

LOW-TEMPERATURE LUMINESCENCE QUENCHING AND LOCAL ORDERING STUDY OF Er-DOPED Ge-S-Ga GLASSES

Z. G. Ivanova^{*}, R. Ganesan^a, K. V. Adarsh^a, V. S. Vassilev^b, Z. Aneva, Z. Cernosek^c,
E. S. R. Gopal^a

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

^aDepartment of Physics, Indian Institute of Science, 560 012 Bangalore, India

^bDepartment of Semiconductors, Chemical Technology and Metallurgy University, 8 Blvd. Kl. Ohridski, 1756 Sofia, Bulgaria

^cInstitute of General and Inorganic Chemistry, University of Pardubice, 565 nam. Legii, 532 09 Pardubice, Czech Republic

Photoluminescence (PL) spectroscopy by excitation with 514.5 nm light at 4.2 and 77 K is applied to $(\text{GeS}_2)_{80}(\text{Ga}_2\text{S}_3)_{20}$: x mol % Er_2S_3 (x=0.3, 0.6, 0.9, 1.8, 2.1 and 2.4) glasses. The compositional dependence of the PL intensity is determined, and a quenching effect accompanied by the strongest absorption at 1.22 μm is established. The influence of temperature on the emission cross-section is investigated by deconvolution of the experimental spectra, and the observed fine features are explained on the basis of the energy level diagram of Er^{3+} ions. The distribution and changes of the structural units at higher Er concentrations are specified by Raman scattering, in the range 50-550 cm^{-1} .

(Received December 2, 2004; accepted January 26, 2005)

Keywords: Chalcogenide glasses, Er-doping, Low-temperature luminescence, Ge-S-Ga glass

1. Introduction

Chalcogenide glasses are of great interest for a variety of photonic applications such as memory switches, frequency converters and optical amplifiers. This is due to their low phonon energy, extended infrared transparency, high refractive index, good thermal and chemical stability, etc. [1]. It has been found that Ge-S-Ga glasses dissolve relatively large amounts of rare-earth elements, which relates to their molecular structure, as formed by the addition of Ga [2]. In particular, erbium doped materials have attracted special attention in the field of integrated optoelectronics technology, because of their Er^{3+} intra-4f emission at 1.54 μm , a standard telecommunications wavelength [1,3]. Photoluminescence (PL) studies have shown that the strength of the broad band excitation of Er^{3+} ions increases in more heavily doped samples. Furthermore, at low temperatures, a direct link between the broad band excitation process and the host glass luminescence has been observed [4]. Recently, Er-doped Ge-S-Ga glasses have been characterized by their physicochemical, structural and fluorescence properties [5,6]. In this report, the influence of Er doping on the PL efficiency of a $(\text{GeS}_2)_{80}(\text{Ga}_2\text{S}_3)_{20}$ glassy host at 4.2 and 77 K and on the local structural features is studied.

^{*} Corresponding author: zojagiv@pronto.phys.bas.bg

2. Experimental details

Bulk glasses of $(\text{GeS}_2)_{80}(\text{Ga}_2\text{S}_3)_{20}$: x mol % Er_2S_3 ($x = 0.3, 0.6, 0.9, 1.8, 2.1$ and 2.4 , i.e. doped with 0.17, 0.35, 0.52, 1.05, 1.22 and 1.39 at % Er, respectively) were prepared by the well known melt quenching technique [5]. The photoluminescence measurements were carried out at 4.2 and 77 K, using a Fourier-Transform Photoluminescence Spectrometer (MIDAC Corp. USA). The samples were excited with an Ar^+ laser radiation of wavelength $\lambda = 514.5$ nm ($E = 2.41$ eV), and the PL signals were analyzed using a Michelson interferometer and detected by a liquid nitrogen cooled Ge photo diode. The interferograms, with a resolution of 2 meV, were recorded by averaging 10 scans. Pulse excitation using the argon laser was used to avoid the possibility of PL fatigue. The infrared transmission spectra were measured on optically polished samples, using a Bruker FTIR spectrophotometer. The Raman spectra were measured at room temperature in a back scattering geometry with a Bruker IFS-55 FRA 106 FT-spectrometer, using the 1064 nm (Nd:YAG laser) excitation line and a Ge-detector cooled by liquid nitrogen.

3. Results and discussion

Fig. 1 presents the compositional dependence of the photoluminescence intensity at temperatures of 4.2 and 77 K. Introducing Er concentrations of up to 1.22 at % result in an increase of the PL efficiency. Further doping leads to a non-uniform distribution of Er atoms and to a decrease in the PL decrease. The intensity becomes remarkably higher with decreasing temperature. In particular, the PL signal at 4.2 K for 1.22 at % Er-doped composition is about three times stronger than that at 77 K.

