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Thermal and spectroscopic properties of Tm^{3+} doped TZPPN transparent glass laser material

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ABSTRACT

In this work a transparent bulk glass with the mol% composition $76TeO_2 \cdot 10ZnO \cdot 9.0PbO \cdot 1.0PbF_2 \cdot 3.0Na_2O$ doped with Tm^{3+} has been synthesized. Results of differential thermal analysis (DTA) indicate a high thermal stability and low tendency to crystallization of this glass. The refractive indices at different wavelengths, the Urbach energy, the optical energy gap, the Sellmeier gap energy and the dispersion energy have been estimated. Spectroscopic quality factor of Tm^{3+} was evaluated from optical absorption spectra. Electric and magnetic dipole transition probabilities, branching ratios, and radiative lifetimes of several excited states of Tm^{3+} have been predicted using calculated intensity Judd–Ofelt parameters. The classical McCumber theory has been applied to evaluate the emission cross-sections for $^3F_4 \rightarrow {}^3H_6$ transition around 1.8 μm. This study shows that TZPPN glass doped with Tm^{3+} ions is a promising candidate for laser applications.

1. Introduction

Considerable scientific effort has been devoted to the investigation of 2 μm *eye-safe* solid-state lasers due to their potential use in atmospheric and space applications, coherent Doppler velocimetry, gas detection, atmospheric wind sensors for full-scale earth observation satellites and medical equipment [1,2]. As the transition of $^3F_4 \rightarrow {}^3H_6$ of trivalent thulium can generate radiations near 1.8 μm, Tm^{3+}-doped laser materials have been widely studied. In addition, the phonon assisted energy transfer process called 'cross-relaxation' (CR: $^3H_4$, $^3H_6 \rightarrow {}^3F_4$, $^3F_4$) makes it possible to obtain two ions in the upper laser level for each pumping photon, which enhances the near 1.8 μm emission and is one of the main reasons for utilizing thulium as an active ion for NIR applications [3–5]. An important feature of Tm^{3+} as an emitter in a host glass is the possibility of continuous tuning in the 1.8–2 μm region depending on the host matrix, thanks to its wide emission peak.

To get efficient Tm^{3+}-doped 1.8 μm optical fiber laser, some factors should be considered for the glass host, such as the highest phonon energy, environmental durability, fiber drawing ability, rare-earth ion solubility and the purity of the starting materials [6]. Oxyhalide-tellurite glasses are well suitable as a host material for infrared lasing due to its high rare earth (RE) ion solubility [6–9]. The composition $75TeO_2$–$10ZnO$–$4.5PbO$–$0.5PbF_2$–$9.4Nb_2O_5$ doped with $0.6Tm_2O_3$ was patented a thermal stability factor of $\Delta T = 104$ °C (the difference between crystallization and glass transition temperature) [10]. Lead(II) oxide (PbO) decreases glass stability: binary TeO_2–PbO glass has thermal stability ($\Delta T = 50$ °C) less than TeO_2–Na_2O ($\Delta T = 120$ °C). By adding intermediate glass structure as Nb_2O_5, Pb–O–Pb linkages were created and the trigonal bipyramid, TeO_4 (tbp) changes to trigonal pyramid TeO_3 (tp) [11]. The goal of the present paper is to study the thermal stability and spectroscopic properties of Tm_2O_3 doped $76TeO_2 \cdot 10ZnO \cdot 9.0PbO \cdot 1.0PbF_2 \cdot 3.0Na_2O$ glass for use as potential optical glasses for laser host or fiber amplifier, depending on the spectroscopic parameters. Hence, the intensity parameters Ω_t ($t = 2, 4, 6$), the electric dipole type transition probabilities (A_{ed}), magnetic dipole type transition probabilities (A_{md}), branching ratios (β) and the radiative lifetimes (τ) of the energy levels of prepared glass were calculated by using the Judd–Ofelt theory, and the emission cross-sections are determined using the McCumber theory.

2. Experiments

A high homogeneity glass with the composition (in mol%) $76TeO_2 \cdot 10ZnO \cdot 9.0PbO \cdot 1.0PbF_2 \cdot 3.0Na_2O \cdot 1.0Tm_2O_3$, denoted as Tm^{3+} doped TZPPN glass, was prepared by the melt quenching technique. The powder mixture was given and heated in a covered gold crucible in a furnace at 850 °C for 30 min and the melt was stirred from time to time. The highly viscous melt was cast at 800 °C on a graphite mold and subsequently, the sample was transferred to an annealing furnace and kept

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for 2 h at 270 °C. Finally, the furnace was switched off and the glass sample was allowed to cool.

All subsequent measurements were carried out at room temperature. The density ρ of the glass sample was measured by a helium pycnometer (AccuPyc 1330 Pycnometer) with an accuracy of $\pm 0.0003\%$. The glass transition temperature (T_g), the softening temperature (T_s), the onset temperature of crystallization (T_x), the peak temperature of crystallization (T_p) and the liquidus temperature were obtained by using differential thermal analysis (Shimadzu DTA 50). The absorption spectrum of the glass was measured at wavelengths in the range from 200 to 3200 nm, using a Shimadzu 3101PC spectrophotometer UV/VIS/NIR with optical path lengths of 1 and 11 mm. From the glassy sample, a prism with the size $30\times15\times15$ mm^3 was cut. The prism was ground and polished using water as liquid component. The prism was used to measure the linear refractive indices at 643.8, 589.3, 546.1, 479.98 and 435.8 nm wavelengths.

