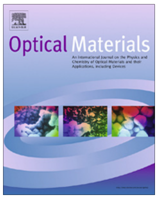
Optical Materials 36 (2013) 221–227

Contents lists available at ScienceDirect

Optical Materials

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



Ho^{3+} ion in a (Ba, La)-tellurite glass: Strong ∼2.0 μm NIR emission and Yb^{3+} aided efficient NIR to vis upconversion

S. Bose, D. Misra, R. Debnath *

School of Laser Science and Engineering, Jadavpur University, Raja S.C. Mullick Road, Kolkata 700 032, India

ARTICLE INFO

Article history:
Received 4 May 2013
Received in revised form 28 August 2013
Accepted 29 August 2013
Available online 26 September 2013

Keywords:
Ho^{3+}-doped (Ba, La)-tellurite glass
NIR emission
Upconversion emission
Crystal field effect
1.972–2.053 μm solid state NIR laser
NIR sensor

ABSTRACT

(Ba, La)-tellurite glasses doped respectively with only Yb^{3+}, only Ho^{3+} and co-doped with (Yb^{3+} + Ho^{3+}) have been prepared and their optical properties are studied. The experimental absorption and the emission spectra of the Ho^{3+} doped glass and calculations of its various Judd–Ofelt parameters, show that the Ho^{3+} ion in the glass has superior absorption and emission transition probabilities and higher emission rates and emission cross-sections. Similar spectroscopic studies on the Yb^{3+}/Ho^{3+} co-doped – glass; on the other hand, demonstrate that the ∼2.0 μm emission of Ho^{3+} of the glass can further be enhanced by phonon assisted non-resonance energy transfer from Yb^{3+}. The derived emission cross-section spectrum of the $^5I_7 \rightarrow {}^5I_8$ transition of Ho^{3+} of the glass and its related gain spectrum, indicate that the glass is prospective for use as a tunable solid state laser medium in this spectral region 1.972–2.053 μm. $Yb^{3+} \rightarrow Ho^{3+}$ energy transfer phenomenon also helps the Ho^{3+} ions of the co-doped glass to exhibit strong green (545 nm) and red (600 nm) upconversion emission upon excitation of its Yb^{3+} ions by 980 nm laser. All the observed superior optical properties of Ho^{3+} ion in the glass have been explained in the light of crystal field effect of the host.

1. Introduction

Rare-earth activated crystals and glasses play vital role in the present day optics, optoelectronics and medical diagnostics [1–16]. They are useful for applications as NIR laser medium [1–8], optical communication [4], optical data storage, light energy upconversion [9–14], bio-labeling [14], solar concentration, solid state lighting [12,13] and anti-Stoke's luminescence cooling [15,16]. There have been a large number of studies on these materials for the last few decades. For applications like solar concentration, fiber amplifier, rare earth doped glasses are more preferred than their crystalline counterpart. Amongst the various factors that determine the optimum optical properties of a rare earth ion in a host, are the phonon structure and crystal field strength of the host. So a host with low phonon energy and higher crystal field strength is most desirable for development of rare earth based efficient optical materials. Of the various oxide glasses tellurite glasses have relatively lower phonon energy and high rare earth dissolution ability [17]. Such glasses are therefore, should function as superior hosts for rare earth incorporation compared to other oxide glasses. One added positive feature in the case of glassy host is that its structure can be modulated by varying its chemical composition. For example, a pure tellurite glass consists [17,21] of structural units like TeO_4 trigonal bipyramids [tbp], TeO_{3+1} distorted trigonal bipyramids [tbp] and some proportion of TeO_3 trigonal pyramids [tp]. These units of the glass are some variant form of the respective units present in the TeO_2 crystal and are connected to each other in the matrix through their oxygen vertices. Addition of a modifier cation generates more and more TeO_3 trigonal pyramids [tp] i.e. more and more nonbridging oxygen in the glass at the cost of (TeO_4 and TeO_{3+1}) units through cleavage of their inter-connectivity bonds [18–20]. The physical and optical properties of the resulting glass also depend on the nature of the modifier cation added. Addition of more and more Na^+ cation to such glass makes the glass more and more fragile while gradual addition of Ba^{2+} to the glass [18–20] causes a gradual decrease of its refractive index and simultaneously makes the glass more and more rigid (Tg increases). It is suggested that in such glass the nonbridging oxygens of the isolated TeO_3 units strongly interact with the modifier Ba^{2+} cations and hence make the glass rigid. Sabadel et al [19] have reported achieving higher Raman gain from a tellurite glass upon adding TiO_2 as modifier oxide. They proposed that the addition of TiO_2 in the network made the structure more polarized. With these knowledge in view and considering the fact that the ionic size of Ba^{2+} is more or less similar to that of any rare earth ion, we expect that in a rare earth containing high barium–tellurite glass the incorporated rare earth ion would also suffer strong interactions with the nonbridging oxygens of the glass

