Thulium-doped Sodium Zinc Molybdenum Tellurite Glasses

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Abstract. Researchers propose and demonstrate Sodium Zinc Molybdenum Tellurite glasses (Na2O-ZnO-MoO3-TeO2 or NZMT) as suitable hosts for rare earth ion thulium (Tm3+) operating at 1.47 μm wavelength. The density, the refractive indices, the optical absorption have been measured. The Judd-Ofelt intensity parameters Ω2, Ω4, Ω6, the radiative rates, the branching ratios, and the fluorescence lifetimes were calculated according to Judd–Ofelt theory. Intense 1.47 μm fluorescence was observed in these glass systems under 973-nm excitation. The bandwidth of the 3H4 → 3F4 transition in NZMT glass is ~100 nm, which is significantly larger than that of fluoride glasses but less than that in KBG glasses. Measured fluorescence lifetimes of the 3F4→ 3H6 and 3H4→ 3F4 decay at room temperature were 2.842 and 0.323 ms respectively, and their quantum efficiencies were approximately 100% and 88.9%. From the data, it appears that Tm3+ doped NZMT glasses are promising materials for waveguide lasers and amplifiers operation at 1.40-1.52 μm wavelength range.

Introduction

Tellurite glasses combine with the attributes of wide transmission region (0.35-6 μm), good glass stability, rare-earth ion solubility, slow corrosion rate, lowest phonon energy spectrum among oxide glass formers, high refractive index, and high nonlinear refractive index [1]. Neodymium (Nd3+)-doped tellurite singlemode fiber laser and Er3+-doped tellurite singlemode fiber laser have been demonstrated recently[2,3]. The signal-gain characteristics of Er3+ doped tellurite fiber amplifiers are clarified based on spectroscopic properties and signal-gain measurements [4].

The complete low-loss window of silica-based optical fibers ranges from 1450 to 1650nm. However, only part of the wavelength regions in the 1550nm range have been used in wavelength division multiplexing (WDM) networks, which is limited by the operating wavelength and bandwidth of erbium doped fiber amplifier (EDFA). To support the need for higher capacity and increased flexibility bandwidth expansion in WDM networks is attractive. Thus, rare earth doped planar waveguides and fiber devices operating at the 1.4 μm wavelength range will be very useful. Tm3+ ion has been shown to provide gain in the 1450-1510 nm window; this is very desirable because it is the next lowest loss window to the erbium (Er3+) emission. Tm3+ ion for 1.47 μm emission has been investigated in a variety of glasses [5-8]. A maximum signal gain of 18 dB has been achieved in a 20m long Tm3+ doped fiber at a signal wavelength of 1.46 μm for a pump power of 150 mW at 0.79 μm [9].

In this paper, Tm3+ doped NZMT glasses suitable for 1.47 μm wavelength operation have been demonstrated. Absorption, emission, radiative lifetimes, and non-radiative properties of the glasses were investigated.

Experiments

Tm3+-doped glasses were prepared from anhydrous sodium carbonate (Na2CO3), zinc oxide (ZnO), molybdenum oxide (MoO3), and tellurium oxide (TeO2) powders. All this powders (99.999-99.5% purity) were obtained from Strem Chemicals Company. The glasses samples used in this research have the following molar composition: 10Na2O-10ZnO-10MoO3-70TeO2. Tm3+-doped NZMT glasses were prepared by doping 1.0 wt% Tm2O3 into the NZMT glass raw chemicals.The glass powders are melted in a platinum crucible by an electrically heated furnace at 750℃. The glasses were subsequently annealed at lower temperatures, and then sliced and polished to dimensions of 20 mm × 20 mm×2 mm.

The density of this sample is 5.31g/cm3. By using the Metricon 2010 prism coupler technique at three wavelengths the refractive indices were obtained. The NZMT glasses refractive indices were 1.950 and 2.011 at 633 nm and 1550 nm wavelength respectively.

