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Spectroscopic properties and Judd–Ofelt analysis of Dy^{3+}-doped and Dy^{3+}, Tm^{3+}-codped Ge–In–S chalcogenide glasses

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ABSTRACT

0.2 wt.% Dy^{3+}-doped and 0.2 wt.% Dy^{3+}, 0.5 wt.% Tm^{3+}-codoped (100-x)$GeS_2 \cdot xIn_2S_3$ (x = 5,10,15,20,25) chalcogenide glasses were prepared. Their spectroscopic properties were analyzed based on absorption (ranges from 500 to 3000 nm) and emission (ranges from 1000 to 4700 nm) measurements. The Judd–Ofelt strength parameters Ω_t ($t = 2, 4, 6$) and the spectroscopy parameters A_{rad}, β and τ_{rad} were calculated, and the σ_{emi} of the 1330, 2930 and 4320 nm fluorescences were estimated. These Dy^{3+}-doped and Dy^{3+}, Tm^{3+}-codoped Ge–In–S chalcogenide glasses are valuable materials for using in 1.3 μm fiber-amplifiers and 2–5 μm mid-infrared laser devices.

1. Introduction

In various chalcogenide glasses, the Ge–Ga-based ones have attracted considerable interest for their possible roles in many optical and photonic applications covering the whole civil, medical and military areas [1,2]. When doped with rare-earth (RE) ions, they always exhibit relatively large RE ions solubility, low non-radiative decay rates and large stimulated emission cross sections [3,4]. Indium (In) has the similar chemical properties with Gallium (Ga) but a larger atomic weight, and the Ge–In-based chalcogenide glasses have a similar structure with the Ge–Ga ones [5], inducing a large RE ion solubility. Larger density and refractive index [6] makes a larger stimulated emission cross section, lower non-radiative decay rate and higher radiative quantum efficiency are expected.

In the several RE ions, Dysprosium (Dy^{3+}) has received particular attention because of its potential applications in 1.3 μm telecommunication and 2–5 μm mid-infrared wavebands. Dy^{3+} has several advantages over Pr^{3+}-based amplifiers for 1.3 μm telecommunication application. Firstly, for populating the $^6H_{9/2}$–$^6F_{11/2}$ level, Dy^{3+} has a good pump band which can be pumped with cheap commercial 808 nm laser diode (LD). Secondly, the emission cross section of the Dy^{3+}:$^6H_{9/2}$–$^6F_{11/2}$ → $^6H_{15/2}$ transition is in general greater than the Pr^{3+}:$^1G_{42}$ → $^3H_4$ in the same host [3]. On the other hand, relatively large branching ratios for the $^6H_{13/2}$ → $^6H_{15/2}$ (~2.86 μm) and $^6H_{11/2}$ → $^6H_{13/2}$ (~4.34 μm) transitions of Dy^{3+} in the chalcogenide glasses make it a very promising candidate material for mid-infrared solid state lasers, which have extensive application prospects in the fields of remote sensing, range finding, environmental monitoring, bio-engineering, medical treatment, and etc. [7,8].

In our previous works, some novel Dy^{3+}-doped Ge–Ga-based chalcogenide or chalcohalide glasses with high RE ion solubility and prominent emission properties were prepared [4,9]. In this work, we investigated the preparation of Dy^{3+}-doped and Dy^{3+}/Tm^{3+}-codoped Ge–In–S glasses for the first time. Their spectral properties excited at 808 nm are presented and Judd–Ofelt analysis is made. Effects of Indium (In) on the intensities of the 1330, 2930 and 4320 nm fluorescences are investigated and discussed. Our work was aimed at the elucidation of the glass composition's influence on the spectroscopic properties in the chalcogenide system and the discovery of a new material for applications in the 1.3 μm telecommunication fiber-amplifier and 2–5 μm mid-infrared laser devices.

