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Mid-infrared emission and Judd-Ofelt analysis of Dy^{3+}-doped infrared Ga-Sb-S and Ga-Sb-S-PbI_2 chalcohalide glasses

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HIGHLIGHTS

- Halide of PbI_2 is successfully introduced into the Dy^{3+} doped GaSbS glasses.
- The introduction of PbI_2 can promote the symmetry and orderliness of the coordination environment nearby Dy^{3+} ions.
- The infrared emission can be improved in the PbI_2-modified GaSbS glass.

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ABSTRACT

Dy^{3+}-doped Ga-Sb-S and Ga-Sb-S-PbI_2 chalcohalide glasses were prepared by traditional melt quenching method. The effect of halide PbI_2 on the physical and optical properties of Dy^{3+} ions was investigated. The density and ionic concentration of the host sample increased with the introduction of PbI_2 halides, whereas the refractive index at 1.55 μm decreased. The Judd-Ofelt parameters showed that Ω_2 increased in PbI_2-modified glass, whereas the Ω_6 value showed the opposite tendency. Infrared emission spectrum also showed that the intensity increased with PbI_2 addition, and considerable enhancement at 2.8 μm was observed in the mid-infrared region. The halide PbI_2 promoted the reduction of phonon energy of the host and the improvement of the laser pump efficiency, which led to the construction of optimized infrared glass materials for optical applications.

1. Introduction

Research of materials applied in fiber amplifiers, especially for the 1.3-μm communication window, has attracted considerable interest after the widespread commercial applications of Er^{3+}-doped silica fiber amplifier with zero dispersion [1–5]. The most successful ZBLAN fluoride fiber gives good quantum efficiency for radiative transitions with losses of the order of 1–10 dB km^{-1} typical and relatively low phonon energy 590 cm^{-1}. However, it cannot cover the entire MIR transmission range because of its hygroscopic nature [6]. Among the studied materials, chalcogenide glasses, which can transmit light from the far visible regions to wavelengths in excess of 15 μm, seem to be ideal candidates as fiber amplifiers [7]. Given their very low phonon energy (350 cm^{-1} for sulfide and 200 cm^{-1} for selenide glasses) and very high refractive index (>2), high MIR emission quantum efficiency of the radiative transitions among the f-f electron energy levels of rare earth (RE) ions is expected [8].

In 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 [9–10]. First, for populating the $^6H_{9/2}$–$^6F_{11/2}$ level, Dy^{3+} has a good pump band, which can be matched with the cheap commercial 808-nm laser diode. Second, the emission cross sections of the Dy^{3+}:$^6H_{9/2}$–$^6F_{11/2}$ → $^6H_{15/2}$ transition is generally greater than the Pr^{3+}:$^1G_4$ → $^3H_4$ in the same host [11]. However, relatively large branching ratios for the $^6H_{13/2} \rightarrow {}^6H_{15/2}$ (∼2.86 μm) and $^6H_{11/2} \rightarrow {}^6H_{13/2}$ (∼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, and medical treatment [12,13]. Dy^{3+} has already been doped into the following chalcogenide bulk glasses: GeAsGaSe [14], GeAs (or Ga)S [15], GeAsSe [16], GeGaSbS [17], GeGaCdS [18], and AsSSeI

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[19]. A few chalcogenide glass systems without Ge or As elements also draw people's attention because of their particular properties. For example, Ga–La–S [20] and Ga–Na–S [21] glasses have been developed as host materials for RE dopants because a large amount of RE ions could be dissolved and dispersed in the low phonon energy hosts homogeneously, making the doped glasses promising candidates for IR amplifiers or lasers.

In this work, we investigated the preparation of Dy^{3+}-doped Ga–Sb–S and Ga–Sb–S-PbI_2 glasses for the first time. Their spectral properties excited at 808 nm were presented, and Judd–Ofelt analysis was performed. Effects of PbI_2 on the intensities of the 1748-, 2426-, and 2880-nm fluorescences were investigated and discussed. Our work aimed to elucidate the influence of glass composition 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

2.1. Sample preparation

$Ga_8Sb_{32}S_{60}$ and $80(Ga_8Sb_{32}S_{60})$-$20PbI_2$ (mol%) chalcohalide glasses were prepared by the melt-quenching method. High purity host glass elements, namely, Ga (5N), Sb (5N), S (5N), and PbI_2 (99.99%) together with 500 ppm Dy^{3+} (99.99%) ions were used to produce the glasses. The ampoule, containing the chalcogenide glass batch, was sealed under vacuum (10^{-5} Pa) and rocked for 16 h at 950 °C in a furnace to achieve melt-homogenization. Then, it was slowly cooled at 650 °C and maintained at this temperature for 2 h to obtain the condensation of the vapors present in the ampoule and their mixing to the melt. The batch is quenched in water at a fast cooling rate to allow the glass formation and to avoid crystallization process. After that, the vitreous sample is annealed near the glass transition temperature (T_g) to relax the internal mechanical stress induced by the quenching process. Finally, the annealed glass was cut and polished to mirror smoothness into slices (Φ10 mm × 2 mm).

