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Luminescent properties of Tb^{3+}- doped TeO_2-WO_3-GeO_2 glasses for green laser applications

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ABSTRACT

Different concentrations of Tb^{3+} -doped oxyfluoro tellurite (TWGTb) glasses were prepared by conventional melt quenching technique and characterized for green laser applications. The Judd-Ofelt theory was applied to evaluate various spectroscopic and radiative parameters. The TWGTb glasses exhibit $^5D_3 \rightarrow {}^7F_{5\text{-}3}$ and $^5D_4 \rightarrow {}^7F_{6\text{-}0}$ transitions when excited at 316 nm radiation. The variation of intensity of $^5D_4 \rightarrow {}^7F_5$ (Green) and $^5D_3 \rightarrow {}^7F_4$ (Blue) transitions and the green to blue (I_G/I_B) intensity ratios were studied as a function of Tb^{3+} ions concentration. The laser characteristic parameters such as effective bandwidth ($\Delta\lambda_{eff}$), stimulated emission cross-section (σ_e), gain bandwidth ($\sigma_e \times \Delta\lambda_{eff}$) and optical gain ($\sigma_e \times \tau_R$) were determined using the three phenomenological Judd-Ofelt intensity parameters. The fluorescence decay profiles of $^5D_4$ metastable level exhibit single-exponential nature for all the samples. Based on the experimental results we suggest that the 1.0 mol% of Tb^{3+} -doped TWGTb glass could be a suitable laser host material to emit intense green luminescence at 545 nm.

1. Introduction

Glasses are the most attractive host materials for optical devices such as lasers, fiber amplifiers, sensors etc. They have been used as promising host materials for rare earth (RE) ions due to their excellent properties such as wide transparency range, low propagation losses and isotropic refractive index. The RE ions doped glasses are of interest in developing solid state lasers, optical amplifiers, waveguides, scintillators, white light emitting diodes [1,2]. The tellurite based glasses are more advisable in designing new class of optical devices to meet the requirement of current technologies due to their low melting temperature, considerably high refractive index, optical non-linearity, enhanced chemical durability and transmittance in visible and near infrared spectral regions [3,4].

Trivalent terbium (Tb^{3+}) ions with $4f^8$ configuration emit intense and strong green emission through $^5D_4 \rightarrow {}^7F_5$ transition (540–550 nm) which is more sensitive to human eye. The Tb^{3+} ions are the most important activators for strong green emission, because the Tb^{3+} ions provide four level laser systems with relatively low pump power for achieving population inversion between $^5D_4$ and $^7F_5$ levels. The first green laser action at 547 nm was demonstrated using Tb^{3+} -doped chelate in solution at room temperature [5]. The higher magnitude of experimental branching ratio of ≥ 0.50 of $^5D_4 \rightarrow {}^7F_5$ transition makes Tb^{3+} -doped material a promising host for green laser applications [6]. In the present work we reported the optical properties of oxyfluoro tellurite glasses containing different concentrations of Tb^{3+} ions. The Judd-Ofelt theory [7,8] has been applied to determine different spectroscopic and laser characteristic parameters. The importance of green ($^5D_4 \rightarrow {}^7F_5$) to blue ($^5D_3 \rightarrow {}^7F_4$) intensity ratio was described in detail. The applicability of studied glasses as green laser host materials was explored.

2. Experimental

2.1. Materials and method of preparation

In order to study the concentration dependent luminescence properties, a series of glasses of chemical composition (85-*x*) TeO_2 + 5 WO_3 + 10 GeO_2 + *x* TbF_3, where $x = 0$, 0.1, 0.5, 1.0 and 2.0 mol%, were prepared by conventional melt quenching technique using high pure TeO_2 ($\geq$99.5%), WO_3 ($\geq$99%), GeO_2 (99.999%) and TbF_3 (99.9%). About 20 g batches of homogeneous mixture of starting materials were melted in alumina crucible at 875 °C for 40 min. The melt was air-quenched and annealed at 300 °C for 10 h to remove thermal

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Table 1
Different physical and optical parameters of TWGTb glasses.

S. No.	Parameter	TWGTb01	TWGTb05	TWGTb10	TWGTb20
1	Sample thickness, l (± 0.01 cm)	0.15	0.15	0.15	0.15
2	Density, ρ (± 0.001 g/cm^3)	5.167	5.195	5.235	5.260
3	Refractive index, n (± 0.001)	2.457	2.461	2.463	2.465
4	Tb^{3+} concentration ((± 0.03 × 10^{-20} ions/cm^3)	0.20	0.99	1.99	3.98
5	Reflection losses, R (± 0.1%)	~18.0	~18.0	~18.0	~18.0
6	Inter-ionic distance, r_i (± 0.01 nm)	3.70	2.16	1.71	1.36
7	Molar volume, V_m ((± 0.02 cm^3)	30.53	30.41	30.24	30.20

strains produced during the quenching process. For convenience, the prepared samples were named as TWG00, TWGTb01, TWGTb05, TWGTb10 and TWGTb20 glasses according to Tb^{3+} concentration x = 0, 0.1, 0.5, 1.0 and 2.0 mol%, respectively.

2.2. Physical and optical characterization

The glass samples were polished for optical quality and used for various characterizations. Applying the Archimedean principle, the densities of prepared samples were determined with distilled water as an immersion liquid. The refractive indices were obtained using Abbes refractometer with sodium vapour lamp as a source of light and 1-bromonaphthalene as an adhesive material. The Fourier transform infrared (FTIR) spectral results show that the TWG00 glass is a suitable candidate for solid state laser due to its low phonon energy (~721 cm^{-1}) and absence of H_2O content [9]. The scanning electron microscope and energy dispersive X-ray spectrum (SEM-EDS) results of TWG00 glass (not shown) provide 18.89 atm% of oxygen, 3.57 atm% of fluorine, 5.28 atm% of tungsten, 5.09 atm% of germanium and 67.17 atm% of tellurium confirming their presence.

