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Spectroscopic studies on Yb^{3+}-doped tungsten-tellurite glasses for laser applications

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ABSTRACT

Tungsten tellurite glasses (TeO_2-WO_3-ZrO_2) doped with various concentrations of Yb^{3+} ions have been prepared by the conventional melt-quenching method and systematically studied their spectroscopic and laser properties. The spectroscopic properties and some of the laser parameters have been evaluated from the measured absorption and emission spectra. Emission cross-sections evaluated from the McCumber and the Fuchtbauer-Ladenburg methods are found to be in good agreement. The absorption and emission cross-sections are found to be in the range of 2.78–1.30 ($\times 10^{-20}$ cm^2) and 3.64–1.83 ($\times 10^{-20}$ cm^2), respectively, when Yb^{3+} ions concentration increases from 0.01 to 3.0 mol%. A significant change in luminescence spectral profile for higher concentration (> 0.1 mol%) of Yb^{3+} ions has been explained as due to reabsorption effects. An initial increase of lifetime for the $^2F_{5/2}$ level up to 0.5 mol% and decrease thereafter for higher concentrations (> 0.5 mol%) of Yb^{3+} ions has been explained with a suitable mechanism. The results of spectroscopic and laser parameters indicate that tungsten-tellurite glasses have potential applications as gain media for lasers and optical amplifiers.

1. Introduction

In recent years, an increasing importance of trivalent rare-earth (RE^{3+})-doped glasses as possible lasing materials have created a significant interest in the study of optical and spectroscopic properties for their applications in glass [1], fiber [2] and waveguide lasers [3]. Among the RE^{3+} ions, ytterbium (Yb^{3+}) ion has attracted a great interest for its excellent properties such as (a) low non-radiative decay rate, (b) simple electronic structure, i.e., the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state, which can avoid non-radiative processes such as excited-state absorption and upconversion, (c) very good sensitizer for other 980 nm pumped RE^{3+} ions [4] and (d) broad absorption and emission bandwidths. These properties can be utilized for the development of high-power (> 50 W cm^{-2}), high-efficiency (> 50%) and ultrafast laser emission [5]. Very recently, the Yb^{3+}-doped glass-ceramics have been utilized for laser cooling of solid state as they exhibit lower maximum phonon energy, higher photoluminescence quantum efficiency and lower background absorption compared to their parent glasses [6,7].

Among different types of glass hosts such as borate, phosphate, silicate and tellurite, the latter have many advantages such as (i) a wider transmission range (0.35–5 μm) compared to silicate glasses (0.2–3 μm), (ii) better corrosion resistance than fluoride glasses [8], (iii) high linear refractive indices (1.8–2.3) and (iv) lower phonon energy among oxide glass hosts (800 cm^{-1}), and (v) high solubility of dopant RE^{3+} ions [9]. The Yb^{3+}-doped tellurite glasses have better spectroscopic properties such as large absorption and emission cross-sections as well as wide fluorescence effective line widths compared to other oxide glasses, and are considered as ideal host materials for fiber lasers and amplifiers [10]. The higher value of linear and non-linear refractive indices and the lower value of phonon energy make the tellurite glasses better suitable for non-linear laser and amplifier applications [7,11].

Tellurium dioxide (TeO_2) is a conditional glass former, the TeO_2 alone cannot form a glass, unlike other glass systems such as silicate and phosphate, because of lone pair of electrons in one of the equatorial positions of the [TeO_4] polyhedron [12,13]. A metal oxide or a transition metal oxide is necessary as an intermediate network modifier to

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form tellurite glasses [14]. Addition of network modifier oxides such as WO_3 and ZrO_2 increases the glass forming ability of the TeO_2 [14,15]. The physical and optical properties of undoped glasses [16] and visible upconversion and broadband near-infrared luminescence properties of Er^{3+}-doped tellurite-tungsten glasses [17] were reported in the literature. However, in the present study spectroscopic and laser properties of Yb^{3+} ions in these glasses are investigated to check their suitability for laser and optical amplifier applications.