2. Experimental procedure

The compositions of the host chalcogenide glasses were (100-x) $GeS_2 \cdot xIn_2S_3$ with x = 5, 10, 15, 20 and 25, while x is the mole percent. More precisely, they were labeled as GINS5, GINS10, GINS15, GINS20 and GINS25, respectively. The raw materials are Ge grains (5 N), In grains (5 N), Dy_2S_3 powers (3 N) and Tm_2S_3 powers (3 N). Details of the preparations were similar to the procedure in the previous paper [9] except that the melting temperature

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is 970 °C in this experiment. The thicknesses of the obtained glass samples were about 4.0 mm.

Differential scanning calorimetry (DSC) and thermal gravity (TG) curves of the prepared glasses were recorded by using a comprehensive thermal analysis apparatus (NETZSCH STA 449C) at a heating rate of 10 °C/min. Typical sample weight was about 15 mg and the error of the characteristic temperatures was about ±1 °C. Density was measured by the Archimedes principle by using CCl_4 as the immersion medium, yielding uncertainties of ±0.015 g/cm^3. The refractive indices were measured by the variable angle spectral ellipsometry (J.A. Woollam WVASE32, U.S.A.). Room-temperature fluorescence spectra were measured by using 808 nm excitation from a laser diode (LD) (the average power is 1 W). The near-infrared fluorescence spectra in the range of 1000–1500 nm and fluorescence decay curves were measured by an InGaAs detector (Judson J22TE2-66C-R05M, U.S.A.) whose rise time is 10 us. During the lifetime measurement, the pulse duration was adjusted to 10 us and the temporal decay was recorded by a storage digital oscilloscope (Tektronix TDS3012B, U.S.A.). The mid-infrared fluorescence spectra in the range of 1650–4700 nm were measured by a liquid-nitrogen cooled InSb detector (Judson J10D-M204-R04M-60, U.S.A.), combining with a model SRB30 DSP lock-in amplifier. Errors in the fluorescence and lifetime measurements are estimated to be ±0.1 nm, ±10 μs, respectively.

3. Results and discussion

3.1. Dy^{3+}-doped glasses

The data from the DSC-TG, refractive indices, densities and ion concentrations are tabulated in Table 1. With the increase of In_2S_3 content, the refractive index, density and ion concentration all increase linearly, which are attributed to the larger atomic weight of Indium (In) in comparison with Germanium (Ge). Whereas the glass transition temperature T_g and crystallization temperature T_x both decrease. It is resulted from the increase in the numbers of the In–S bonds with more ionicity and the structural degradation in the glass. A maximum criterion $\Delta T\,(=T_x-T_g)$ is presented for 0.2Dy-GINS10 glass, suggesting that more different chemical bonds and disordered micro-structural units enhancing the dimensionality of the glass network [10], therefore the glass becomes more stable with the appropriate addition of In_2S_3. By and large, thermal stability of Ge–In–S glass is weaker than that of Ge–Ga–S glass with a similar composition ratio, and the doping of RE ions decrease the thermal stability in comparison with the blank glass sample [11].

Fig. 1 is the Vis–NIR absorption spectra of the 0.2 wt.%Dy^{3+} doped GINS serial glasses in the wavelength region of 500–3000 nm. The short-wavelength absorption edge of the glass lies at 532, 572, 576, 586 and 600 nm, respectively, and shifts to the long wavelength gradually with the addition of In_2S_3. The absorption bands at 916, 1110, 1300, 1704, 2826 nm are strong, whereas that of 808 nm is weak, indicating that the pumping efficiency of 808 nm LD will be

Table 1
The glass transition temperature T_g, crystallization temperature T_x, criterion $\Delta T\,(=T_x-T_g)$, density d, refractive index nD (589 nm) and Dy^{3+} ion concentration N_o of 0.2 wt.%Dy^{3+} doped GINS serial glasses.

Host glass	T_g[a] (°C)	T_x[b] (°C)	ΔT (°C)	d (g/cm^3)	n_D	N_o (×10^{25}/m^3)
GINS5	425	509	84	2.92	2.08	2.083
GINS10	385	492	107	3.00	2.12	2.220
GINS15	367	465	98	3.18	2.17	2.348
GINS20	350	422	72	3.29	2.23	2.436
GINS25	332	401	69	3.32	2.27	2.455

[a] T_g is defined as the temperature that an endothermic step shown in the DSC curve.
[b] T_x is the onset temperature of crystallization.

