Photoluminescence and local structure in GeS_2-Ga_2S_3-Er_2S_3 glasses

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In this report, some main results on the photoluminescence (PL) of $(GeS_2)_{80}(Ga_2S_3)_{20}$ glasses doped with different amounts of Er (from 0.2 to 1.4 at %) have been performed. The broad PL band centred at ~1540 nm has been characterized, according to the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition in the energy Stark splitting diagram of Er^{3+} state. The influence of Er content on the PL line-shape at 300, 77 and 4.2 K has been studied. A quenching effect at 1.22 at % Er has been established from the development of the emission cross-section by increasing Er^{3+}-doping level. Decreasing temperature down to 4.2 K, a narrowing effect of the emission cross-section has been observed, which leads to improved PL efficiency. The distribution and changes of the basic structural units in the glasses studied have been defined by Raman scattering in the range of 50-550 nm.

1. Introduction

Erbium doped chalcogenide glasses have been intensively studied for their possible applications in telecommunications because of the Er^{3+} intra-4f emission at ~1.54 μm [1-5]. Some chalcogenide glasses with low phonon energy, high infrared transmittance and high refractive index can be considered as efficient hosts for rare earth doping. In particular, the molecular structure formed by introduction of Ga into Ge-S glasses determines the relatively large solubility of rare earth elements [2,4,6].

Recently, we have studied the influence of Ga content, excitation wavelength and temperature on the photoluminescence properties of Er-doped Ge-S-Ga glasses [7-9]. It has been found that PL intensity increases about 30 times at 0.35 at % Er-doped $(GeS_2)_{75}(Ga_2S_3)_{25}$ glasses [7]. The observed decrease both of the optical energy gap and the host luminescence with Er doping confirms our suggestion that erbium may reduce the number of native defects, improving the structure [8]. The PL efficiency considerably increases by temperature decreasing down to 4.2 K, accompanied by a well expressed narrowing effect of the emission cross-section [9]. Photoluminescence in Er-implanted amorphous Ge-S-Ga thin films has been studied in our earlier paper [10]. In the present paper, some main results on the peculiarities in photoluminescence and local ordering of Er-doped $(GeS_2)_{80}(Ga_2S_3)_{20}$ glasses as a function of Er^{3+} doping concentration have been summarized.

2. Experimental

Bulk glasses with starting compositions of $(GeS_2)_{80}(Ga_2S_3)_{20}$: xEr_2S_3, where x=0.3, 0.6, 0.9, 1.8 and 2.4 mol % (corresponding to 0.17, 0.35, 0.52, 1.05, 1.22 and 1.39 at % Er, respectively) were prepared from appropriate mixtures of GeS_2, Ga_2S_3 and Er_2S_3. The synthesis procedures of GeS_2 and Ga_2S_3 compounds are described in Ref. [7]. Commercial Er_2S_3 was used as the dopant. The materials were loaded into evacuated to ~10^{-3} Pa silica ampoules, flame sealed, heated up to about 1000 °C for 24 h in a rocking furnace and quenched in ice water. The amorphous state and homogeneity of the samples were checked by X-ray diffraction and electron microscopy.

The photoluminescence and Raman spectra were measured at room temperature with excitation line 1064 nm of Nd:YAG laser in back scattering geometry by FT-spectrometer IFS-55FRA 106 (Bruker) with a Ge-detector cooled by liquid nitrogen. Laser power 50 mW was applied and 50 scans were averaged. A Fourier-Transform Photoluminescence Spectrometer (MIDAC Corp. USA) was used for the low-temperature PL measurements at 77, 4.2 K, and at 300 K as well. The samples were excited with Ar^+ laser (λ=514.5 nm) with 200 mW cm^{-2} power density. The PL signals were detected by a liquid-nitrogen cooled Ge- photodiode and were recorded by averaging out 10 recorded scans by resolution of 2 meV.