In this paper, the effect of Yb^{3+} ions concentration on spectroscopic properties of Yb^{3+}-doped tungsten-tellurite glasses has been investigated by considering the reabsorption effects. From the measured absorption spectra, emission and laser performance properties are evaluated. The emission cross-sections, evaluated from McCumber and Futchbauer-Landenburg methods, have been compared to those of other reported Yb^{3+}-doped glasses. The better emission and laser properties show that these glasses are promising candidates as gain medium for high power solid state laser applications [18].

2. Experimental

The starting chemicals of TeO_2, WO_3, ZrO_2 and Yb_2O_3 with a purity of 99.99% (Aldrich, USA) were weighed in an electronic balance, with an accuracy of ± 0.0001, according to the molar composition of $70TeO_2$-(25-x)WO_3-$5ZrO_2$-xYb_2O_3, where x = 0.01, 0.05, 0.1, 0.5, 1.0, 2.0 and 3.0 mol% and hereafter referred as TWZYbx. A 30 g batch was fairly mixed in agate mortar for getting a homogeneous mixture. The well-mixed powder was taken in a platinum crucible and melted in the temperature range of 940–980 °C (± 1 °C), depending on the Yb^{3+} concentration, for 50 min using a high temperature furnace. Glasses were suddenly quenched on preheated brass mold at 320 °C. Annealing was done at 320 °C for 16 h and then allowed to cool down to room temperature (RT) in steps of 20 °C per hour. Finally, the samples were cut and polished with a size of 20 × 20 × 2.15 mm^3 for optical and spectroscopic measurements.

Densities of TWZYb glasses were measured by Archimedes' method using water as an immersion liquid with an accuracy of ± 0.0001 g. The refractive indices were measured by Brewster's angle method using diode laser (λ = 650 nm) with a precision of 0.01. Optical absorption spectra were measured with a Perkin Elmer Lambda-950 spectrometer in the wavelength range of 870–1040 nm with a spectral resolution of 1.0 nm. The near infrared emission spectra were measured in the wavelength range of 900–1070 nm with 0.5 nm spectral interval by exciting the samples with 910 nm wavelength from a Ti: sapphire laser (Spectra Physics 3900S) pumped by a 10 W cw Ar^+ laser (Spectra Physics). The decay curves for the $^2F_{5/2}$ level were measured by exciting with a 950 nm laser from optical parametric oscillator (EKSPLA/NT342/3/UVE) and the signal was detected with the help of a digital oscilloscope (Tekronix 2430). All the measurements were made at RT.

3. Results and discussion

3.1. Absorption and emission cross-sections

Densities, refractive indices and nominal Yb-Yb inter-atomic distances of TWZYb glasses are collected in Table 1. As can be seen, the density increases from 4.788 to 5.634 with increase in Yb^{3+}-ion concentration from 0.01 to 3.0 mol%. This can be explained by considering the molecular weight of Yb_2O_3 (394.08 g/mol), which is higher than TeO_2 (159.6 g/mol), WO_3 (231.84 g/mol) and ZrO_2 (123.22 g/mol). With the gradual replacement of WO_3 by Yb_2O_3, the average molecular weight increases which results in higher densities. Decrease in inter-atomic distances also supports higher density of the glasses at higher Yb^{3+} concentrations. The values of refractive index of the TWZYb glasses are found to be in the range of 2.01–2.22 at 650 nm, which are found to be higher than those of TeO_2-ZnO (2.02–2.10 at 643.8 nm) [19] and TeO_2-$LiNbO_3$ (2.06–2.11 at 632.8 nm) [20]. The higher refractive index of TWZYb glasses might find application in optoelectronic devices [7,11,21].

Table 1
The glass label, molar composition and their physical properties (density (d ± 0.1%, g/cm^3)), Yb^{3+} ions concentration (C ± 0.1%, × 10^{20} ions/cm^3), nominal Yb^{3+}-Yb^{3+} distance (r ± 1%, Å) and refractive index (n ± 1%, at 650 nm) of Yb^{3+}-doped tungsten tellurite glasses.

