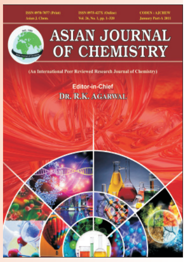
Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5891-5894

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18311



Effect of Tm^{3+} Sensitization to Ho^{3+} Doped GeO_2-B_2O_3-BaF_2-Al_2O_3-ZnO_2-Na_2O Glass on Spectral Properties†

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AJC-15816

A series of Tm^{3+}/Ho^{3+} sensitized 65GeO_2-7BaF_2-10B_2O_3-4Al_2O_3-4ZnO_2-10Na_2O glass samples were synthesized by using high temperature melting method. The spectral properties were systematically studied when Ho^{3+} concentration was 0.1, 0.3, 0.5 mol % and Tm_2O_3 changed from 0.3 to 2.5 mol %. Differential thermal analysis showed that ΔT was higher than 190 °C, which illustrated this kind of matrix glass have better thermal stability. The absorption cross section peak height, free energy of Ho^{3+} from $^5I_8$ to $^5I_7$ and emission cross section were calculated according to Mc-Cumber theory. Under the excitation of 808 nm laser diode, fluorescence intensity at 1954 nm reached the highest value when the concentration of Ho^{3+} was 0.1 mol % and Tm^{3+} was 0.7 mol %. However the fluorescence intensity reduced greatly when Ho^{3+} concentration was 0.5 mol % and Tm^{3+} exceeded 1.5 mol %. The sensitized function and influence of different Tm^{3+}/Ho^{3+} doped ion ratios on the spectral properties was studied.

Keywords: Adsorption, Growth from high temperature solutions, Glasses, Rare earth compounds.

INTRODUCTION

With the development of 2 μm fiber laser in medicine application, the study on infrared optical fiber materials is more and more urgent. Infrared fiber materials mainly includes crystalline and glass material. Compared with crystal material, glass has many advantages, *e.g.*, adjustable chemical composition, high solubility of rare earth ions, controllable preparation process and be drawn to fiber easily, which is an ideal matrix material for rare earth active ions[1]. Therefore, glass material becomes the focus of research on infrared optical fiber materials. The research of infrared optical materials on heavy metal oxide glass mainly is to gain the red shift of transmission wavelength. The high transmittance can weaken the bonding energy between the glass network to gain larger atomic weight and decrease the phonon energy so that the absorption can shift to the long wavelength direction. In view of fluoride glass has low phonon energy (about 540 cm^{-1}), its chemical stability and mechanical properties are bad[2], so it has not yet achieved good practical value. The common matrix material is silicate glass, but it has high phonon energy (about 1100 cm^{-1}), the non radiation transition energy loss caused by multi-phonon relaxation is dominant, which leads to the decrease of Tm^{3+} quantum efficiency and can not get the ideal amplification effect. The solubility of rare earth ions in silicate glass is very poor and the doped concentration is low[3]. Germanate matrix glass is selected because it not only has good mechanical and optical properties but high solubility of rare earth ions. It has also lower phonon energy (about 900 cm^{-1}) to inhibit the non radiation transition effectively and improve its luminous efficiency greatly[4]. Selected Tm^{3+} sensitized Ho^{3+} co-doped ions due to that the laser output efficiency of Ho^{3+} doped glass is relatively low. Ho^{3+}/Tm^{3+} co-doped is the most effective way to gain 2 μm light, which has important application in medical treatment[5]. The level of transition from $^5I_8$ to $^5I_7$ of Ho^{3+} can emission 2 μm wavelength. Due to that $^5I_7$ of Ho^{3+} has longer lifetime and larger stimulated emission cross section[6,7], the laser material can obtain better spectral performance for a new generation of infrared laser device.

This paper chooses Tm^{3+} sensitized Ho^{3+} doped 65GeO_2-7BaF_2-10B_2O_3-4Al_2O_3-4ZnO_2-10Na_2O matrix glass system, the influence of different Tm^{3+}/Ho^{3+} sensitized proportion on spectral properties are studied. Spectral parameters are calculated according to Mc-Cumber theory. Selecting a suitable infrared optical fiber material among the samples provides theory basis for the good performance mid-infrared laser optical fiber.