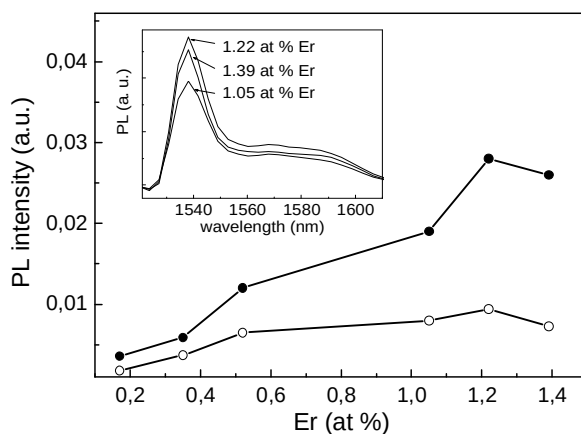


Fig. 1. Compositional dependence of the PL intensity at 4.2 K (●) and 77 K (○). The quenching effect is shown in the inset.

The influence of temperature on the emission cross-section of the quenching composition is shown in Fig. 2. The PL band resulting from 514.5 nm excitation is centred at around 1540 nm, which is associated with the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition in the Er^{3+} ion [4]. It is seen that the PL intensity increases with decreasing temperature, with the peak also becoming sharper and more intense. With increasing temperature, the population of the upper sublevels of the $^4\text{I}_{13/2}$ level also increases, and causes splitting of the main band [7]. The observed features can be specified by deconvoluting the experimental spectra. At 4.2 K (Fig. 2 a), the total PL band may be presented as a sum of three Gaussian sub-bands, centred at $\sim 1538, 1546$ and 1577 nm. The sub-band at 1538 nm is very strong and intense, resulting in a narrow main peak. At 77 K (Fig. 2 b), this sub-band is drastically reduced at the expense of that at 1577 nm, and a new sub-band at 1524 nm appears. All these features lead to a broadening of the PL emission cross-section.

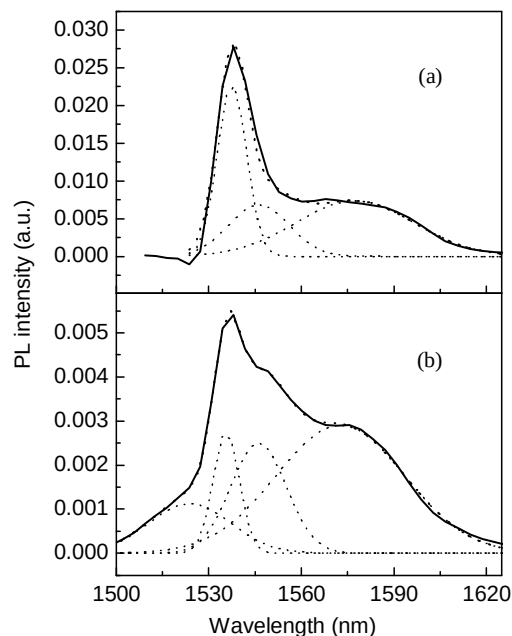


Fig. 2. Deconvoluted PL spectrum for 1.22 at % Er doping at 4.2 K (a) and 77 K (b).

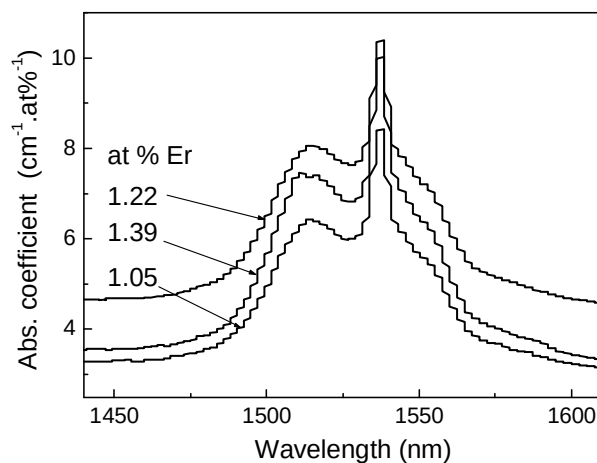


Fig. 3. Absorption spectra for 1.05, 1.22 and 1.39 at % Er doping.