Using Cary 5000 double-bean spectrophotometer the absorption spectra were obtained from 300nm to 2600nm. The fluorescence spectra were measured with a SPEX 500M monochromator and detected by a liquid-nitrogen-cooled germanium detector. The fluorescence lifetime of the 3F4 and 3H4 level of Tm3+ ion is measured with a 980nm laser diode light pulses and an InGaAs photodetector.

Results and Discussion

The absorption spectrum of Tm3+ doped tellurite glasses is shown in Fig. 1, from which an energy-level diagram of Tm3+ is constructed (Fig. 2). The absorption bands can be ascribed to transitions from the ground state (3H6) to the excited states of the Tm3+ ion. The band assignments are also indicated in this figure. The absorption spectra show wavelengths that may be used as pump lights for laser and optical amplifiers. Four possible pump transitions are 3H6→1G4 (465 nm), 3H6→3F2 (658 nm), 3H6→ 3F3 (687 nm) and 3H6→ 3F4 (793 nm).

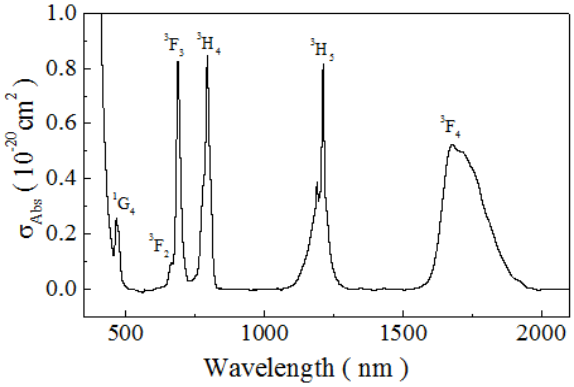

Fig. 1 Absorption cross section of Tm^{3+} in NZMT glasses

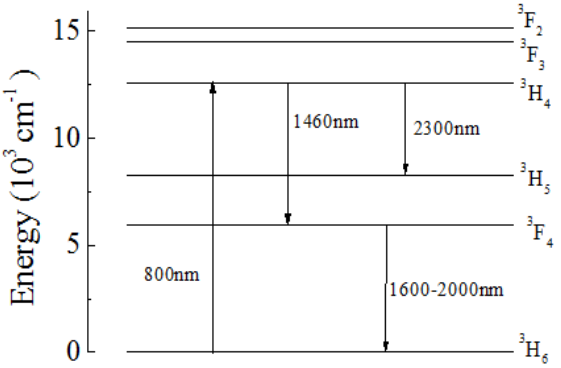

Fig. 2 Energy level diagram of Tm^{3+} in NZMT glass

A Judd-Ofelt analysis is employed to determine the radiative transition within the 4f n configuration of a rare earth ion [10,11]. The emission probability of electric dipole transition is dominated by the Judd-Ofelt Ω t parameters [12], which are functions of crystal field and radial integral of 4f and 5d electrons. The line strength for an electric-dipole transition between a ground state J and an excited state J' is calculated as

$$S_{ed}[J;J'] = \sum_{t=2,4,6} \Omega_t \left\langle \alpha SL, J \left\| U^{(t)} \right\| \alpha' S' L', J' \right\rangle^2,$$

(1)

where Ω_t is the Judd-Ofelt parameters, J is the total angular momentum of initial state, J' is the total angular momentum of final states, αSL is defined all other quantum numbers needed to specify the states and $\langle \| U^{(t)} \| \rangle$ is denoted the double reduced matrix elements of unit tensor operators for the corresponding transition.

