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Optical properties of Er-doped GeS_2-Ga_2S_3 glasses♣

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Erbium doped chalcogenide glasses are of great interest in integrated optoelectronics technology, due to their Er^{3+} intra-4f emission at the standard telecommunication wavelength of 1.54 μm. In this report, the optical absorption and photoluminescence (PL) of chalcogenide $(GeS_2)_{80}(Ga_2S_3)_{20}$ glasses doped with 0.6 and 1.8 mol % Er_2S_3 have been evaluated. The role of the excitation wavelength on the emission cross section at ~ 1540 nm, attributed to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} ion, has been specified, and basic optical properties have been determined. For this purpose, the Judd-Ofelt (J-O) theory has been applied to calculate the intensity Ω_λ parameters. Consequently, radiative properties such as the radiative transition probabilities (A_R), the total radiative transition probabilities (A_T) and the radiative lifetimes (τ_R) have been determined. In particular, the present glasses have exhibited relatively high τ_R values, of about 3.4 ms. The influence of the Er-doping level on the PL line-shape at ~1540 nm has been specified by such spectroscopic parameters as the full width at half maximum and the stimulated emission cross-section (σ_e) for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.

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1. Introduction

During recent years, chalcogenide Ge-S-Ga glasses have been considered as promising hosts for rare-earth (RE) elements. Much attention has been turned to the enhancement of the photoluminescence from RE ions suitable for integrated photonics [1-3]. In particular, glasses heavily doped with Er^{3+} ions are rather promising materials for the engineering of short wavelength optical amplifiers working at 1.54 μm [2,4]. The developments in telecommunication technologies have driven the required characteristics for host materials – a wide transparency to the infrared wavelengths, a high refractive index, a low phonon energy (i.e. low radiation losses), etc. [4]. All these properties have been realized in Ge-S-Ga glasses. Especially, the introduction of Ga into Ge-S glasses leads to a significant modification of the structure, to allow a relatively large RE solubility [4].

Recently, we have studied the compositional trends in the physicochemical, optical and structural properties of erbium doped Ge-S-Ga glasses, by incorporating Er from 0.1 to 1.4 at % [5-7]. The peculiarities in the main PL band at 1540 nm, as a function of Er-doping level, excitation wavelength and temperature have been specified.

In the present work, the basic optical parameters of $(GeS_2)_{80}(Ga_2S_3)_{20}$ glasses doped with 0.6 and 1.8 mol % Er_2S_3 have been estimated on the basis of their absorption and emission, using the Judd-Ofelt (J-O) theory [8,9]. The role of the excitation wavelength has also been evaluated.

2. Experimental

Starting compositions of $(GeS_2)_{80}(Ga_2S_3)_{20}$ doped with 0.6 and 1.8 mol % Er_2S_3 were selected in this work. The glasses were prepared by the well known technique of conventional rapid quenching of melts in ice-water (the details are given in [5]) The absorption spectra were measured on optically polished samples with thicknesses of ~1 mm by a Perkin Elmer Lambda 900 UV-VIS-NIR spectrophotometer in the wavelength region 600-1700 nm. The PL spectra were measured at room temperature under excitation by a Nd:YAG laser (λ = 1064 nm) [5] and an Ar^+-ion laser (λ = 514.5 nm) [6]. The amorphous state and uniformity of the samples were checked by X-ray diffraction and electron microscopy.

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2.1. Theoretical background

According to the Judd-Ofelt theory of the 4f-4f intensity model [8,9], the oscillator strength of a transition between two multiplets ψJ and $\psi' J'$ is given by the equation

$$f(\psi J;\psi' J') = \frac{8\pi^2 mc\nu}{3h(2J+1)}\left[\frac{(n^2+2)^2}{9n}\right] \times \sum_{\lambda=2,4,6} \Omega_\lambda (\psi J \| U^\lambda \| \psi' J')^2 \quad (1)$$

where m is the electron mass, c is the speed of light, e is the electron charge, h is Planck's constant, $\frac{(n^2+2)^2}{9n}$ is the Lorentz local field correction for the absorption, n is the refractive index, and $\|U^\lambda\|^2$ is the doubly reduced matrix element of the unit tensor operator of rank λ calculated from the intermediate coupling approximation. In our case, we have utilized the reduced matrix elements reported in [10]. The Judd-Ofelt intensity parameters Ω_λ (λ = 2, 4, and 6) can be determined from a least squares fit, by equalizing the experimental and calculated oscillator strengths, and on their basis, the spontaneous radiative probabilities between ψJ and $\psi' J'$ levels are calculated by