3. Results and discussion

The measured at room temperature PL spectra of the glasses studied are summarized in Fig. 1. At the used excitation wavelength of 1064 nm only the $^4I_{13/2}$ level in the energy diagram of Er^{3+} ion can be excited, therefore the obtained PL band at ~ 1540 nm is due to the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition [5]. The influence of Er concentration is clearly expressed by the enlarged emission cross-section up to 1.22 at % Er, following by a considerable decrease of PL intensity at 1.39 at % Er, moreover, the amplitude of the corresponding band is lower than that at 1.05 at % Er-doping. Obviously, a non-uniform distribution of Er atoms probably occurs in such case, accompanied by Er clustering, which causes the quenching effect of the Er^{3+} emission.
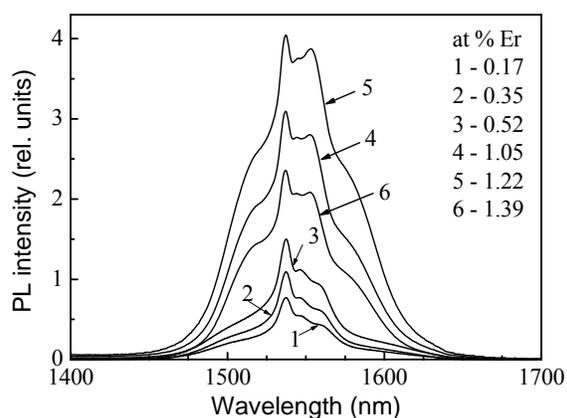
Fig. 1. Photoluminescence spectra of the glasses studied under 1064 nm excitation at room temperature.

Fig. 2. Photoluminescence spectra of the glasses studied under 514.5 nm excitation at 4.2 K.

The low-temperature emission at 77 and 4.2 K is excited by 514.5 nm radiation, corresponding to the host absorption. The influence of erbium on the PL line at 4.2 K is shown in Fig. 2. Comparing the results with those at room temperature in Fig. 1, a narrowing effect of the mean PL peak at ~ 1540 nm is well pronounced. PL quenching with the Er content increase up to 1.22 at % Er is maintained, only the subsequent decrease of the emission cross-section at 1.39 at % Er is not so strongly manifested as at room temperature (Fig. 1).

The role of temperature on the line-shape of the emission cross-section can be clearly defined by deconvolution of the experimental PL spectra. As an example, the observed fine features of Er^{3+} emission at 514.5 nm excitation for the quenching sample are illustrated in Fig. 3. The PL spectrum at room temperature exhibits rather broad total band, which can be presented as a sum of four Gaussian sub-bands, centred at ~ 1520, 1538, 1554 and 1570 nm (Fig. 3a). Following the energy Stark splitting diagram of Er^{3+} [5,11], they are attributed to the transitions F_{21}, F_{11}, F_{12} and F_{13}, respectively. It should be mentioned that the observed broadening is mainly due to the enhanced development of the sub-bands at 1520 and 1570 nm. At 77 K, a new band at 1546 nm appears at the expense of that at 1554 nm, the intensity of the sub-band at 1520 nm drastically decreases and as a result the PL global band becomes more narrow (Fig. 3 b). With decreasing the temperature down to 4.2 K, the intensity of the sub-bands at 1546 and 1570 nm decreases, while that at 1520 nm disappears (Fig. 3 c). The amplitude of the sub-band at 1538 nm, coinciding with the total one, considerably increases and a well pronounced narrowing effect is exhibited. Consequently, with the temperature decrease the population of the second sub-level of the $^4I_{13/2}$ manifold also decreases and the Er^{3+} emission occurs mainly by the transition F_{11}, assisted by F_{12} and F_{13} ones.
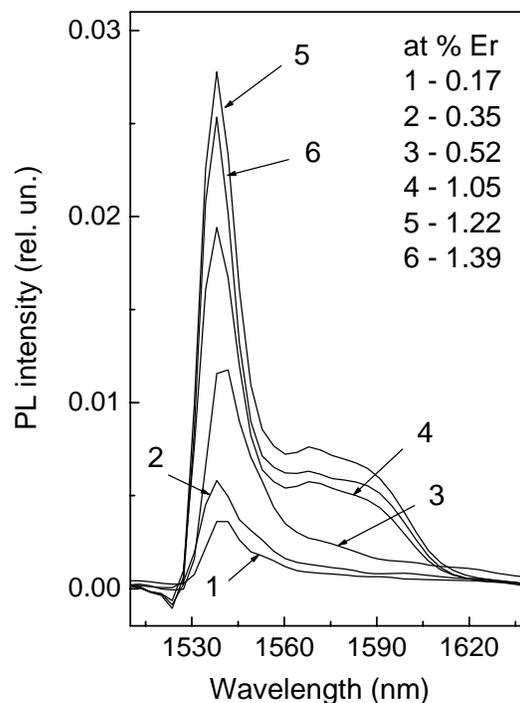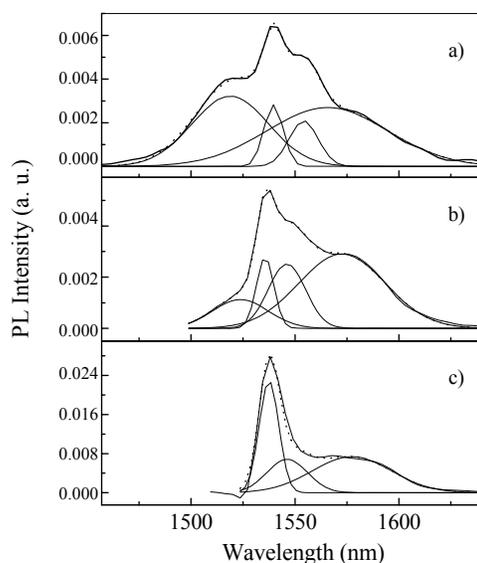