From the absorption spectrum, the measured oscillator strength fmeas of the transitions are obtained by integrating absorption coefficients for each band using the following expression

$$f_{meas} = \frac{2303mc}{\pi e^2 N_A} \int \varepsilon(\nu) d\nu = 4.318 \times 10^{-9} \int \varepsilon(\nu) d\nu \quad (2)$$

where m is the mass of the electron, e is the charge of the electron, c is the velocity of light, $\varepsilon(\nu)$ is the molar absorption coefficient, ν is the light frequency and N_A is the Avogadro number. The experimental oscillator strengths of the transitions from the ground $^3H_6$ level to seven excited levels are determined by numerical integration of the corresponding absorption bands in Fig. 1.

The refractive indices of the glasses are measured using prism coupler 2010 with a prism (2.0<n>2.4). The refractive indices at 633 nm and 1550 nm are 2.0112 and 1.9261, respectively. Since the experimental oscillator strengths contain electric-dipole and magnetic-dipole contributions, the magnetic-dipole contribution is subtracted from the experimental oscillator strengths to obtain the magnetic-dipole contribution. The magnetic-dipole contribution, fmd, is obtained from the refractive index of the investigated glasses and the quantities, f [13]. For each wavelength, the refractive index was calculated using Cauchy's relation: using Cauchy's relation:

$$n = A + \frac{B}{\lambda^2}$$

(3)

A = 1.9092, B = 40870x104nm2

$$f_{md} = nf',$$

(4)

The relation between line strength S_{ed} and oscillator strength f for each electric dipole transition (at average frequency ν) is given by

$$f_{calc}(J, J') = \frac{8\pi^2 mc(n^2+2)^2}{3h\bar{\lambda}(2J+1)9n} S_{ed}(J;J'),$$

(5)

Where h is Planck's constant, n is the refractive index of the host, $\bar{\lambda}$ is the mean wavelength of the transition. From the integrated absorbance, three intensity parameters Ω_t (t=2,4,6) were determined by using a least-square fitting approach.

Accuracy of the least-squares approximation was evaluated by the root mean-square (rms) deviation from the measured oscillator strengths, Which is defined as

$$rms = \left(\frac{\sum (f_{meas} - f_{cal})^2}{no.\ of\ \ transition - no.\ of\ \ parameters} \right)^{1/2}.$$

(6)

The measured and calculated oscillator strengths, the electric-dipole line strengths S_{ed} for some transitions, and the Judd-Ofelt intensity parameters of of Tm^{3+}-doped NZMT glasses are presented in TABLE I. The Judd-Ofelt intensity parameters Ω_t, determined by using a least-squares fitting approach, are found to be $\Omega_2 = 4.74 \times 10^{-20}$ cm^2, $\Omega_4 = 1.20 \times 10^{-20}$ cm^2, and $\Omega_6 = 1.33 \times 10^{-20}$ cm^2.

Table 1 The measured and calculated oscillator strengths, the electric-dipole line strengths Sed for some transitions, and the Judd-Ofelt intensity parameters of Tm^{3+} in NZMT glasses

Transition	**Energy[cm^{-1}]**	f_{exp} **[10^{-6}]**	f_{cal} **[10^{-6}]**	f_{md} **[10^{-6}]**	S_{ed} **[10^{-20}]**
$^3H_6 \rightarrow {}^3F_4$	5961	3.4913	3.4835		3.7394
$^3H_6 \rightarrow {}^3H_5$	8254	2.5048	2.1356	0.5278	1.5125
$^3H_6 \rightarrow {}^3H_4$	12602	4.2463	4.1879		2.0631
$^3H_6 \rightarrow {}^3F_{3,2}$	14513	4.7364	4.6023		1.8726
$^3H_6 \rightarrow {}^1G_4$	21482	1.3537	1.3261		0.3480
Ω_2 [10^{-20} cm^2]				4.74	
Ω_4 [10^{-20} cm^2]				1.20	
Ω_6 [10^{-20} cm^2]				1.31	
Root-mean-square deviation [10^{-6}]				0.154	

