

## PHOTOLUMINESCENCE OF $\text{Er}^{3+}$ IONS IN $(\text{GeS}_2)_{80}(\text{Ga}_2\text{S}_3)_{20}$ GLASSES

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The photoluminescence (PL) efficiency of  $(\text{GeS}_2)_{80}(\text{Ga}_2\text{S}_3)_{20}$  glasses doped with 0.17, 0.35 and 1.05 at % Er has been investigated. The PL has been excited by laser diodes operating at 982 and 532 nm. These wavelengths correspond to direct excitation of  $^4I_{15/2} \rightarrow ^4I_{11/2}$  transitions in  $\text{Er}^{3+}$  ions and to absorption in the host material, respectively. The PL band is presented as a sum of four Gaussian sub-bands. For all compositions, the PL band excited at 532 nm has been found to be narrower than that excited at 982 nm. The effect of broadening can be attributed to the development of broad Gaussian sub-bands centered at 1553 and 1600 nm, with the simultaneous reduction of sharp band centered at 1540 nm.

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### 1. Introduction

Rare-earth (RE)-doped sulfide glasses are extensively investigated for their possible applications in active optical devices such as fiber-optic amplifiers, infrared (IR) light sources and sensors [1,2]. These materials are known to have low phonon energies, decreasing the rate of non-radiative recombination of RE-excited states and increasing the radiative efficiencies of the RE-emissions. The multi-phonon absorption edge in these glasses is shifted to longer wavelengths (as compared to oxide glasses), making them suitable for the manufacture of IR fiber-optic amplifiers operating in the 2-10  $\mu\text{m}$  wavelength range. Moreover, these glasses have high refractive indices, which yield large emission cross-sections for the RE dopants. It should be noted that these glasses also have good thermal stability against devitrification. Among other sulfide glasses, the Ge-S-Ga system is of particular interest because of the enhanced solubility of REs in this system [3,4]. In the present paper, we investigate and discuss photoluminescence in Er doped  $(\text{GeS}_2)_{80}(\text{Ga}_2\text{S}_3)_{20}$  glasses.

### 2. Experimental details

Glasses with the composition,  $(\text{GeS}_2)_{80}(\text{Ga}_2\text{S}_3)_{20} : x \text{ mol \% of } \text{Er}_2\text{S}_3$  ( $x = 0.3, 0.6$  and  $1.8$ , i.e. doped with 0.17, 0.35 and 1.05 at % Er, respectively) were synthesized by mixing and melting the appropriate amounts of  $\text{GeS}_2$ ,  $\text{Ga}_2\text{S}_3$  and  $\text{Er}_2\text{S}_3$  in evacuated quartz ampoules at about  $1000^\circ\text{C}$ , with subsequent quenching in a mixture of ice and water. A stepwise heating regime was employed, for several hours, for the synthesis of  $\text{GeS}_2$  and  $\text{Ga}_2\text{S}_3$  due to the high vapor pressure of sulphur at higher temperatures [5].  $\text{Er}_2\text{S}_3$  was obtained as an Er salt from Alfa Aesar (Johnson Matthey

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Company, 99.9 %). Steady state photoluminescence (PL) spectra were measured using an ORIEL Cornerstone 1/8m monochromator and an ORIEL cooled InGaAs photodiode. The PL was excited using laser diodes (LDs) operating at wavelengths of 982 and 532 nm.

