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Dy^{3+}-doped Ge-In-S-CsI chalcohalide glasses for 1.3 µm optical fiber amplifier

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Dy^{3+}-doped Ge-In-S-CsI chalcohalide glasses were prepared by the well-established melt-quenching technique, and the thermal stabilities, absorption spectra, densities, refractive indics, fluorescence spectra and lifetimes were investigated. The intensity parameters Ω_t *(t=2, 4, 6)*, transition probabilities, exited state lifetimes and the branching ratios were calculated by using the Judd-Ofelt theory. The radiative quantum efficiencies and emission cross sections of 1.3µm emission were then confirmed. The $64GeS_2{\cdot}16In_2S_3{\cdot}20CsI$ glass with good thermal stability (the glass transition temperatures T_g is 360°C and the difference between the onset crystallization temperature T_x and T_g is 149°C), long fluorescence lifetime (τ_{mea}= 154µs) and high radiative quantum efficiency (η=20.9%) is considered to be an attractive host material for 1.3 µm optical fiber amplifiers.

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1. Introduction

Chalcogenide and chalcohalide glasses doped with rare earth ions have been extensively investigated for optical amplifer at 1.3µm because of their high refractive indices and low phonon energies in comparison with fluoride and oxide glasses [1-4]. Particularly, attentions have been given to the Dy^{3+}-doped ones. Dy^{3+} has several advantages over Pr^{3+}-based amplifiers for 1.3µm telecommunication applications. First, for populating the $^6H_{9/2}$-$^6F_{11/2}$ level, Dy^{3+} has a good pump bands which can be pumped with a cheap commercial laser diode. Second, the emission cross section of the $^6H_{9/2}$-$^6F_{11/2}$ level is in general greater than the Pr^{3+}:$^1G_4$ level in the same host [5].

Several experimental attempts have been made to explore the Dy^{3+}-doped chalcogenide glasses fiber at 1.3µm. The As-S and Ge-S glasses exhibit a good thermal stability but poor rare earth solubility [6]. Ga-La-S glasses possess a high refractive index (2.4) and a high rare earth ions solubility limit. Unfortunately, Ga-La-S glasses have problems with thermal stability [7]. According to the report [8], when Gallium (Ga) added into Ge-S glasses, the rare earth ions solubility limit was significantly increased. Wei et al. [9] thoroughly investigated Ge-Ga-S glasses doped with Dy^{3+}, in which the highest Dy^{3+} solubility limit was about 1.4 wt% ($Ge_{25}Ga_5S_{70}$ glasses). However, the lifetime of the Dy^{3+}:$^6F_{11/2}$-$^6H_{9/2}$ levels of this glass was only 38 µs [1]. In order to further improve the optical and thermal properties, Jong Heo et al. added alkali halides into Ge-Ga-S glasses and made a meaningful improvement [2, 10].

It is well known that Indium (In) has the similar chemical properties with Gallium (Ga) but larger atomic weight, which results in much higher refractive index. Indium (In) also has the ability to improve rare-earth solubility limits in chalcogenide glasses [8]. What's more, CsI was introduced as the net modifier to optimize the Ge-In-S glasses, which acquire lower phonon energies [11, 12]. Nevertheless the works concerned with rare-earth doped Ge-In-S-CsI glasses are rarely reported.

In this work, the design and preparation of Dy^{3+}-doped Ge-In-S-CsI glasses were presented. Their absorption spectra, refractive indics, fluorescence spectra and lifetimes were investigated. The intensity parameters Ω_t *(t=2, 4, 6)*, transition probabilities, excited state lifetimes and the branching ratios were calculated by using the Judd-Ofelt theory. The radiative quantum efficiencies and emission cross sections of 1.3µm emission were confirmed. It is promising that Dy^{3+}-doped Ge-In-S-CsI glasses are a good candidate for 1.3 µm optical fiber amplifiers.

2. Experimental

2.1. Sample preparation

Considering that stoichiometric composition could result in high Dy^{3+} solubility limits [13], the compositions of the host chalcohalide glasses were $(1-x)(80GeS_2 \cdot 20In_2S_3) \cdot xCsI$ with x=0, 10 and 20, while x is the mole percent. For more concise, these glasses were labeled as S1, S2 and S3, respectively. The glasses were prepared by the well-established melt-quenching technique from the elements Ge, In, S (99.999% purity) and the compound CsI, Dy_2S_3 (99.9% purity). The mixture was placed in a fused silica ampoule and then sealed while being continuously evacuated down to a pressure of 10^{-4} Pa. The mixture was heated to 600 °C with a rate of 1 °C /min and raised to 1050°C within 5 h. Melted at this temperature for 12 h and then cooled down to 820-920 °C in 2 h depending on the glass composition. Then stopped the rock and preserved the temperature for 3h. Finally, the mixture was cooled to room temperature in water, and then transferred to an annealing oven, which was held at T_g for 5 h. The samples were cut into the form of disk and polished for measurements.