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†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

EXPERIMENTAL

The sample formula was $65GeO_2$-$7BaF_2$-$4ZnO_2$-$10B_2O_3$-$10Na_2O$-$4Al_2O_3$-xHo_2O_3-yTm_2O_3, where x was (0.1, 0.3, 0.5), x:y was (1:3,1:5,1:7, 1:10). Glass samples were marked G1, G2, G3, G4...G9. The raw materials were analytically pure reagents. The total amount of different optical reagents was 15 g. A mortar was used to grind the powder and mix evenly. It was melted in a silicon molybdenum rod resistance furnace that was preheated at 1250 ºC and then clarified at 1300 ºC for 1 h. Pouring it onto the steel die that was preheated to 450 ºC and kept at a uniform near the glass transformation temperature for 1 h. Then it was cooled to the room temperature at the speed of 20 ºC/h. The glass samples were processed into the size of 20 mm × 20 mm × 2 mm to meet the spectral test requirement.

Glass density was measured by Archimedes method and calculated according to the formula of d = m/v, where d is glass density, m is glass quality, v is sample volume. Refractive index was measured by V prism, the light source is sodium lamp. Differential thermal curves were measured by TAS-100 differential thermal analyzer that is produced by the Japanese Rigaku company. The absorption spectra was tested by UV/VIS/NIR 900 fluorescence spectrophotometer, wavelength range was from 300-3000 nm; bandwidth was 0.05-5.0 nm; wavelength accuracy was +0.08 nm; repeatability of wavelength was less than 0.02 nm. Fluorescence spectral was tested by fluorolog-3-211 near ultraviolet/visible/infrared fluorescence system that was produced by JY company. Pump source was 808 nm semiconductor laser. All tests were carried out at room temperature.

RESULTS AND DISCUSSION

Physical performances: The density and refractive index of Tm^{3+} sensitized Ho^{3+} doped Germanate glass samples were listed in Table-1. The density rose with the increasing of Tm^{3+} when Ho^{3+} concentration was 0.1 mol %. When Ho^{3+} was 0.3 or 0.5 mol %, glass density decreased firstly and then increased with increasing of Ho^{3+} concentration. The influence of Tm^{3+} concentration on the glass density was obvious mainly because there was a close relationship between density and glass structure, which depended on the quality of glass atoms, packing tightness and coordination number[8]. While the refractive index increased with the increasing of the rare earth ions concentration. In order to study the thermal stability of the glass samples, differential thermal curve was tested. The temperature range was 20-1000 ºC, differential thermal curve of the samples were shown in Fig. 1.

There was an obvious peak in the range from 430-600 ºC. It can be seen that T_g was about 430 ºC and T_x was 620 ºC. The thermal stability of the glass was usually measured by the value of T_x-T_g, so it was 190 ºC, which indicated that the glass had a good thermal stability and ability to resistance crystallization.

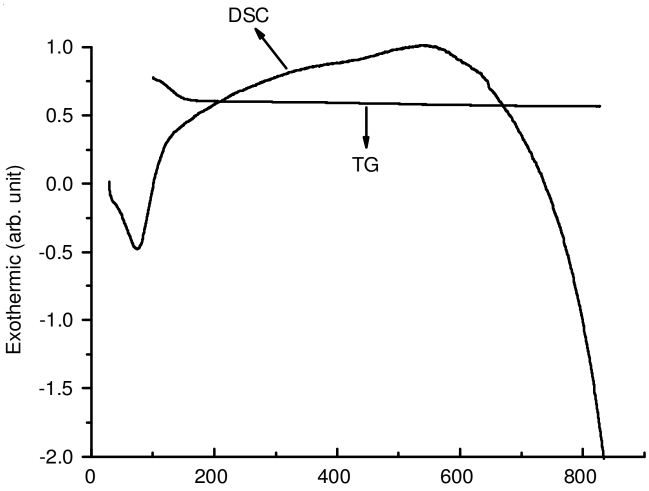

Fig. 1. Differential thermal curve of glass sample

Absorption spectra: Fig. 2 showed the absorption spectra of Tm^{3+} sensitized Ho^{3+} doped Germanate glass in the wavelength range of 500-2000 nm at room temperature, when Ho^{3+} and Tm^{3+} concentrations ratio were 0.1 and 0.5 mol %, respectively. It can be seen that there were six strong absorption bands located at 1951, 1670, 1212, 791, 686 and 537 nm. They were corresponding to the characteristic level transition: $^5I_7$ to $^5I_8$ of Ho^{3+}, $^3H_6$ to $^3H_4$, $^3H_5$, $^3F_3$, $^3F_4$ of Tm^{3+}, respectively. The strongest absorption peak at 686 nm was the overlapping of two transitions of $^5I_8$ to $^5I_5$ of Ho^{3+} and $^3H_6$ to $^3F_4$ of Tm^{3+}.