2.2. Characterization

Measurements include density, refractive index, Vis–NIR transmission spectra, and optical spectra. Densities were measured by Archimedes method in CCl_4 liquor. The Perkin–Elmer Lambda 950 UV/VIS/NIR spectrophotometer was used to analyze near-infrared absorption spectra of the glass samples. The infrared luminescence spectra ranging from 1200 nm to 3500 nm were measured with an Edinburgh FLS 980 fluorescence spectrometer equipped with a T3015R4UO monochromator and a liquid-nitrogen cooled steady state InSb detector. The pumped light source adopted an 808-nm laser with power of 400 mW. All optical properties were measured on the polished plate-like samples at room temperature.

3. Results and discussion

3.1. Physical and thermal properties

The prepared glasses are black and homogeneous, which have no obvious defects and bubbles through infrared optical lens observation. An amorphous property was proven by XRD spectra. The density and refractive index data are measured and listed in Table 1. As can be seen, with incorporation of PbI_2 in the host, the density increased and the refractive index declined. Generally, the iodine acts as network terminator in the network structure and breaks down the connectivity of Sb–S and/or Ga–S bonds; therefore, the density should be decreased. Another influence on the density is the large atomic mass of PbI_2 (153.7), which is considerably larger than the average atomic mass of the Ga-Sb-S glass host (63.8). These two factors have contradicting effects, which can consequently lead to the maximum forming ability in the glass system and can primarily increase density because of the large atomic masses of Pb and I. As for the refractive index proportional to the polarization of the element, the larger value of I^- than S^{2-}-decreased the refractive value of the whole glass sample. The high refractive index (n) can lead to the increase of the stimulated emission cross-section (σ) of the doped (RE) ions in the glasses according to the empirical formula ($\sigma \sim (n^2+2)^2/n$). The concentration of doped Dy^{3+} can be calculated by the glass density and chemical composition, namely the quantity of Dy^{3+} per volume. The results are listed in the Table 1. The ionic concentration of Dy^{3+} increased with the introduction of metal iodides, indicating the improved RE ion solution ability in the glass system.

Table 1
Physical property of Dy^{3+}-doped chalcogenide glass samples.

Sample name	Density (g/cm^3)	Refractive index at 1.55 μm	Ionic concentration (cm^{-3})
GaSbS: Dy	4.157895	2.72	3.0817×10^{19}
GaSbS-PbI_2:Dy	4.531532	2.69	3.3586×10^{19}

3.2. Absorption spectra and Dy^{3+} energy transition

Fig. 1 presents the absorption spectra of Dy^{3+}-doped Ga-Sb-S and Ga-Sb-S-PbI_2 glass samples. Notably, the absorption spectra located in the wavelength range of 600–3500 nm before and after addition of metal iodides were similar. The main absorption bands centered at 808, 917, 1115, 1300, 1710, and 2830 nm, which belong to the transitions of Dy^{3+} from ground state $^6F_{3/2}$ to the excited states $^6F_{7/2}$, $^6F_{9/2}(^6H_{7/2})$, $^6F_{11/2}$ ($^6H_{9/2}$), $^6H_{11/2}$, and $^6H_{13/2}$, respectively. Obviously, the Dy^{3+} absorption intensity increased in the PbI_2-modified sample, which is attributed to the large density of metal iodides. After PbI_2 was introduced, the solution concentration of Dy^{3+} increased in the glass host with higher density, leading to strong absorption. In addition, the near-infrared absorption edge lies in the wavelength of 800 nm, which generated a light blue shift after PbI_2 was added in the glass matrix. According to the fact, the shortwave absorption edge of the glasses is related to the electrical transition between valence band and conduction band. The addition of anions I with a higher electronegativity than that of sulfur led to the blue shift of λ_{vis}, because high electronegativity indicates strong combination with electrons and high excitation energy. Meanwhile, the band broken effect of I^- ions in the glass network formed many nonbridge sulfur and iodides. The polarization rate of I^- is smaller than that of S^{2-}. Therefore, the weak polarization effect induced the blue shift of shortwave absorption edge. Herein, the energy structures and their related absorption cross sections are conjected according to the absorption spectra.

As seen in Fig. 2, different energy transitions of Dy^{3+} are demonstrated according to the absorption spectra. The absorption cross section of Dy^{3+} transition energy is calculated for both glass samples. The results show that the absorption cross section values were approximately 0.312×10^{-19} and 0.353×10^{-19} cm^2 for Ga-Sb-S: Dy and Ga-Sb-S-PbI_2: Dy glasses, respectively, in the wavelength of 1300 nm and approximately 0.113×10^{-19} and 0.14×10^{-19} cm^2 in the wavelength of 2880 nm for the two glasses. The increased absorption cross section indicated that the pump efficiency of the RE ions improved in the PbI_2-modified glass sample.