Fig. 3. Deconvoluted PL spectra under 514.5 nm excitation: a) room temperature, b) 77 K, c) 4.2 K.

The local ordering features of the glasses studied are specified by Raman scattering analysis (Fig. 4). It is known that the basic structural units (s. u.) in Ge-S-Ga glasses are GeS_4- and GaS_4- tetrahedra connected through bridged sulfur [12,13]. In fact, the strongest band at ~340 cm^{-1} is due to the symmetric stretching vibration of $[GeS_{4/2}]$ s.u., while that ~110 cm^{-1} is associated with symmetric bending vibration of $[GeS_{4/2}]$ s. u.
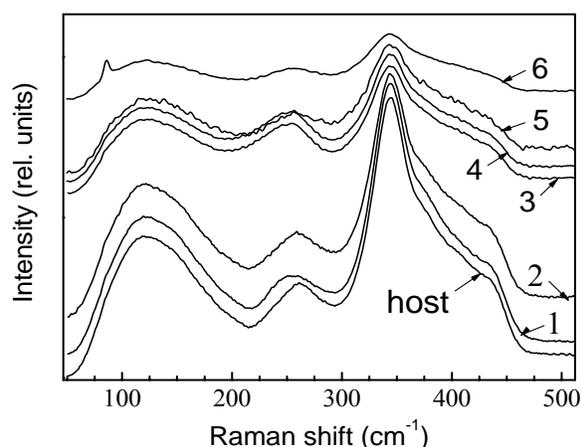
Fig. 4. Raman spectra of the glasses studied (the number notation is the same as in Fig. 1).

The shoulder at ~380 cm^{-1} is known as a companion band which is due to the vibration of two edge-shared GeS$_4$ tetrahedra Since Ga is in trivalent bonding state, the GaS$_4$ tetrahedron has one negative charge because of the deficiency of sulfur, resulting in the creation of defects such as [GaS$_4$]$^{1-}$. On the other hand, the atomic mass of Ga is similar to that of Ge, so that the frequency of GaS$_4$ vibration is only slightly larger than that of the GeS$_4$ tetrahedra and the corresponding Raman bands can not be distinguished in the range of 340-390 cm^{-1}. The broad band at ~ 440 cm^{-1} is assigned to the vibration of two corner-shared S$_3$Ge-S-GeS$_3$ tetrahedra, while that at 260 cm^{-1} is ascribed to the vibration of two tetrahedra with ethane-like S$_3$Ge(Ga)-(Ga)GeS$_3$ type of bonds [13].

It is clearly seen that the introduction of Er$_2$S$_3$ leads to decrease in the amplitude of all the bands. The variation of Raman bands is clearly illustrated from the deconvoluted spectrum of the host and that at maximum Er doping (Fig. 5, Table 1).