3. Result and discussion

3.1. Density, thermal stability, Urbach and optical energy gap

The measured density of Tm^{3+}-doped TZPPN glass sample is 5.798 ± 0.001 g/cm^3. The concentration of Tm^{3+} ions can be calculated by;

$$N = [RE\ \text{mol}\%]\frac{\rho}{M}2A_v \tag{1}$$

where ρ is the glass density, [*RE* mol%] is the molar percent concentration of rare-earth oxide based on the glass molar, M is the molecular weight of Tm:TZPPN glass and A_v is the Avogadro's number. The concentration of Tm^{3+}-doped TZPPN glass is $N=4.427\times10^{26}$ ions/m^3.

The DTA profile of the Tm^{3+} doped TZPPN glass is shown in Fig. 1. The glass stability parameter ΔT, is important for glass technology and is considered as a measure of the degree of disorder in glassy state. It is attributed to the stability against crystallization and can be determined from the characteristic temperatures T_g, T_s, T_x, and T_m from the DTA profile using the following equation: $\Delta T = T_x - T_g$.

The temperatures are $T_g=288$ °C, $T_s=323$ °C, $T_x=452$ °C and $T_m=551$ °C (see Table 1a). For the studied glass, the glass stability is $\Delta T=164$ °C. The prepared glass has a fairly low tendency towards crystallization. The value ΔT of our prepared glass is higher than other tellurite glasses [6–10] used in optical applications.

The optical absorption coefficient, $\alpha(\nu)$, at wavelengths near the optical band edge in many amorphous semiconductor shows an exponential

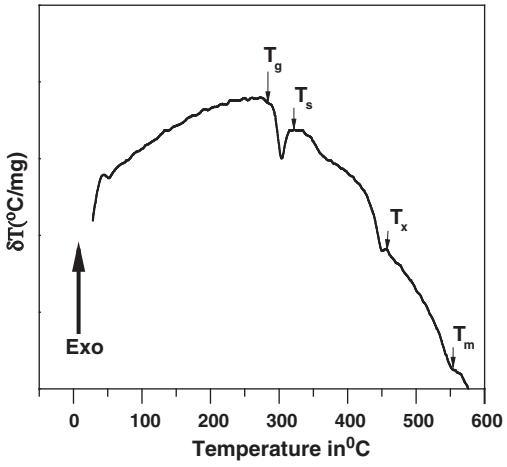

Fig. 1. DTA profile of the TZPPN glass doped with Tm^{3+} ions.

Table 1a
The physical parameters obtained for Tm^{3+} in TZPPN glass.

Parameters	
Density ρ (in g·cm^{-3})	5.798
Glass transition temperature T_g (in °C)	288
Softening temperature T_s (in °C)	323
Onset crystallization temperature T_x (in °C)	452
$S=T_x-T_g$ (in °C)	164
Melting temperature T_m (in °C)	551
Abbe number	17.9
Band gap E_g (in eV)	2.5
Urbach energy E_e (in eV)	0.043
Sellmeier energy gap E_s (in eV)	6.581
Dispersion energy E_d (in eV)	20.484

dependence on the photon energy, $h\nu$, and obeys an empirical relation due to Urbach [12],

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_e) \tag{2}$$

where ν is the frequency of radiation; α_0 is a constant; and E_e is related to the width of the tail of localized states in the band gap.

The physical origin of E_e can be attributed to the phonon-assisted indirect electronic transitions. Tauc [13] reported that the exponential variation of α with $h\nu$ is due to transitions between localized states and will vary from sample to sample, whereas Davis and Mott [14] assumed that the value of E_e will be approximately the same for most amorphous semiconductors. In the studied glass, the values of Urbach energy have been calculated by taking the reciprocals of slope of the linear part of the $\ln\alpha(\nu)$ vs. $h\nu$ curve in the lower photon energy regions (see Fig. 2a). The as calculated value is 0.043 eV which indicates the homogeneity of the glass.

The absorption coefficient for indirect transition is as follows [15]:

$$\alpha(\omega) = \frac{A\left(\hbar\omega - E_{opt}\right)^r}{\hbar\omega} \tag{3}$$

where $\alpha(\omega)$ is the absorption coefficient; A is a constant; E_{opt} is the optical band edge and $\hbar\omega$ is the photon energy of the incident radiation. r is an index which can be assumed to possess values of 1/2, 3/2, 2 and 3, depending on the nature of the transition. The optical band edge is obtained by extrapolating from the linear range in the plots of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ as shown in Fig 2b. The value of the optical energy gap for the studied glass equals 2.5 eV. McSwain et al. [16] suggested that the shift from higher to lower energies or a change in the absorption band characteristics can be related to a transition to nonbridging oxygens which bind excited electrons less tightly than bridging oxygens. Therefore, the optical energy gap of the present glass in Table 1a is in good agreement with oxychloride-tellurite glasses [17]. Sahar et al. [17] reported that the value of the optical energy gap in $TeO_2/ZnO/ZnCl_2$ glasses which is around 2.5 eV could be used for a longer wavelength application. Our present glass has the similar value of the optical energy gap and hence provides a possibility that this glass may be applicable in the optical device components.

The linear refractive index depends on the radiation wavelength and is given by the Wemple relation [18].

$$\frac{1}{n^2(E)-1} = \frac{E_s}{E_d} - \frac{E^2}{E_s E_d} \tag{4}$$

where E_s is the so-called Sellmeier gap energy and E_d is the dispersion energy. Fig. 3 shows a plot of $1/(n^2(E)-1)$ versus E^2 for the prepared glass. From the linear regression, values of E_s and E_d of 20.484 eV and 6.581 eV, respectively, have been obtained.