Some of the important parameters are summarized in Table 1. As can seen Table 1, it is clear that with increase of Tb^{3+} ions concentration, the values of density and refractive index increase, while the inter-ionic distance and molar volume decrease. The decrease in molar volume supports the increased values of density with increase of Tb3+ ions concentration. The reflection losses [R = (n-1/n+1)^2] are found to be ~18.0% indicating most of the incident light energy will be transmitted through the studied glasses. The optical absorption measurements were carried out on Perkin Elmer Lambda 950 spectrophotometer. The photoluminescence (PL) excitation, emission and fluorescence lifetime measurements were recorded on a Jobin YVON Fluorolog-3 spectrofluorimeter. All the measurements were carried out at room temperature only.

3. Results and discussion

3.1. Absorption spectra and intensity parameters

The optical absorption spectra of TWGTb glasses contain five absorption bands peaked at about 514, 1800, 1895, 1945 and 2192 nm and they are assigned to $^7F_6 \rightarrow {}^5D_4$, $^7F_6 \rightarrow {}^7F_0$, $^7F_6 \rightarrow {}^7F_1$, $^7F_6 \rightarrow {}^7F_2$ and $^7F_6 \rightarrow {}^7F_3$ transitions, respectively [10]. The intensity of absorption bands increase with increase of Tb^{3+} concentration without any remarkable change in their peak positions showing the uniform distribution of Tb^{3+} ions in TWGTb glasses. For reference, the optical absorption spectrum of TWGTb10 glass is shown in Fig. 1. The inset of Fig. 1 indicates the variation of intensity of $^7F_6 \rightarrow {}^7F_1$ (1895 nm) transitions as a function of Tb^{3+} concentration.

The intensities of observed absorption bands have been evaluated using integrated area under the absorption bands and expressed in terms of experimental oscillator strengths (f_{exp}) [11].

$$f_{exp} = 4.2 \times 10^{-9} \int_{\nu_1}^{\nu_2} \varepsilon(\nu)\, d\nu \quad (1)$$

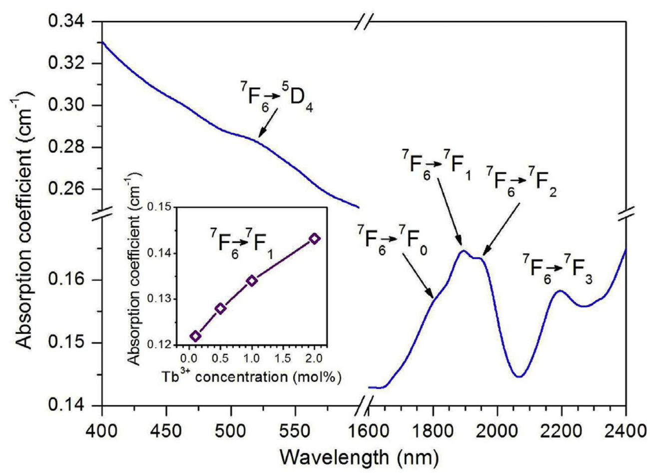

Fig. 1. Optical absorption spectrum of TWGTb10 glass. Inset shows the variation of intensity of $^7F_6 \rightarrow {}^7F_1$ (1895 nm) transitions as a function of Tb^{3+} concentration.

where ν_1 and ν_2 represent the first and end positions of a particular absorption band. The parameter $\varepsilon(\nu)$ is the molar absorption coefficient of an absorption band at energy ν (cm^{-1}) and it is given as

$$\varepsilon(\nu) = \frac{1}{N.\ l} \log\left(\frac{I_0}{I}\right) \quad (2)$$

where N is the concentration of Tb^{3+} ions (in mol/l), l is the sample thickness. The term log (I_0/I) represents the optical density. The calculated oscillator strengths (f_{cal}) and hence the J-O intensity parameters, Ω_λ (λ = 2, 4 and 6) have been determined by least-square fit method. The oscillator strength of a transition between an initial energy level aJ and a final energy level bJ' is given by

$$f_{cal}(aJ \rightarrow bJ') = \frac{8\pi^2 m c \nu}{3h(2J+1)} \left[\frac{(n^2+2)^2}{9n} .\ S_{ed} + n\ .\ S_{md}\right] \quad (3)$$

where m represents mass of an electron, c is the speed of light, n is the refractive index of the medium, h is the Plank's constant and $(2J + 1)$ is the degeneracy of ground energy state. The terms S_{ed} and S_{md} represent the electric and magnetic dipole linestrengths and they can be defined as follows.

$$S_{ed}(aJ \rightarrow bJ') = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda |\langle aJ \| U^\lambda \| bJ' \rangle|^2 \quad (4)$$

$$S_{md}(aJ \rightarrow bJ') = \frac{e^2h^2}{16\pi^2m^2c^2} |\langle aJ \| L + 2S \| bJ' \rangle|^2 \quad (5)$$

where 'e' is the charge of an electron. The small root mean square deviation (δ_{rms}) of ± 0.10 × 10^{-6} shows the good fit between f_{exp} and f_{cal} and the best set of three phenomenological J-O (Ω_λ) intensity parameters. The observed values of f_{exp} and f_{cal} are summarized in Table 2. In case of TWGTb10 glass, the J-O intensity parameters are determined as $\Omega_2 = 5.34 \times 10^{-20}$ cm^2, $\Omega_4 = 4.85 \times 10^{-20}$ cm^2 and $\Omega_6 = 1.22 \times 10^{-20}$ cm^2. These parameters follow $\Omega_2 > \Omega_4 > \Omega_6$