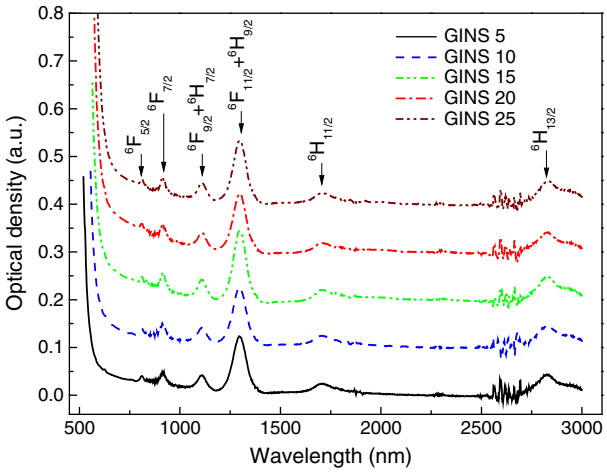

Fig. 1. Absorption spectra of GINS serial glasses doped with 0.2 wt.% Dy^{3+}.

low. The absorption cross section (σ_{abs}) at 808 nm was calculated to be 0.96, 1.14, 1.16, 1.18 and 1.23×10^{-21} cm^2, respectively.

The Judd–Ofelt intensity parameters of Dy^{3+} among the GINS serial glasses were then calculated and summarized in Table 2. With the increase of In_2S_3 content, the values of Ω_2 and Ω_4 decrease rapidly, whereas the Ω_6 increases markedly. According to the previous work on GINS glasses' structure [5,11], the addition of In_2S_3 will convert the original [GeS_4] tetrahedra forming structure to [GeS_4] and [InS_4] mixed-tetrahedra forming one. Therefore the symmetry decreases and the covalence has also been reduced because of weaker electronegativity of the In (1.78) compared with Ge (2.01). Generally, a lower symmetry of polyhedra and a higher covalency of bonds inside the hosts surrounding the rare-earths results in larger Ω_2. Considering the decrease of Ω_2 in the GINS serial glasses, the decrease of covalence symmetry is therefore suggested to play a dominant role whereas the influence of the covalence's symmetry can be ignored. Furthermore, the value of Ω_6 increases with the addition of In_2S_3, reflecting the fact that more ionic bonds and lower rigidity of glass are presented.

The fluorescence spectra of 0.2 wt.% Dy^{3+} doped GINS serial glasses are shown in Fig. 2. Three major emission bands were observed at around 1140, 1330 and 1750 nm, and obviously their intensities have a strong compositional dependence. From GINS5 to GIN25, the intensities of the 1140 and 1330 nm fluorescence increase first and reach strongest values when the In_2S_3 content is 15–20%, and then decrease abruptly to the weakest values when the In_2S_3 content is 25%. Whereas a contrary trend is detected for the 1750 nm fluorescence. No obvious shift of fluorescence band center was observed in this system, which is different with our previous works in Ge–Ga-based chalcogenide glasses [4,9].

The radiative transition probabilities (A_{rad}), branching ratios (β) and radiative lifetimes (τ_{rad}) of the excited states of Dy^{3+} were evaluated following the Judd–Ofelt theory and summarized in Table 3. The measured effective line widths ($\Delta\lambda_{eff}$) of 1330 and 1750 nm fluorescences and the measured lifetimes (τ_{mea}) of 1330 nm fluorescence were also listed. The radiative quantum efficiency η were calculated from $\eta=\tau_{mea}/\tau_{rad}$.

Table 2
Judd–Ofelt intensity parameters of Dy^{3+}-doped GINS serial glasses in comparison to other hosts.

Host glass	J–O parameters (×10^{-20} cm^2)		
	Ω_2	Ω_4	Ω_6
GINS5	11.69	3.52	0.53
GINS10	11.56	2.69	1.14
GINS15	10.98	1.98	1.67
GINS20	9.60	1.87	1.75
GINS25	9.58	1.78	1.79