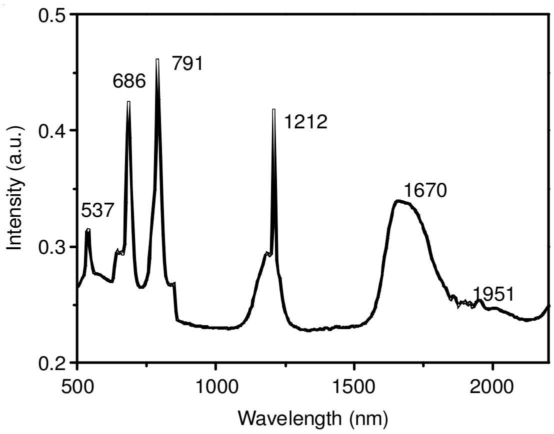

Fig. 2. Absorption spectra of sample

$$N_0 = \frac{d}{M_x} \times m \times 6.02 \times 10^{23} \tag{1}$$

The doped concentration of rare earth ions can be calculated by eqn. 1, where m is the molar concentration of rare earth ions; N_0 is the number of rare earth ions in a unit volume; d is the sample density; M_x is the average molecular weight.

$$\sigma_{abs} = \frac{2.303\log(I_0/I)}{Nd} \tag{2}$$

TABLE-1
DENSITY AND REFRACTIVE INDEX OF Tm^{3+}/Ho^{3+} SENSITIZED GLASS SAMPLE

Number	G_1	G_2	G_3	G_4	G_5	G_6	G_7	G_8	G_9
Ho^{3+}:Tm^{3+} (mol)	0.1:0.3	0.1:0.5	0.1:0.7	0.1:1.0	0.3:0.9	0.3:1.5	0.3:2.1	0.5:1.5	0.5:2.5
d (g/cm^3)	4.513	4.527	4.542	4.580	4.569	4.587	4.562	4.543	4.597
Nd	1.605	1.609	1.617	1.617	1.618	1.621	1.624	1.626	1.627

TABLE-2
PARAMETERS OF Ho^{3+}/Tm^{3+} CO-DOPED GLASS

Number	m.w.	Density (g/cm^3)	N_{Ho} (10^{19} /cm^3)	N_{Tm} (10^{19}/cm^3)
G_1	101.88	4.513	5.33	15.99
G_2	102.44	4.527	5.34	26.6
G_3	102.99	4.542	5.39	37.17
G_4	103.82	4.580	5.43	53.11
G_5	104.09	4.569	15.25	47.56
G_6	105.73	4.587	15.67	76.43
G_7	106.26	4.562	15.7	108.55
G_8	107.34	4.543	25.47	76.43
G_9	108.93	4.597	25.48	127.31

Absorption cross section of $^3H_6$ to $^3F_4$ of Tm^{3+} can be calculated according to eqn. 2[9,10], where I_0 and I is the incident and transmit light intensity; N is the doping concentration of Ho^{3+}, that is $15.25 \times 10^{19} cm^{-3}$; d is sample thickness (about 2 mm). The calculated results were that absorption cross section of the strongest absorption peak at 1950 nm was 9.8×10^{-19} cm^2, the absorption cross section peak height of Ho^{3+} was about 4.6×10^{-19} cm^2 in Fig. 3. The relationship between emission cross section and absorption cross section is followed as eqn. 3:

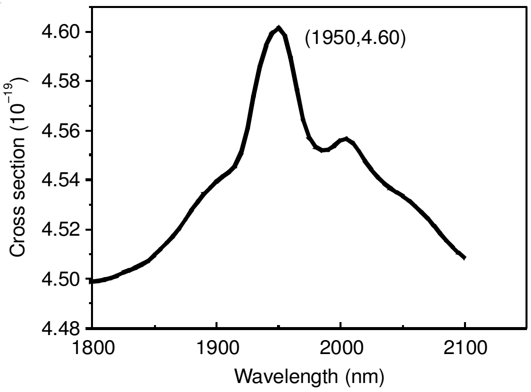

Fig. 3. Absorption spectra at 1950 nm of Ho^{3+}

$$\sigma_e(\lambda) = \sigma_a(\lambda)\exp\left(\frac{\varepsilon - hc\lambda^{-1}}{KT}\right) \qquad (3)$$