### 3. Results and discussion

The normalized PL spectra of the glasses studied excited at wavelengths of 982 and 532 nm are summarized in Fig.1 a, b, respectively. These wavelengths were chosen intentionally, because they correspond to direct excitation of the  $^4I_{15/2} \rightarrow ^4I_{11/2}$  transition in  $\text{Er}^{3+}$  ions and to absorption predominantly in host material, respectively. The PL emission band is close to 1.54  $\mu\text{m}$ , which is associated with the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition in the  $\text{Er}^{3+}$  ion. It can be clearly seen that at higher Er contents, the PL band excited by the 982 nm radiation (Fig. 1 a) is broader than that excited by radiation at 532 nm (Fig. 1 b). The tentative explanation is based on the concept of so-called “physical clusters” or “clusters of interaction”, via which the excitation can migrate from one  $\text{Er}^{3+}$  ion to another [6,7]. The mechanisms of energy transfer and migration are widely discussed elsewhere [2,8]. In the case of direct stimulation of the  $^4I_{15/2} \rightarrow ^4I_{11/2}$  transition in  $\text{Er}^{3+}$  ions, the time of energy migration is limited by the sum of the lifetimes of the  $^4I_{13/2}$  and  $^4I_{15/2}$  manifolds. In the case of excitation by LD operating at 532 nm, the energy can be transferred from the matrix to higher manifolds, and the resulting migration time can be longer. The positions of  $\text{Er}^{3+}$  ions inside a cluster are non-equivalent, due to statistical variations of the Er and Ga local concentrations. (Ga is known to be extremely important for RE activation in chalcogenide glasses [3,9]). This “non-equivalence” implies that some  $\text{Er}^{3+}$  ions are faster emitters of light than others. The longer migration time in the case of 532 nm excitation means that the energy has more chance to reach the “fast emitters” which will control the emission in this case. It is reasonable to assume that the PL band of the “fast emitters” alone is narrower than that of entire quantity of  $\text{Er}^{3+}$  ions forming the cluster. It should be noted that at low concentrations of Er, the dominant concentration of Ga may destroy clusters and “equalize” all positions of the  $\text{Er}^{3+}$  ions. Our experimental data confirm this assumption. The comparison of Fig. 1(a) and 1(b) shows that the PL spectra in glasses containing quite a low concentration of Er (0.17 at %) are independent of the excitation wavelength.

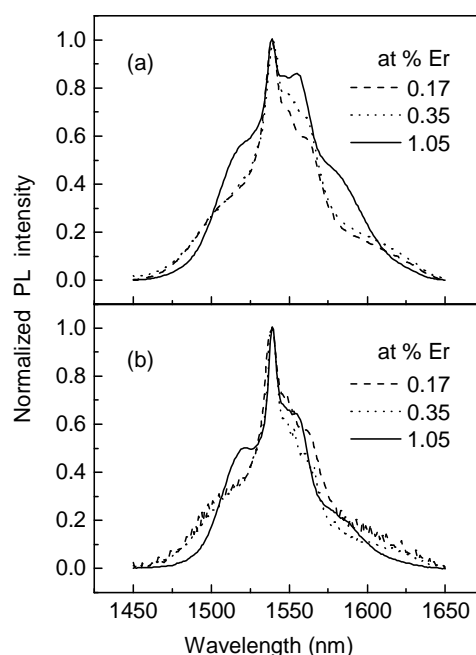


Fig. 1. Normalized PL spectra of the glasses studied at 982 nm (a) and 532 nm (b) excitation.

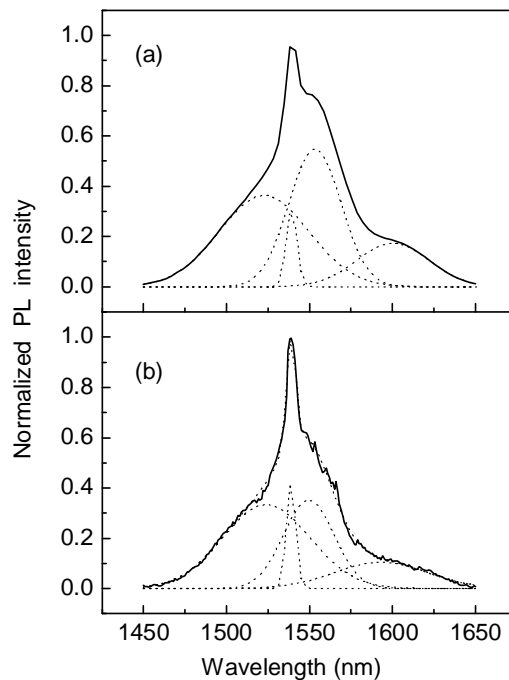


Fig. 2. Deconvoluted PL spectra for 0.35 at % Er doping at 982 nm (a) and 532 nm (b) excitation.