2.2. Measurements

The Dy^{3+} contents of the samples were confirmed by ICP-AES. The Vis-NIR absorption spectra were recorded by a Shimadzu UV-VIS-NIR Scanning Spectrophotometer. The refractive indices were measured by the variable angle spectral ellipsometry (WVASE32, J.A.Woollam, USA). DTA measurement was carried out by Perkin-Elmer differential thermal analyzer instrument (DTA7, USA) under N_2 at 10 °C /min. The fluorescence spectra and decay curves were recorded by an InGaAs detector (Judson, USA) when pumped by a laser diode at 808 nm.

3. Results and discussion

3.1. Thermal properties

The glass transition temperatures, T_g and the onset crystallization temperatures, T_x of individual glasses are given in Figure 1. The T_g is in the range of 325-360 °C. The T_x could be found in 449-474 °C range. With increasing of CsI content, T_g drops regularly and T_x increase slightly, which is attributed to the decrease of the dimensionality of the glassy network [11]. It is known that the criterion T_x-T_g is a critical parameter to evaluate the thermal stability and fiber-drawing property of glasses. The glass with the value of T_x-T_g > 100 °C is usually considered to have the ability to be drawn into fibers. It is shown that the valuses of T_x-T_g for these glasses are greater than 100 °C when CsI is added, indicating that they have good thermal stability and are preferable for fiber drawing.

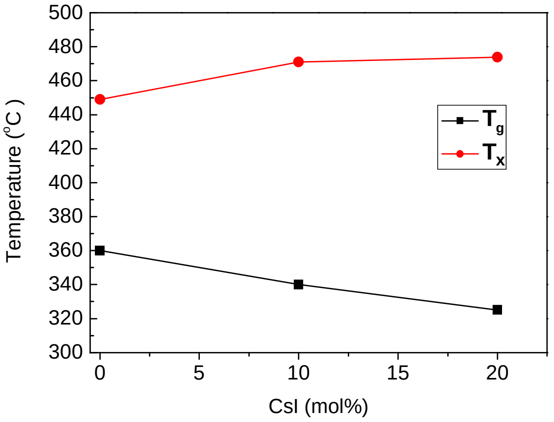

Fig. 1. T_g and T_x as a function of CsI content.

3.2. Optical properties

Fig. 2 shows the Vis-NIR absorption spectrum of S1 glass doped with 10,000 ppm Dy^{3+}. Optical absorption peaks at 760, 812, 916, 1112, 1298, 1710 and 2830 nm corresponding to electron transitions from Dy^{3+} ground state $^6H_{15/2}$ to $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6H_{7/2}$-$^6F_{9/2}$, $^6H_{9/2}$-$^6F_{11/2}$, $^6H_{11/2}$ and $^6H_{13/2}$ levels are observed. The location and spectral shape of the Dy^{3+} absorption bands are similar to those in oxide glasses. But the intensities are much stronger due to the high covalency and large refractive index of the chalcohalide glass [14].

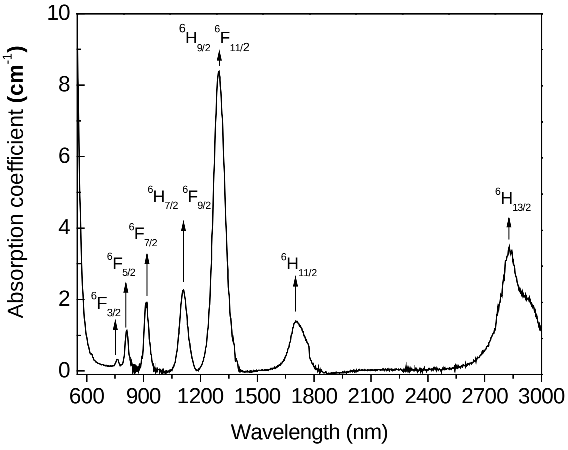

Fig. 2. Absorption spectrum of 10,000 ppm Dy^{3+} -doped Ge-In-S glass (thickness 2 mm)

Fig. 3 gives the effect of CsI addition in the Ge-In-S glasses on the short-wavelength absorption edges (defined as the wavelength where the half maximum of glass transmittance). It can be seen that with the addition of CsI changed from 0 to 20 mol%, the edge is shifted from 544 to 473 nm, and the color of the samples changed from red to yellowish accordingly. This is in favor of choosing proper excitation source. The blue-shift of the short-wavelength absorption edge can be explained by the electronegativity of the iodine atoms which reduces the electron delocalization in the glass network, and consequently, increases the bandgap energy [7].

