal oxides like BaO , CaO , PbO and their chlorides and fluorides, as network modifiers. They are also found suitable for enhancing the upconversion efficiency and stability of the TeO_2 glass [8–10]. The glasses particularly based on mixed oxide–fluoride systems combine the properties of both, i.e. good optical transparency of fluorides and good chemical and thermal properties associated with oxide glasses [11,12]. So it is expected that the mixed glasses including tellurite and fluoride should bring the interesting properties of the glass. Several studies have been focused on the properties of RE^{3+} -doped fluoride modified tellurite glasses in recent times [12–15].

The motive of the present work is to study the enhancement in luminescence efficiency of Er^{3+} ions in $\text{TeO}_2\text{--Na}_2\text{O--PbX}$ ($\text{X} = \text{O}$ and F) ternary glasses. In our previous work [16], we had synthesized binary glasses $\text{TeO}_2\text{--M}_2\text{O}$ ($\text{M} = \text{Li}$, Na and K) in order to see the effect of alkali modifiers on the fluorescence/upconversion efficiency of Er^{3+} ions. Our observations

* Corresponding author. Tel.: +91 542 230 7308; fax: +91 542 236 889.
E-mail address: sbrai49@yahoo.co.in (S.B. Rai).

show that the fluorescence intensity of Er^{3+} ions increases with different alkali modifiers in the order of $\text{K}_2\text{O} < \text{Li}_2\text{O} < \text{Na}_2\text{O}$. So, it was concluded that Na_2O is the best amongst the other alkali modifiers. Now, to enhance fluorescence intensity further, we have added PbO/PbF_2 in $\text{TeO}_2\text{--Na}_2\text{O}$ binary glass and the results are reported here.

2. Experimental

$\text{TeO}_2\text{--Na}_2\text{O--PbX}$ glasses used in the present work were synthesized by the conventional melting and quenching method. The starting materials were analytical grade 99.9% pure TeO_2 , Na_2CO_3 , PbO , PbF_2 and Er_2O_3 . The compositions were taken within the glass forming region and is expressed in mol% as



where $x = 0.5, 1.0, 1.5$ and 2.0 mol% and $y = 0.0, 4.0, 6.0, 8.0, 10.0, 12.0$ and 15.0 mol%.

The appropriate batches were thoroughly mixed and melted in Pt crucible with continuous stirring in an electric furnace at 900°C for 20 min and then the melt was poured on a copper plate kept at 500°C . The annealing was done in order to minimize the stress in the glasses. The samples were polished carefully to meet the requirement for optical measurements. Emission spectra of these glasses were measured using 0.5 m Spex monochromator equipped with S-20 photo-multiplier tube as a detector. Two excitation wavelengths were used to monitor the upconversion, first 797 nm line from a Ti:Sapphire laser and second 532 nm line from a Nd:YVO₄ laser. The IR spectra were recorded on a FTIR spectrophotometer (Perkin Elmer, RX 1). For comparison of fluorescence intensities amongst the glasses with different rare-earth content, spectra were recorded in the same experimental conditions and at the same excitation power, keeping modifier and former composition same. Absorption intensity of the $^4\text{S}_{3/2} \leftarrow ^4\text{I}_{15/2}$ transition was measured using halogen lamp and monochromator assembly. The absorption coefficient for a particular transition was determined from the following formula:

$$\alpha(\lambda) = 2.303 D_0(\lambda)/\ell \quad \text{and} \quad D_0(\lambda) = \log_{10} I/I_0$$

where ℓ is the sample thickness, I and I_0 are the absorbed and the total incident photon intensity, respectively.

3. Results

The ternary glass system $\text{TeO}_2\text{--Na}_2\text{O--PbO/PbF}_2$ has limited glass forming region, although these glasses have been found better in efficiencies than the binary glass systems. In our observations, the glass transparency decreases as PbO/PbF_2 content reaches beyond the 10.0 mol% limit. All the glass samples below this limit show good optical transparency and homogeneity. The solubility and homogeneity of glass samples were checked from Er^{3+} concentration dependent absorption measurements for $^4\text{S}_{3/2} \leftarrow ^4\text{I}_{15/2}$ transition, shown in Fig. 1. It shows good linearity with the increase in Er^{3+} concentration

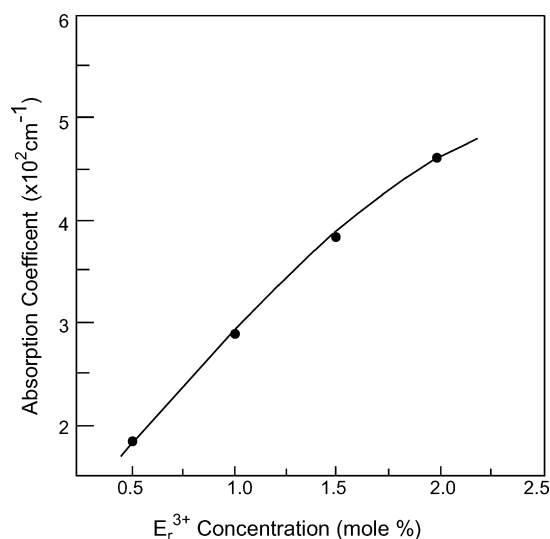


Fig. 1. Absorption coefficient vs. Er^{3+} concentration for the $^4\text{S}_{3/2} \leftarrow ^4\text{I}_{15/2}$ transition in $\text{TeO}_2\text{--Na}_2\text{O--PbO}$ glasses.

from 0.5 to 2.0 mol%. Some deviation from the linear behaviour is found at higher concentrations, which may occur due to saturation effect. The effect of the concentration of Er^{3+} ions on the fluorescence intensity is observed and found that the quenching starts when the Er_2O_3 concentration goes above 1.0 mol% (Fig. 2).

3.1. Physical properties of glass

The different physical properties of the samples are measured as these parameters are important factor in the production of laser glass materials. The glass densities and refractive indices were measured by employing the Archimedes and the Brewster's law, respectively, to evaluate different parameters for glass samples. Table 1 gives results for the $79\text{TeO}_2\text{--}10\text{Na}_2\text{CO}_3\text{--}10\text{PbF}_2\text{--}1\text{Er}_2\text{O}_3$ glass.

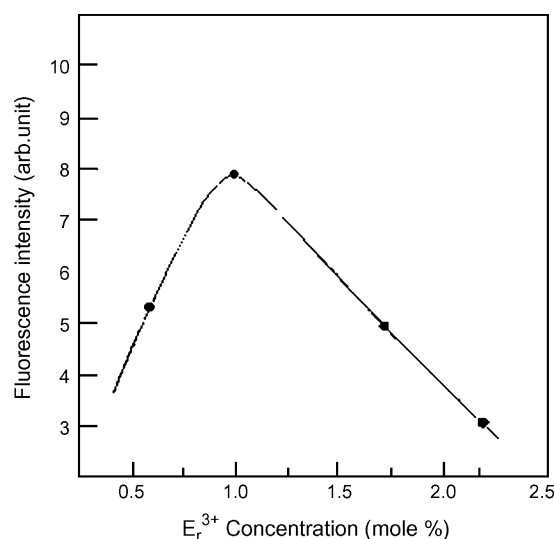


Fig. 2. The fluorescence intensity vs. Er^{3+} concentration graph for the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition in $\text{TeO}_2\text{--Na}_2\text{O--PbO}$ glasses.

Download English Version:

<https://daneshyari.com/en/article/1235896>

Download Persian Version:

<https://daneshyari.com/article/1235896>

[Daneshyari.com](https://daneshyari.com)