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* Corresponding author. Tel.: +91 33 24146372; fax: +91 33 24146372.
E-mail address: drdebnathr@gmail.com (R. Debnath).

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http://dx.doi.org/10.1016/j.optmat.2013.08.027

which in turn, should influence the optical properties [22] of the former.

Considering the importance of ~2.0 µm emission of Ho^{3+} in developing eye-safe high power NIR fiber laser, in the present work we have prepared three high Ba containing-tellurite glasses doped respectively with Yb^{3+}, Ho^{3+} and ($Ho^{3+} + Yb^{3+}$) and studied their optical properties both by experiment and Judd-Ofelt theory [23,24]. The results show that the Ho^{3+} ions in this glass exhibit superior optical properties compared to those reported in many other hosts.

2. Experimental

Three tellurite glasses of base composition TeO_2 (70–65), ZnO (15–10), MO (20–15); [M = Ba, Sr] and $LaO_{3/2}$ (10–5) doped respectively with Yb^{3+}, Ho^{3+} and ($Ho^{3+} + Yb^{3+}$) were prepared. The Yb^{3+} containing glass had 2 mol% Yb^{3+}, while the only Ho^{3+} and ($Ho^{3+} + Yb^{3+}$) containing glasses had 2 mol% Ho^{3+} and (2 mol% Yb^{3+} + 0.5 mol% Ho^{3+}) respectively. All the batch materials were of AR grade (Sigma Aldrich, E Merck). The glasses were prepared by melting, in each case, approximately 10 g of the respective batch at a temperature 800–850 °C for an hour in a Pt crucible. The glass melt in each case was then cast on a mould and annealed at 300 °C for 24 h. Plate shaped polished samples were then made out of the respective glasses for spectroscopic studies.

The density of the Ho^{3+} containing glass ($D = 5.72$ g/cc) was measured by using Archimedes method. The concentration of the Ho^{3+} in the only Ho^{3+}-glass was calculated to be 4.63×10^{20} ions cm^{-3}. The IR spectrum of the glass was recorded in an IR spectrometer (Shimadzu, Japan). The refractive indices of the glass at different wavelengths, were measured by using an UVISEL Ellipsometer (Horiba Jobin Yvon, model HR 460FUV AGAS). The base glass corrected absorption spectra of the glasses were recorded at 303 K in a UV–VIS–NIR absorption spectrometer (Shimadzu, Japan) by using in each case polished base glass sample of respective similar thickness as the reference.

The fluorescence and the fluorescence-excitation spectra of the glasses were recorded in a UV–VIS–NIR spectrofluorimeter (photon Technology, USA) The upconversion emission spectra of the (Ho^{3+}, Yb^{3+}) co-doped glass were recorded in the same spectrofluorimeter by using a 980 nm diode laser (photon Technology, USA) of variable power (1–1000 mW) as the excitation source. Front surface luminescence measurement technique was adopted in each case of luminescence study. The emission in each case was collected in the perpendicular direction to the direction of excitation and then focused to the detector.

3. Results and discussions

3.1. IR spectrum and structural properties of the glass

Fig. 1 shows the FTIR absorption spectrum of the host glass. It shows strong bands at 754, 695, 615 and 425 cm^{-1}. Out of these bands, the band at ~754 cm^{-1} is known to represent [19] the stretching vibrations of $Te–O^-$ bond in TeO_{3+1} and in $[TeO_3]^-$ trigonal pyramids of the glass.