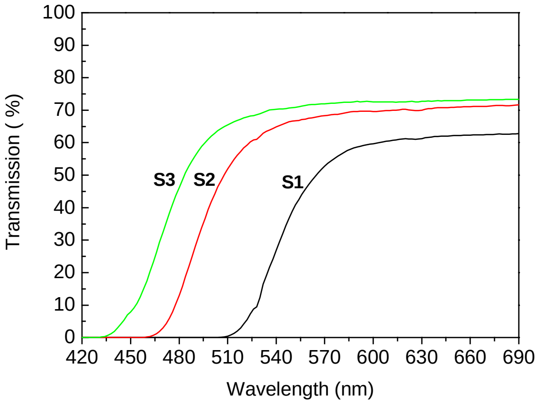

Fig. 3. Effect of CsI addition on the short-wavelength absorption edges of Dy^{3+}doped Ge-In-S-CsI glasses

Spectral dependencies of the refractive index were determined by the variable angle spectral ellipsometry. The refractive index collected as a function of wavelength at 375-1200 nm flowing the Cauchy dispersion formula, $n=A+B/\lambda^2+C/\lambda^4$ (where n is refractive index, A, B and C are constants, λ is the wavelength) are shown in Figure 4. A decrease of the refractive index is observed when the CsI amount was added, which is in accordance with the previous experimental results [11]. According to the Lorentz-Lorenz equation, the refractive index decreases as the ionic polarizabilities of glass constituents decrease [15]. Such a decrease was attributed to the smaller polarizability of I^{-} ions compared to the cations (Ge^{4+} and In^{3+}).

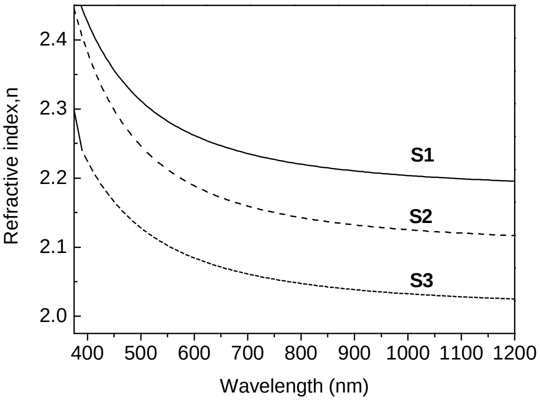

Fig. 4 Spectral dependencies of the refractive index of Dy^{3+}doped Ge-In-S-CsI glasses

Fig. 5 shows the emission spectra of S2 glasses doped with different concentration of Dy^{3+} ions. The observed emission bands near 1.1 and 1.3 μm originate from the optical transitions of Dy^{3+}: $^6F_{5/2}\rightarrow{}^6H_{13/2}$, $^6F_{9/2}$-$^6H_{7/2}\rightarrow{}^6H_{15/2}$, and $^6F_{11/2}$-$^6H_{9/2}\rightarrow{}^6H_{15/2}$, respectively. The inset figure shows the energy scheme of Dy^{3+} in our samples. It is found that the intensity of fluorescence decreases with increasing amount of Dy^{3+} ions. Obviously, the $^6F_{11/2}$-$^6H_{9/2}$ level for the 1.3 μm emission in Dy^{3+} suffers from strong concentration quenching effects at high concentrations. Such effects could include cross-relaxational energy transfer, upconversion and energy transfer to defect sites or impurity centers.

In principle, the longer the lifetime becomes, the more frequently the stimulated emission events occur. Therefore, the emission lifetime should be maximized. The 1.3 μm emission lifetimes of samples corresponding to S1, S2, and S3 doped with 1000 ppm Dy^{3+} were measured to be 110, 130, 154 μs. The lifetimes of the emission increase with the increasing CsI content.