The integrated absorption cross section is given as eqn. 4:

$$\Sigma_{abs} = \int \sigma_{abs}(\lambda)d\lambda \qquad (4)$$

The spontaneous radiative transitions probability is according to eqn. 5:

$$A = 8\frac{\pi c}{\lambda^4}\int \sigma_{abs}(\lambda)d\lambda = 8\frac{\pi c}{\lambda^4}n^2\int \sigma_{abs}(\lambda) \qquad (5)$$

where λ is the average wavelength of absorption bands; n is the corresponding refractive. Therefore, the stimulated emission lifetime can be obtained. The formula of stimulated emission lifetime is given as eqn. 6:

$$\tau_{rad} = \frac{1}{A} \qquad (6)$$

$$\varepsilon = \kappa T \ln\left[\frac{c^2 A}{8\pi n^2 \tau \int \nu^2 \sigma_s(\nu)\exp\left(-\frac{h\nu}{kT}\right)d\nu}\right] \qquad (7)$$

where k is Boltzmann constant; ε is the free energy from the ground state to the excited states; λ is the fluorescence emission wavelength; T is sample temperature; K is 1.38×10^{-23} J/k; h is 6.6×10^{-34} J s; C is the speed of light in vacuum (C is 3×10^8 m/s). The free energy of $^5I_8$ to $^5I_7$ was 5139 cm^{-1} according to formula (7). The calculated parameters of Ho^{3+}/Tm^{3+} co-doped glass were shown in Table-3.

TABLE-3
PARAMETERS OF $^5I_8$ TO $^5I_7$ OF Ho^{3+}

Number	Concentration (mol %)	FWHM (nm)	Height (10^6)	λ_p (nm)
G1	0.1:0.3	25.93	25.49	1954.27
G2	0.1:0.5	25.93	30.58	1954.27
G3	0.1:0.7	27.46	67.35	1954.46
G4	0.1:1.0	26.02	12.22	1954.08

The transition absorption and stimulated emission cross sections of Ho^{3+} from $^5I_8$ to $^5I_7$ at 1953nm increased when Ho^{3+} concentration was 0.1 mol % and Tm^{3+} increased from 0.3-1.0 mol %. The radiative transition probability decreased and reached the highest value of 149.93 when Ho^{3+}/Tm^{3+} ratio was 1:3. On the other hand, the absorption cross section, emission cross section and radiative transition probability all decreased with the increasing of Tm^{3+} concentration, which indicated the rare earth ion solubility of Germanate glass was limited. When rare earth ions increased higher than a certain concentration, there would be a reunion phenomenon.

Fluorescence spectra: Fig. 4(a) is the fluorescence spectra under the conditions of 808 nm pumped of Tm^{3+} sensitized H_O^{3+} doped Germanate glass. It is observed that there was an obvious emission band at 1953 nm, which attributes to $^5I_8$ to $^5I_7$ transition of H_O^{3+}. Fluorescence intensity gradually increased with the increase of Tm^{3+} when Ho^{3+} was 0.1 mol %. When Tm^{3+} was 0.7 mol %, the fluorescence intensity reached the maximum value of 67.35×10^6. Therefore, the best proportion of Ho^{3+}/Tm^{3+} is 1:7. Higher than this proportion, the fluorescence intensity decreased significantly. These parameters were shown in Table-4.

The fluorescence intensity increase with the increasing of Ho^{3+}/Tm^{3+} concentration proportion when Ho^{3+} was 0.3 mol %, which reached the highest value when the two ions ratio is 1:5 [Fig. 4(b)]. The sensitized proportion of Ho^{3+} and Tm^{3+} had an important influence on the luminescence properties.

Fig. 4(c) indicated the fluorescence intensity decreased significantly when Ho^{3+} was 0.5 mol % and Tm^{3+} exceeded 1.5 mol %. Increasing Tm^{3+} concentration would cause the fluorescence quenching. So the solubility of Tm^{3+} was 1.5 mol %. From the above analysis, the sensitization of Tm^{3+} to Ho^{3+} could increase the peak height by an order of magnitude.