By using the Judd-Ofelt intensity parameter Ω_t, some important radiative properties are calculated. The radiative transitions probabilities A from the *J* to the *J'* levelsis calculated from the following equation [14]

$$A[(S,L)J:(S',L')J'] = \frac{64\pi^4 e^2 n}{3h(2J+1)\lambda^3}\left[\frac{(n^2+2)^2}{9}\right]\sum_{t=2,4,6}\Omega_t\left\langle (S,L)J\left\|U^{(t)}\right\|(S',L')J'\right\rangle^2, \qquad (7)$$

where h is Planck Constant, e is the charge of the electron, n is the refractive index, λ is the mean wavelength of the transition, J is the total angular momentum of the initial state, <||U||> is the double reduced matrix element of unit tensor operators calculated in the intermediate-coupling approximation.

The branching ratios for the different transitions from |(S,L)*J* to lower level (S,L')*J'*| is given by

$$\beta[(S,L)J:(S',L')J'] = \frac{A[(S,L)J:(S',L')J']}{\sum_{S\ L',J'} A[(S\ L\ J\ ,S)\ L',J')]}, \qquad (8)$$

The radiative lifetime is expressed as the following equation

$$\tau_{rad} = \left\{\sum_{S',L',J'} A[(S,L)J:(S',L')J']\right\}^{-1} = A_{total}^{-1} \qquad (9)$$

The quantum efficiency of the |(S, L)J> manifold is defined as

$$\eta = \tau_{meas}/\tau_{rad} \qquad (10)$$

whereτ_{meas} andτ_{rad} are the experimentally determined and radiative lifetime, respectively.

Table II gives the spontaneous transition probabilities *A*, the branching ratios b, and the calculated lifetimes τ_{rad} in Tm^{3+}-doped NZMT glasses。

Fig. 3 shows the emission spectra of Tm^{3+} doped NZMT glass in the range of 1300-1650 nm. Fluorescence bands at 1.47 μm ($^3H_4 \rightarrow {}^3F_4$) was observed from the glass doped with 1.0 wt. % Tm_2O_3. Because of limitations of the spectrometer, only part of the spectrum of the the $^3F_4 \rightarrow {}^3H_6$ transition in the 1600–2000 nm can be observed. The bandwidth of the $^3H_4 \rightarrow {}^3F_4$ transition is ~100 nm, which is significantly larger than that of fluoride glasses but less than that in KBG glasses [15,16]

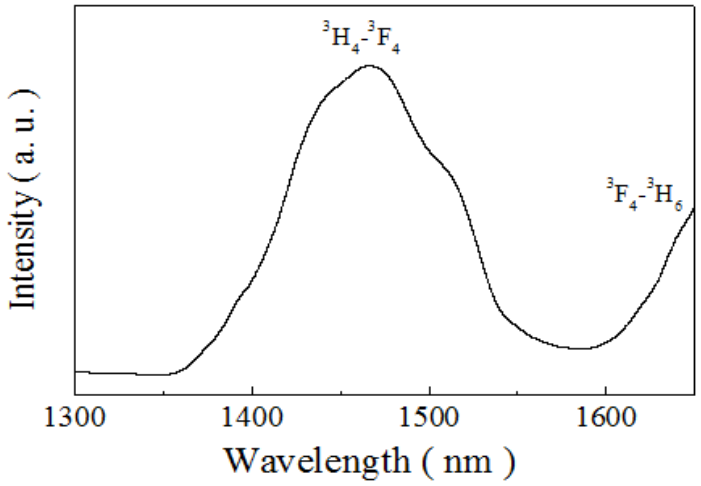

Fig. 3 Fluorescence spectrum of Tm^{3+} doped NZMT glass in the range of 1300-1650 nm

Measured fluorescence lifetimes of the $^3F_4 \rightarrow {}^3H_6$ and $^3H_4 \rightarrow {}^3F_4$ decay at room temperature were 2.842 and 0.323 ms respectively, and their quantum efficiencies were approximately 100% and 88.9%. From the data, it appears that Tm^{3+}-doped NZMT glasses are promising materials for use in lasers and optical amplifiers operating in the 1.47 μm wavelength range.