Relative higher intensity of the ~754 cm^{-1} bands of the spectrum clearly indicates presence of appreciable number of TeO_3 units in the glass each of which has non-bridging oxygen. Since presence of greater number of non-bridging oxygen in a glass increases possibility of greater electrostatic interactions with an incorporated ion of large ionic size, it is expected that the incorporated Yb^{3+} and Ho^{3+} ions of the present glass would experience greater electrostatic interactions with the surroundings. This phenomenon in turn should have some positive influence on the optical properties of the incorporated Ho^{3+} ion.

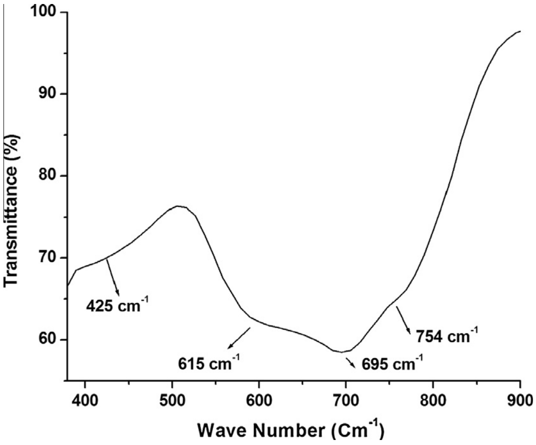

Fig. 1. FTIR spectrum of the glass.

3.2. Absorption of Ho^{3+} of the glass: calculations of its various optical parameters

The VIS–NIR absorption spectrum of the Ho^{3+}-doped glass is shown in Fig. 2. The spectrum of the (Yb^{3+}/Ho^{3+}) Co-doped glass is shown in the inset. The spectrum of the Ho^{3+}-doped glass exhibits its absorption bands peaking respectively at 1953, 1153, 895, 644, 539, 487, 451 and 420 nm. Comparing the energies and the absorption strength of the bands with those of the reported corresponding absorption bands of Ho^{3+} in various crystals and other glasses [1–9] the observed bands in the present case can easily be assigned to the electronic transitions from the $^5I_8$ ground state to the $^5I_7$, $^5I_6$, $^5I_5$, $^5F_5$, ($^5F_4 + {}^5S_2$), $^5F_3$, ($^5F_1 + {}^5G_6$) and $^5G_5$ excited states of the ion respectively.

The absorption spectrum of the (Yb^{3+}, Ho^{3+}) co-doped glass (Inset of Fig. 2) shows as expected, in addition to the above mentioned Ho^{3+} absorption bands a strong absorption band of Yb^{3+} ion (~978 nm) due its $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition.

The electric dipole transitions between the $4f^n$ states of a rare earth ion in its free state are parity forbidden. But such transitions become partially allowed when the ion is incorporated in a host. This happens because of noncentrosymmetric interactions of the

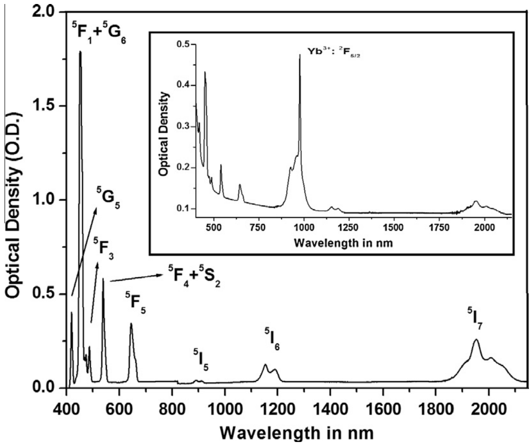

Fig. 2. Base glass corrected absorption spectrum of Ho^{3+} in the Tellurite glass. (Sample-thickness $d = 1.96$ mm); Inset: Absorption spectrum of the (Yb^{3+}, Ho^{3+}) co-doped glass.