The optical absorption spectra of the compositions with 1.05, 1.22 and 1.39 at % Er, obtained from the corresponding transmission spectra, are presented in Fig. 3. They are normalized with respect to Er concentration, and reflect how much light is absorbed by 1 at % Er. The optical activation of Er atoms is clearly expressed by the obtained $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition band. The shape of the absorption line strongly depends on the concentration - the absorption is largest at 1.22 at % Er, corresponding to the quenching composition. The influence of Er on the local structure of these compositions is specified by their Raman spectra (Fig. 4). The peaks at around 340 and 120 cm^{-1} are attributed to symmetrical bending vibrations of GeS_4 tetrahedra, while the shoulder at 370 cm^{-1} is assigned to the vibration of two edge-shared tetrahedra. In addition, the increased width of the 340 cm^{-1} band is considered to be due to the formation of GaS_4 tetrahedra, leading to a cross-linked glassy network. Since the atomic mass of Ga is similar to that of Ge, the frequency of the GaS_4

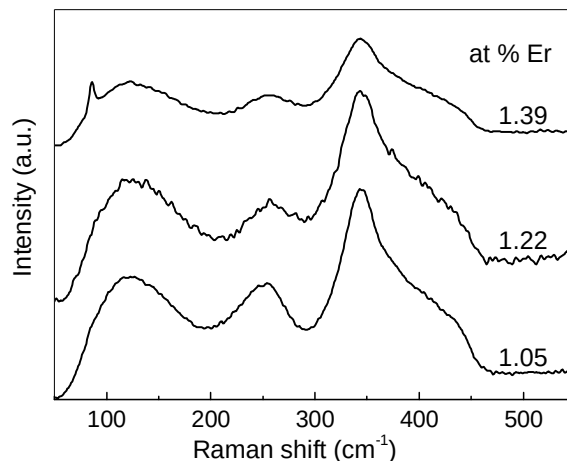


Fig. 4. Raman spectra for 1.05, 1.22 and 1.39 at % Er doping.

vibration is only slightly larger than that of the GeS_4 one. The band at 265 cm^{-1} is associated with the formation of $\text{S}_3\text{Ge}(\text{Ga})-(\text{Ga})\text{GeS}_3$ bonds. The wide band at about 430 cm^{-1} is assigned to the vibration of two corner-shared tetrahedra, through a bridged sulphur. The introduction of erbium decreases the amplitude of the bands at 265 and 340 cm^{-1} , resulting in the disruption of metal Ga-Ga bonds and the formation of corner-shared tetrahedra with non-bridged sulphurs. Furthermore, edge-shared GaS_4 tetrahedra are dissociated into corner-shared ones, with the creation of non-bridged sulphurs. The Er^{3+} ions are expected to act as charged compensators for these non-bridged sulphur atoms. It has been found [2] that a chemical reaction between Ga_2S_3 and Er_2S_3 , forming the ternary Er_3GaS_6 compound, can also cause enhanced Er^{3+} solubility.

4. Conclusions

The evaluation of the obtained results has shown that: (i) the introduction of 1.22 at % Er into a $(\text{GeS}_2)_{80}(\text{Ga}_2\text{S}_3)_{20}$ glassy host leads to a photoluminescence quenching effect at 4.2 and 77 K accompanied by strongest absorption; (ii) the global PL band at the higher temperature is rather broadened. This is due to both the drastically decrease of the sub-band at 1538 nm at the expense of that at 1577 nm and the appearance of a new sub-band at 1524 nm; (iii) Er^{3+} ions modify the structure, by breaking the tetrahedra connected through bridged sulphur atoms, and act as charge compensators for the formed non-bridged sulphurs.

References

- [1] M. J. E. Dignonet, *Rare-Earth-Doped Fiber Lasers and Amplifiers*, Marcel Dekker, Inc., New York-Basel, (2001).
- [2] J. Heo, J. M. Yoon, S.Y. Ryon, *J. Non-Cryst. Solids* **238**, 115 (1998).
- [3] A. Polman, *J. Appl. Phys.* **82**, 1 (1997).
- [4] D.A. Turnbull, B.G. Aitken, S. G. Bishop, *J. Non-Cryst. Solids* **244**, 260 (1999).
- [5] Z. G. Ivanova, Z. Aneva, Z. Cernosek, E. Cernoskova, V. S. Vassilev, *J. Mater. Sci.: Materials in Electronics* **14**, 761 (2003).
- [6] Z. G. Ivanova, V.S. Vassilev, E. Cernoskova, Z. Cernosek, *J. Phys. Chem. Solids* **64**, 107 (2003).
- [7] N. A. Bhat, K. S. Sangunni, K. S. R. K. Rao, *J. Non-Cryst. Solids* **319**, 192 (2003).