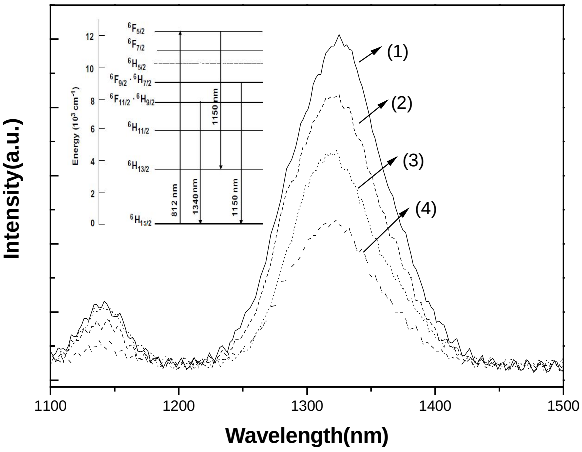

Fig. 5 Emission spectra of S2 glasses doped with (1) 1000ppm, (2) 2000ppm (3) 4000ppm and (4) 10000ppm Dy^{3+} ions.

3.3. Judd-Ofelt analysis

Judd-Ofelt analysis [16, 17] was used to determine the intensity parameters and other optical characteristics. Its application requires the computation of three intensity parameters Ω_2, Ω_4, and Ω_6 by a least-square fitting procedure. The Judd-Ofelt parameters Ω_t of Dy^{3+} in Ge-In-S-CsI glasses and other hosts are shown in Table 1. It can be seen that Ω_2 decreased with increasing CsI content while Ω_4 and Ω_6 showed similar change with increasing CsI content. Generally, Ω_2 is the most sensitive to the local structure and increases with the asymmetry of the local structure and the degree of covalence [1]. Ω_4 and Ω_6 is greatly affected by the ionic packing ratio of the host composition, which is reciprocally related to the host composition [18]. Therefore, the smaller Ω_2 value for Dy^{3+} in S2 and S3 glasses, compared with those of other Dy^{3+}

doped glasses, is the direct consequence of highly symmetrical and les covalent nature of the chemical bonds in Ge-In-S-CsI glasses. The observed decrease in Ω_4 and Ω_6 values with the addition CsI is due to the increasing ionic packing ratio of the host composition.

Table 1 Judd-Ofelt parameters of Dy^{3+} in various glasses

Host glasses	Ω_2	Ω_4	Ω_6	Reference
Ga-La-S	11.3	1.0	1.3	[19]
Ge-Ga-S	11.9	3.58	2.17	[1]
ZBLA	3.22	1.35	2.38	[20]
Phosphate	5.5	1.31	1.88	[21]
Tellurite	8.59	1.48	2.43	[21]
S1	11.32	1.1	1.94	This work
S2	6.45	0.76	0.57	This work
S3	5.29	0.43	0.29	This work

From the J-O parameters, the radiative emission probability of a transition is given by,

$$A\left(\alpha J,\alpha' J'\right)=\frac{64\pi^4 v^3}{3h\left(2J+1\right)}[\frac{n\left(n^2+2\right)^2}{9}\times S_{ed}+n^3\times S_{md}] \quad (1)$$

The total spontaneous emission transition rate of a manifold (A_{total}), the calculated radiative lifetime τ_{cal} of the excited state, the fluorescence branching ratio β and the radiative quantum efficiency of a level were detemined by,

$$A_{\text{total}}=\sum_{\alpha' J'} A\left(\alpha J,\alpha' J'\right)=\frac{1}{\tau_{cal}}, \quad (2)$$

$$\beta=\frac{A\left(\alpha J,\alpha' J'\right)}{A_{\text{total}}}, \quad (3)$$

$$\eta=\frac{\tau_{mea}}{\tau_{cal}} \quad (4)$$

Where h is Planck's constant, n is the index of refraction at the mean wavelength, J and J' are the total angular momentum of the initial and final states, respectively, the S_{ed} and S_{md} are the line strength for electric dipole and magnetive dipole transitions, τ_{mea} is the measured lifetime, respectively.