Table 2 Calculated Spontaneous Emission Probabilities, Branching Ratios, and Lifetimes of Tm^{3+}-doped NZMT glasses

Transition	$\bar{\lambda}$ **[nm]**	A_{ed} **[s^{-1}]**	A_{md} **[s^{-1}]**	A_{total} **[s^{-1}]**	β_{ij}	τ_{rad} **[μs]**
$^1D_2 \rightarrow {}^1G_4$	1486	323		323	0.004	13
$^1D_2 \rightarrow {}^3F_2$	778	1590	61	1651	0.022	
$^1D_2 \rightarrow {}^3F_3$	745	2348	101	2449	0.032	
$^1D_2 \rightarrow {}^3H_4$	657	3768		3768	0.049	
$^1D_2 \rightarrow {}^3H_5$	504	241		241	0.003	
$^1D_2 \rightarrow {}^3F_4$	450	48673		48673	0.638	
$^1D_2 \rightarrow {}^3H_6$	357	19187		19187	0.251	
$^1G_4 \rightarrow {}^3F_2$	1634	16		16	0.004	219
$^1G_4 \rightarrow {}^3F_3$	1494	67	4	71	0.016	
$^1G_4 \rightarrow {}^3H_4$	1177	405	34	439	0.096	
$^1G_4 \rightarrow {}^3H_5$	778	1276	154	1430	0.313	
$^1G_4 \rightarrow {}^3F_4$	646	294	9	303	0.066	
$^1G_4 \rightarrow {}^3H_6$	470	2314		2314	0.506	
$^3F_2 \rightarrow {}^3F_3$	17513	0	0	0	0	393

$^3F_2 \rightarrow {}^3H_4$	4215	13		13	0.005	
$^3F_2 \rightarrow {}^3H_5$	1506	265		266	0.105	
$^3F_2 \rightarrow {}^3F_4$	1069	1038		1038	0.408	
$^3F_2 \rightarrow {}^3H_6$	670	1225		1225	0.482	
$^3F_3 \rightarrow {}^3H_4$	5552	5		5	0.001	216
$^3F_3 \rightarrow {}^3H_5$	1558	647		647	0.139	
$^3F_3 \rightarrow {}^3F_4$	1138	117	63	180	0.039	
$^3F_3 \rightarrow {}^3H_6$	686	3806		3806	0.820	
$^3H_4 \rightarrow {}^3H_5$	2166	27	11	33	0.014	363
$^3H_4 \rightarrow {}^3F_4$	1432	187	24	211	0.077	
$^3H_4 \rightarrow {}^3H_6$	784	2504		2504	0.910	
$^3H_5 \rightarrow {}^3F_4$	4226	12	1	13	0.025	1836
$^3H_5 \rightarrow {}^3H_6$	1225	447	84	531	0.975	
$^3F_4 \rightarrow {}^3H_6$	1725	361		361	1	2770

Conclusions

The optical properties of Tm^{3+} doped NZMT glassglasses are investigated. The Tm^{3+} 1.47 μm emission is very desirable since it is the next lowest loss to the Er^{3+} window. The bandwidth of the $^3H_4 \rightarrow {}^3F_4$ transition in tellurite glass is ~100 nm, which is significantly larger than that of fluoride glasses but less than that in KBG glasses. Measured fluorescence lifetimes of the $^3F_4 \rightarrow {}^3H_6$ and $^3H_4 \rightarrow {}^3F_4$ decay at room temperature were 2.842 and 0.323 ms respectively, and their quantum efficiencies were approximately 100% and 88.9%. Those results indicate that Tm^{3+} doped KBG glass is a promising candidate for optical amplifier operation at 1.40-1.52 μm.

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