Label	Glass composition	d	C	r_i	n
TWZYb001	$70TeO_2$ + 24.99 WO_3 + $5ZrO_2$ + $0.01Yb_2O_3$	4.7882	0.0336	66.75	2.01
TWZYb005	$70TeO_2$ + 24.05 WO_3 + $5ZrO_2$ + $0.05Yb_2O_3$	4.8105	0.1661	39.18	2.06
TWZYb01	$70TeO_2$ + 24.9 WO_3 + $5ZrO_2$ + $0.1Yb_2O_3$	4.8248	0.3318	31.11	2.11
TWZYb05	$70TeO_2$ + 24.5 WO_3 + $5ZrO_2$ + $0.5Yb_2O_3$	4.8376	1.6487	18.23	2.15
TWZYb10	$70TeO_2$ + 24 WO_3 + $5ZrO_2$ + $1.0Yb_2O_3$	4.8651	3.3029	14.46	2.18
TWZYb20	$70TeO_2$ + 23 WO_3 + $5ZrO_2$ + $2.0Yb_2O_3$	4.9625	6.6759	11.44	2.20
TWZYb30	$70TeO_2$ + 22 WO_3 + $5ZrO_2$ + $3.0Yb_2O_3$	5.6342	11.2668	9.61	2.22

The potential laser performance parameters of Yb^{3+}-doped glasses can be evaluated from the absorption and emission spectra [18]. The absorption spectra of present glass samples for different Yb^{3+}-concentrations in the NIR region are shown in Fig. 1(a). All the TWZYb samples show peak absorption centered at 977 nm corresponding to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. The absorption coefficient of the 977 nm peak increases with increasing Yb^{3+} concentration and is shown in inset of Fig. 1(a). A linear dependence in intensity confirms the incorporation of the Yb^{3+}-ions into the TWZ glass matrix [22]. Owing to positional disorder, the RE^{3+} luminescence centers in TWZ matrix are characterized by a marginal change in spectroscopic parameters resulting in small inhomogeneous broadening of spectral lines [see Fig. 1(a)]. The local environment of Yb^{3+} centers in the TWZ glass network also consists of O^{2-} anions with statistically-distributed structural parameters (rare earth ion oxygen inter-atomic distances and coordination numbers) in the first coordination shell (positional disorder) that is seen in the inhomogeneous broadening of the optical absorption and emission bands. Moreover, a glass network is characterized by a short-range order which in the second (cationic) coordination sphere around the luminescence centers leads to the further inhomogeneous broadening of spectral lines [23]. The Stark splitting for the ground and excited state manifolds of Yb^{3+} ions is shown in Fig. 1(b). Moreover, some of the important spectroscopic parameters are determined by using either the reciprocity method [24] or the Futchbauer-Landenburg formula [25]. On the basis of the reciprocity method described by McCumber [24], the emission cross-section can be obtained from measured absorption spectrum. The absorption cross-section for the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ions can be obtained by using the following Eqs. [26,27],

$$\alpha = \frac{2.303 \log\left(\frac{I_0}{I}\right)}{l} \tag{1}$$

$$\sigma_{abs} = \frac{\alpha}{N} \tag{2}$$

where N is the Yb^{3+} ion concentration (in ions/cm^3) and l is the thickness (in cm) of the glass sample. The emission cross-section can be calculated using the reciprocity method described by McCumber [24] from the measured absorption cross-section (σ_{abs}),

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda)\frac{Z_l}{Z_u}\exp\left(\frac{E_{ZL} - hc\lambda^{-1}}{KT}\right) \tag{3}$$

where Z_i and Z_u are the partition functions of the lower and upper levels, respectively, and E_{ZL} is the zero line energy, which is equal to the energy gap between the lowest Stark components of the upper and