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

where ψJ and $\psi' J'$ are the initial and final states, ν is the energy gap between the states, and S_{ed} and S_{md} are the electric and magnetic dipole line strengths, respectively. Then, the total radiative transition probability of an excited state is given by the sum of the spontaneous emission rates of all the excited states:

$$A_T(\psi J) = \sum_{\psi' J'} A_R(\psi J;\psi' J'). \quad (3)$$

The radiative lifetime of an excited state (ψJ) can be extracted from the total radiative transition probability using the relation

$$\frac{1}{\tau_R} = A_T(\psi J) \quad (4).$$

The stimulated emission cross-section, which is a very important parameter that influences the potential laser performance, is determined by the Fuchtbauer-Ladenburg relation [11]:

$$\sigma_e = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}} A_R(\psi J;\psi' J') \quad (5)$$

where the λ_P and $\Delta\lambda_{eff}$ values are the wavelength and effective bandwidth of the emission peak, respectively.

3. Results

The optical absorption bands at ~1540 nm of the present samples are shown in Fig. 1. It is seen that the line-shape strongly depends on the erbium concentration, being broadened in the more heavily doped sample. The experimental oscillator strength (f_{exp}) is directly proportional to the area of the absorption band. The obtained Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, and 6) are summarized in Table 1. The accuracy of the applied least-square fitting method between the experimental and the calculated oscillator strengths was checked by the obtained small root-mean-square (*rms*) deviation (± 0.117 for 0.6 mol % Er_2S_3 and 0.033 for 1.8 mol % Er_2S_3). On the basis of the obtained Ω_2, Ω_4 and Ω_6 values, the total radiative transition probability of the excited state was calculated, and consequently the radiative lifetime (τ_R) for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions was determined (Table 1).

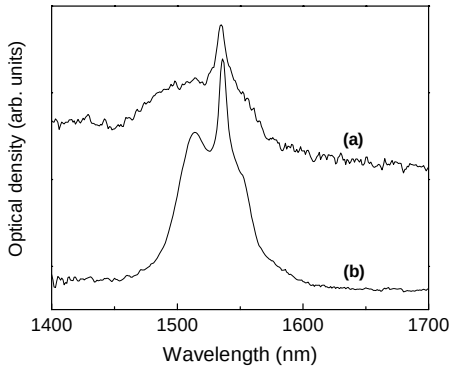

Fig. 1. Absorption bands of the Er_2S_3-doped $(GeS_2)_{80}$ $(Ga_2S_3)_{20}$ glasses: (a) 0.6 mo l % Er_2S_3 and (b) 1.8 mol % Er_2S_3.

Table 1. Radiative and spectroscopic parameters of Er-doped $(GeS_2)_{80}(Ga_2S_3)_{20}$ glasses

Er_2S_3 content (mol %)	**0.6**	**1.8**
Peak PL wavelength (μm)	1.54	1.55
Optical energy gap, E_g^0 (eV)	2.77	2.63
J–O intensity parameters, Ω_λ ($\times 10^{-20}$ cm^2)		
Ω_2	1.287	0.560
Ω_4	0.418	0.787
Ω_6	1.019	0.614

Radiative life time, τ_R (ms)	2.96	3.78
FWHM (nm)		
λ_{exc} = 1064 nm	36.7	78.1
λ_{exc} = 514.5 nm	23.5	40.8
Stimulated PL cross-section, σ_e ($\times 10^{-21}$ cm^2)		
λ_{exc} = 1064 nm	14.48	5.291
λ_{exc} = 514.5 nm	22.47	9.933

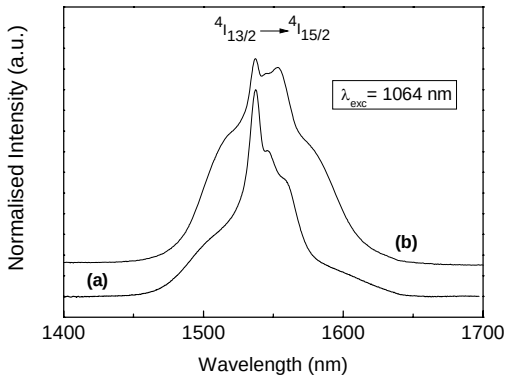

Fig. 2. Normalized PL bands of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in Er^{3+} of the glasses at λ_{exc}=1064 nm: (a) 0.6 mol % Er_2S_3 and (b) 1.8 mol % Er_2S_3.