Conclusion

In the Tm^{3+} sensitized to Ho^{3+} doped $65GeO_2$-$7BaF_2$-$10B_2O_3$-$4Al_2O_3$-$4ZnO_2$-$10Na_2O$ glass series, fluorescence intensity reaches the highest value of 67.35×10^6 when Ho^{3+} is 0.1 mol % and Ho^{3+}/Tm^{3+} ratio is 1:7. When Tm^{3+} changed from 0.3 to 1.0 mol %, the absorption, emission cross sections and lifetime increased, while the transition probability reduced. It reached the maximum of 149.93 when Ho^{3+}/Tm^{3+} 1:3. The fluorescence intensity decreased significantly when the Ho^{3+}

TABLE-4
FLUORESCENCE SPECTRA PARAMETERS

Number	Ho^{3+}:Tm^{3+} (mol)	σ_{abs} (1953 nm) × 10^{-20} (cm^2)	δ_e (1953 nm) × 10^{-20} (cm^2)	Σ_{abs} × 10^{-20} (cm^2)	τ_{rad} (ms)	A (s^{-1})
G_1	0.1:0.3	0.907	1.009	11.16	6.67	149.93
G_2	0.1:0.5	0.905	1.007	9.57	7.74	129.18
G_3	0.1:0.7	0.960	1.068	8.21	8.94	111.91
G_4	0.1:1.0	0.981	1.091	5.79	12.63	79.13
G_5	0.3:0.9	0.197	0.219	6.65	11.01	90.84
G_6	0.3:1.5	0.193	0.215	4.07	17.95	55.71
G_7	0.3:2.1	0.190	0.212	2.29	31.76	31.49
G_8	0.5:1.5	0.60	0.170	2.23	32.48	30.78
G_9	0.5:2.5	0.17	0.190	1.70	42.55	23.50

was 0.5 mol % and Tm^{3+} exceeded 1.5 mol %, which indicated the dissolving capacity of Tm^{3+} is 1.5 mol %. When Ho^{3+} doping concentration was different, the proportion of sensitization had a different influence on the luminescence properties.

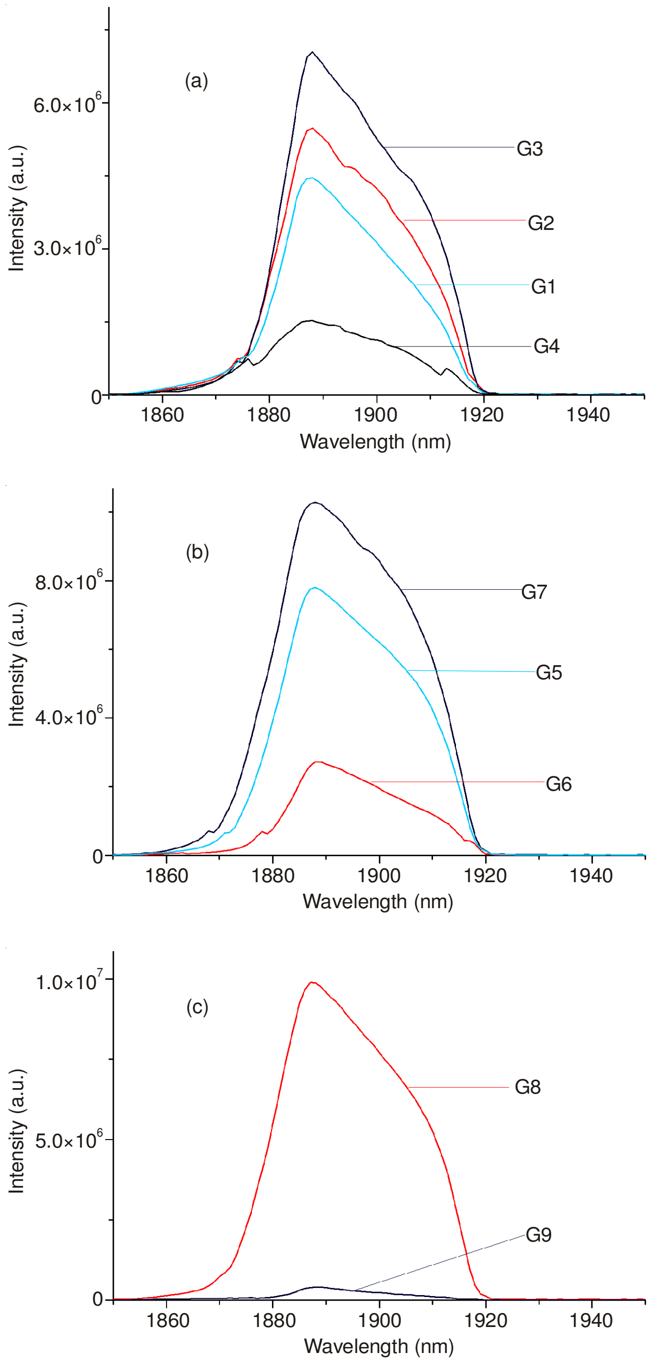

Fig. 4. Fluorescence spectra of sample

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