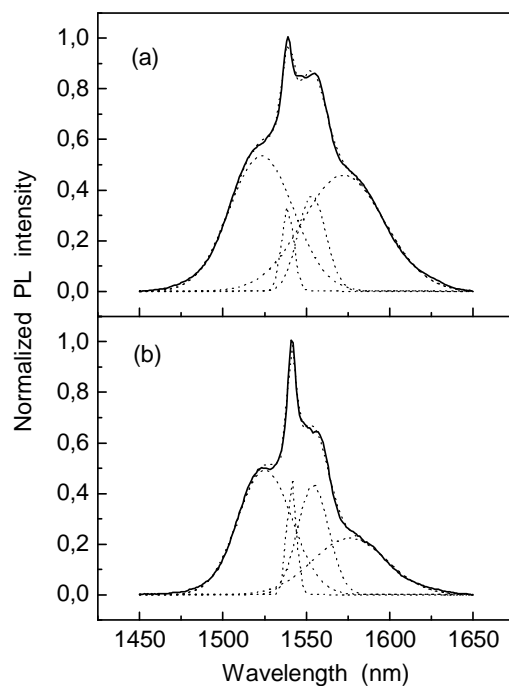


Fig. 3. Deconvoluted PL spectra for 1.05 at % Er doping at 982 nm (a) and 532 nm (b) excitation.

The PL spectra may be deconvoluted into the sum of four Gaussian sub-bands, which facilitates the comparison of PL spectra measured in samples with varying Er concentrations under different excitations (Figs. 2, 3). It should be noted that this deconvolution is quite arbitrary, and these sub-bands should not be confused with real Stark components. Three sub-bands centered at

about 1520, 1540, 1553 nm are detected in all samples. A fourth one is centered at 1600 nm in glasses with Er concentrations lower than 0.35 at %, and shifts to 1574 nm at higher Er concentrations. It is natural to assume that this fourth long wavelength sub-band is generated by radiative transitions from lower occupied levels of the  $^4I_{13/2}$  manifold into upper empty levels of the  $^4I_{15/2}$  manifold. Therefore, the shift of the sub-band to lower wavelengths with Er doping implies a narrowing of the manifolds, which may correspond to a smaller Stark splitting due to the reduction of the effective crystal field. This effect may be caused by the partial “deficit” of Ga, which is known to be an activator of Er in chalcogenide glasses [9]. In our heavier doped glasses with  $C_{Er} = 1.05$  at %, the ratio of the Ga to Er concentrations ( $C_{Ga}/C_{Er}$ ) is less than 8. Therefore, some  $Er^{3+}$  ions inevitably fall out of the most favorable octahedral Ga surroundings and may experience a smaller crystal field. In practice, an even larger concentration of Ga  $C_{Ga}/C_{Er} > 10$  is needed to achieve the homogeneous activation of  $Er^{3+}$  ions.

Figs. 2 and 3 show that the sub-band positions are stable against the variation of PL excitation wavelength. Therefore, the PL lineshape variations appearing under the 982 and 532 nm excitations may be attributed to changes in the partial intensities of the sub-bands centered at 1540 and 1600 nm at  $C_{Er} \leq 0.35$  at % (or 1570 nm at  $C_{Er} = 1.05$  at %). This effect is highly improbable in an isolated ion, where this reconstruction would mean that the distribution of excited electrons within manifolds is not thermodynamic. Therefore, we conclude that this is a “cooperative” effect related to the non-equivalency of different  $Er^{3+}$  ion sites, as discussed above.

#### 4. Conclusions

The PL spectra of Er doped  $(GeS_2)_{80}(Ga_2S_3)_{20}$  glasses, excited by laser diodes operating at 982 and 532 nm, are broad emission bands centered around  $\sim 1540$  nm. The chosen excitation wavelengths correspond to the direct excitation of  $^4I_{15/2} \rightarrow ^4I_{11/2}$  transitions in  $Er^{3+}$  ions, and to absorption in the host material, respectively. The PL bands excited at 982 nm have been found to be broader than those excited at 532 nm. We have attempted to deconvolute the PL spectra into a sum of Gaussian sub-bands, and have shown that the sub-band positions are stable against variation of the PL excitation wavelength. The broadening may be attributed to the change of the partial intensities of the different sub-bands. An increase of the Er of concentration shifts the long wavelength sub-band from 1600 nm to 1574 nm, which may be associated with a smaller Stark splitting due to the reduction of the effective “crystal field” (or local field) caused by the deficit of Ga in heavily doped glasses.

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