The normalized PL spectra of the glasses studied, measured at room temperature under direct excitation of Er^{3+} ions (λ_{exc} = 1064 nm), are presented in Fig. 2. A broadening PL effect with increasing Er_2S_3 content from 0.6 to 1.8 mol % is observed, accompanied by an increase in the full width at half maximum (FWHM) of about two times (Table 1). This effect is even more pronounced under excitation by absorption via the host at λ_{exc} = 514.5 nm (Fig. 3). Additionally, the comparison of PL bands in Figs. 2 and 3 shows a narrowing of the PL effect under excitation via the host - the FWHM values decrease from 37 to 24 nm for 0.6 mol % Er_2S_3 and from 78 to 41 nm for 1.8 mol % Er_2S_3.

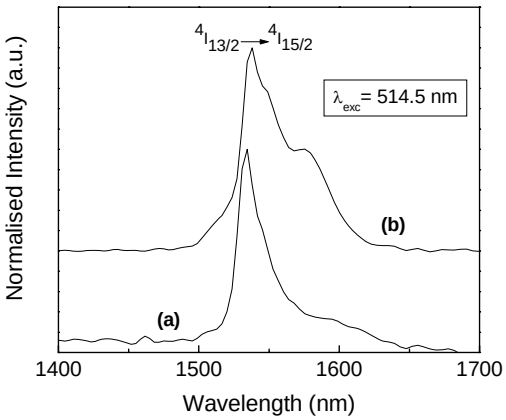

Fig. 3. Normalized PL bands of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in Er^{3+} of the glasses at λ_{exc}=514.5 nm: (a) 0.6 mo l % Er_2S_3 and (b) 1.8 mol % Er_2S_3.

On the other hand, enlargement of the stimulated emission cross-section of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition for lower Er doping at 514.5 nm excitation was found.

4. Discussion

The radiative properties of rare-earth ions in different host materials can be described by application of the Judd-Ofelt theory. The J-O intensity parameters are important for evaluation of the local structure and bonding arrangements of RE ions in the glassy matrix. It should be noted that compared to other similar chalcogenide glasses, the present ones possess relatively high radiative lifetimes, 2.96 and 3.78 ms at 0.6 and 1.8 mol % Er_2S_3, respectively. In a previous paper [7], a shift of the absorption edge towards lower energies of these glasses has been observed, and consequently, the corresponding optical energy gap (E_g^0) decreases from 2.77 to 2.63 eV (Table 1).

The observed broadening effect of both the absorption and the photoluminescence bands with increasing Er_2S_3 content from 0.6 to 1.8 mol % (Figs. 1-3) means that the emission is exhibited by more optically active Er^{3+} ions at higher doping levels. Such behaviour could also be attributed to a self-absorption effect [12].

The role of the Er content on the PL line-shape is demonstrated by FWHM enlargement at excitation wavelengths corresponding both to intra 4f-shell transition in Er^{3+} ions (λ_{exc} = 1064 nm, from 37 to 78 nm) and to absorption in the Urbach tail of the glassy host (λ_{exc} = 514.5 nm, from 24 to 41 nm). However, the stimulated emission cross-section of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, which is of greatest practical importance, is highest at the lower Er doping level of 0.6 mol % Er_2S_3.

5. Conclusions

The study of $(GeS_2)_{80}(Ga_2S_3)_{20}$ glasses doped with 0.6 and 1.8 mol % Er_2S_3 has shown that: (i) the emission is connected with the occupation of different microscopic environments by the active Er^{3+} ions at higher doping levels, which should be attributed to a self-absorption effect; (ii) the obtained radiative lifetimes, about 3.2 ms, are relatively high by comparison with similar Er^{3+}-doped chalcogenide glasses; (iii) the introduction of increasing amounts of Er^{3+} leads both to a broadened PL band under direct excitation of Er^{3+} ions and by absorption via the host. A narrowing PL effect in the latter case is observed, whereas the stimulated emission cross-section of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is mostly enhanced at the lower Er doping level.

Acknowledgements

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