Total radiative transition rates, branching ratios, radiative lifetimes, measured lifetimes and the radiative quantum efficiency are shown in Table 2. The branching ratios, β of $^6H_{9/2}+^6F_{11/2}\rightarrow^6H_{15/2}$ transitions of these samples are 90.8%, 92.6% and 93.2%, respectively. The radiative lifetime of 1.3 µm emission levels increased from 236 µs for S1 glass (1000 ppm Dy^{3+}) to 305 µs for S3 glass containing 20 mol% of CsI. So the lifetime enhancement makes the glass potential material of 1.3 µm laser amplifier. Such lifetime enhancement was attributed to the refractive index change in the modified glasses and this in turn decreased the intrinsic spontaneous radiative transition rate [22]. Other explanation is related to change in the symmetry of the crystal field and decrease in the local refractive index in the vicinity of rare earth sites [23]. The local structure of Dy^{3+} was modified by CsI, and as a result the local refractive index near Dy^{3+} is significantly smaller than the overall macroscopic value [22, 24] Such variation lead to changing of the local field correction factor which is usually used to describe radiative intra-4f-configurational transitions of a lanthanide ion.

Table 2 Total radiative transition rates A_{rad}, and branching ratios β, radiative lifetimes τ_{rad}, measured lifetimes τ_{mea} and the radiative quantum efficiency η for Dy^{3+} in Ge-In-S-CsI glasses.

Sample	*Transition*	*Wavenumber* (cm^{-1})	A_{ed} (s^{-1})	A_{md} (s^{-1})	A_{rad} (s^{-1})	β (%)	τ_{rad} (µs)	τ_{mea} (µs)	$\eta=\tau_m/\tau_c$ (%)
S1	$^6H_{9/2}+^6F_{11/2}\rightarrow^6H_{11/2}$	1849	30.6	0.0	30.6	0.7	236	110	46.6
	$\rightarrow^6H_{13/2}$	4180	379.2	0.0	379.2	8.6			
	$\rightarrow^6H_{15/2}$	7463	4023.2	0.0	4023.2	90.8			
S2	$^6H_{9/2}+^6F_{11/2}\rightarrow^6H_{11/2}$	1849	12.1	0.0	12.1	0.6	489	130	26.6
	$\rightarrow^6H_{13/2}$	4180	139.4	0.0	139.4	6.8			
	$\rightarrow^6H_{15/2}$	7463	1893.6	0.0	1893.6	92.6			
S3	$^6H_{9/2}+^6F_{11/2}\rightarrow^6H_{11/2}$	1849	7.7	0.0	7.7	0.6	738	154	20.9
	$\rightarrow^6H_{13/2}$	4180	84.0	0.0	84.0	6.2			
	$\rightarrow^6H_{15/2}$	7463	1263.0	0.0	1263.0	93.2			

It is known that the product of $\sigma_{em}\times\tau_{\mathrm{mea}}$ is a figure of merit of laser potential [25]. The emission cross sections (σ_{em}) of 1.3 µm were calculated basing on the McCumber equation [26]

$$\sigma_{em}=\frac{\lambda_p{}^4}{8\pi cn^2\Delta\lambda_{eff}}A\left(\alpha J,\alpha' J'\right) \tag{5}$$

Where λp is the peak fluorescence wavelength, $\Delta\lambda_{eff}$ is the effective linewidth defined as full width in half maximum (FWHM), respectively. For comparison, the $\sigma_{em}\times\tau_{\mathrm{mea}}$ for the $^6H_{9/2}$-$^6F_{11/2}\rightarrow{}^6H_{15/2}$ transition of Dy^{3+}-doped chalcogenide glasses are shown in Table 3. The $\sigma_{em}\times\tau_{\mathrm{mea}}$ indicates that the Dy^{3+}-doped chalcohalide may be a vialable candidate for optical fiber amplifiers at 1.3µm.

Table 3 The σ_{em}, τ_{mea} of Dy^{3+}-doped in different chalcogenide glasses

Host glasses	σ_{em}	τ_{mea}	$\sigma_{em}\times\tau_{\mathrm{mea}}$	Reference
Ga-La-S	3.8	59	220	[19]
Ge-Ga-S	4.35	38	165.3	[1]
S1	3.84	110	421.9	This work
S2	1.94	130	252.6	This work
S3	1.42	154	217.9	This work

4. Conclusions

In summary, Dy^{3+}-doped Ge-In-S-CsI glasses have been successfully prepared with good optical and chemical quality. The T_g is about 325-360 °C and ΔT ranges from 89 °C to 147 °C. There Judd-Ofelt parameters are obtained and radiative parameters are calculated. The lifetime at 1.3 µm was enhanced with increasing amount of CsI. Such enhancement of lifetime is associated with the change of the refractive index in the modified glasses and in the vicinity of rare earth sites. All of these results indicate that the Dy^{3+} -doped Ge-In-S-CsI glass is a very promising candidate material for lasers, amplifiers, and high brightness sources in the near- and mid-infrared.

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