Table 1. Data from Raman spectra deconvolution

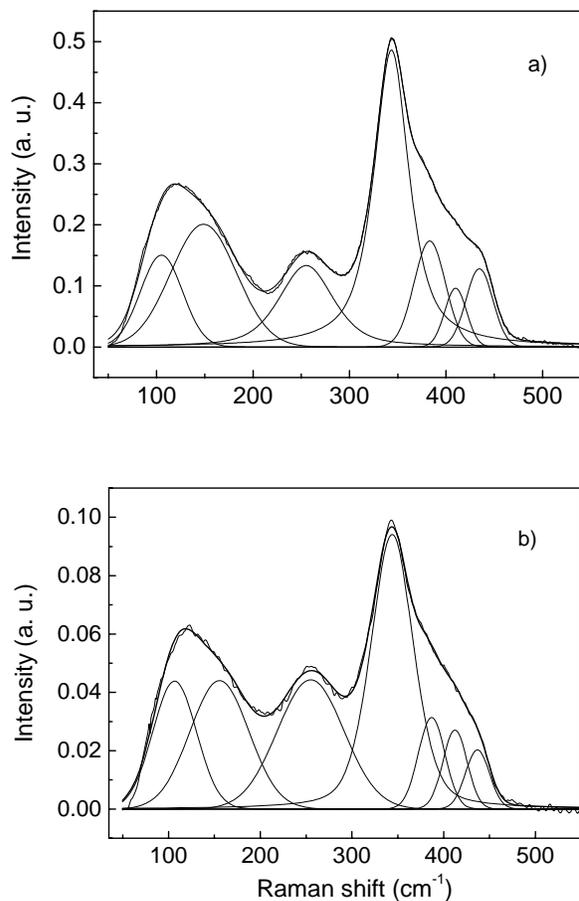| Raman shift (cm^{-1})	host		1.4 at % Er	
	Area	Height (a. u.)	Area	Height (a. u.)
107	8.22	0.15	2.61	0.04
156	17.13	0.20	3.54	0.04
255	11.71	0.13	4.04	0.04
344	30.76	0.49	6.39	0.09
387	7.06	0.17	1.14	0.03
412	2.74	0.10	0.89	0.03
437	4.46	0.13	0.67	0.02
total	82.07		19.28	

Fig. 5. Deconvolution of Raman spectra for: a) host, b) at 1.4 at % Er doping level.

In particular, the height decrease of the 260 cm^{-1} band about three times with addition of Er$_2$S$_3$ could be a sign for the dissociation of Ge-Ge bonds This is accompanied by a decrease of one at 340 cm^{-1}, about five times, which is associated with the formation of tetrahedral with non-bridging sulfurs.. Increasing Er$_2$S$_3$ concentration, edge-shared GaS$_4$ tetrahedra are converted into corner-shared ones with non-bridged sulfurs. The presence of the [GaS$_4$]$^{1-}$ tetrahedra determines the role of Er^{3+} ions as charge compensators for these non-bridged sulfurs. Therefore, while, in general a variety of defects may be induced by doping, in the present case the incorporation of Er^{3+} ions in the glassy host decreases the number of structural defects [8].

4. Conclusions

The photoluminescence of the studied Er-doped (GeS$_2$)$_{80}$(Ga$_2$S$_3$)$_{20}$ glasses is exhibited by a broad emission band at ~1540 nm, which is related to the ^{4}I$_{15/2}$→^{4}I$_{13/2}$ transition. Decreasing temperature down to 4.2 K, a well pronounced narrowing effect of the PL line-shape has been established. This is connected with the drastically increase

of PL intensity of the sub-band at 1538 nm and disappearance of the sub-band at 1520 nm. Consequently, with temperature decrease the population of the second sub-level of the $^4I_{13/2}$ manifold also decreases and the Er^{3+} emission occurs predominately by the transition F_{11} in the corresponding Stark splitting diagram. Introduction of erbium modifies the local structure by converting the edge-shared GaS_4 tetrahedra into corner-shared ones with non-bridged sulphurs, which are charge compensated by the Er^{3+} ions.

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