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Optical properties of Er-doped As-S-Ge chalcogenide glasses

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We have investigated Er-doped $(As_2S_3)_{30}$ $(GeS_2)_{70}$ chalcogenide glasses (0.01; 0.1; 0.5 and 1 at.% Er) by X-ray diffraction, photoluminescence, and optical transmittance measurements. The amorphous character of the samples was controled by standard X-ray techniques. Transmission spectra of investigated glasses were recorded in the wavelength interval from 200 to 2500 nm. Absorption edge and optical band gap were determined by extrapolating linear parts of the absorption spectra. It was concluded that this range of Er doping concentrations does not have great influence on the values of these parameters. The photoluminescence results indicate emission peaking at around 1550 nm, for the samples with Er content above 0.5 at%, which makes them interesting for the applications as active chalcogenide glasses.

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1. Introduction

The development of optoelectronics resulted in an increased interest in special glasses such as fluoride, chalcogenide, and oxide glasses of heavy metals with the aim of using them as a matrix material for doping with rare-earth ions. Investigations have shown that chalcogenide glasses appeared to be very suitable materials for this purpose. An especially distinguishing characteristic is their high transparency in the IR spectral range and high values of the refractive index. Transparency of matrix materials, with no absorption transitions in the IR region, is of special importance since this is exactly the region in which rare-earth ions exhibit emission transitions [1, 2, 3].

This interest is primarily related to the transitions within the 4f orbital of the rare-earth ion, which appear in the near or middle range of the IR spectrum [1]. Chalcogenide glasses doped with Er^{3+} ions are used in optical fibers as passive fibers in the power transmission systems, but also as active fibers in lasers (Er: YAG-2,97 μm, CO-5,3 μm, CO_2-10,6 μm) [4, 5, 6]. The use of Er^{3+}-doped amplifiers is based on its 4f transitions occurring in the "c-band" region of wavelengths, that is between 1530 and 1560 nm [7].

The breakthtough made in the area of these wavelengths is of great importance in optoelectronics, and it is thought that chalcogenide glasses doped with rare earths will take the leading role of optical amplifiers similar to the one that transistor had in the era of the development of elctronics [7]. If an external light source is used to excite rare-earth ions, it is possible to achieve light amplification without conversion of the signal into the electrical one. Er^{3+} ions have already been widely used for making optical amplifiers. Intensive investigations are being currently in progress with the aim to find out the most appropriate matrix from the group of chalcogenides, to serve as the carrier of these ions, and along these lines, the As-S-Ge chalcogenide glasses were synthesized, containing Er as dopant. Optical parameters of the system were determined, which represents a significant basis for the assessment of the possibility of using these chalcogenides in optoelectronics.

2. Experimental

Glass samples were synthesized by the cascade heating to the maximal temperature and annealing in air, according to the previously described procedure [8]. Their amorphous character was checked by polarization microscopy (Zeiss Axioskop 40A Pol), whereas the X-ray control of the structural disorder of the glasses was carried out on a Brucker D8 powder diffractometer with a copper anticathode.

Transmission spectra of the prepared samples were recorded on a NIR Perkin-Elmer, Model Lambda-950 instrument, in the wavelength range from 200 to 2500 nm. Preparation of samples in the form of plane-parallel plates was performed with the aid of abrasive powders of different grain size, and then by polishing with alumina powder on a silk cloth, to achieve a mirror-like appearance. Transmittance was recorded for several thicknesses, reducing them down from the initial one to a thickness of 0.10-0.35 mm. The values of the plate smallest thicknesses are shown in Table 1.

Table 1. Thicknesses of the thinnest plates of the samples

x (at % Er)	d (mm)
0	0.31
0.1	0.22
0.01	0.11
0.5	0.37
1.0	0.18

Fluorescence spectra were recorded at room temperature on a Fluorolog-3 Model FL3-221 (HORIBA Jobin-Yvon) instrument in the spectral range from 1200 to 1600 nm. The radiation source was a xenon lamp. The excitation spectrometer of the setup consisted of two monochromators connected in series, to obtain high-quality radiation. The radiation thus defined was directed to the sample and then to the detector. The detector in the IR region was a semiconductor (InGaAs) detector, cooled to the temperature of liquid nitrogen.

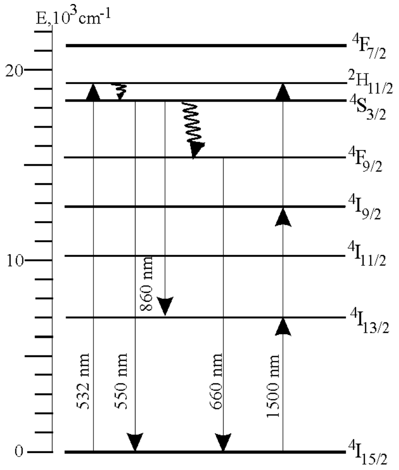

Fig. 1. Energy levels of Er^{3+}, emission and non-emission transitions.

Sample excitation was performed with the aid of light of wavelength 537 nm, corresponding to the inner transition of 4f electrons between $^4H_{11/2}$ and $^4I_{15/2}$ states of Er, Figure 1 [9, 10].

3. Results and discussion

Study of the glass samples by polarization microscopy in orthoscopic illumination mode showed no optically active centers, which indicates that the samples prepared were dominantly amorphous.

The diffractograms recorded are shown in Fig. 2. It is possible to observe the presence of a crystalline phase in the amorphous matrix, and the peaks (marked by arrows in Fig. 2) were identified to belong to the crystalline structural units As_2S_3, whose formation was not, obviously, prevented during annealing of the samples.

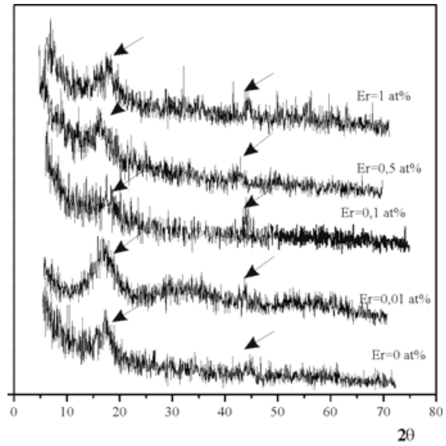

Fig. 2. X-ray diffractograms of powdered samples from the $[(As_2S_3)_{30}(GeS_2)_{70}]_{1-y}(Er_2S_3)_y$ system.

Fig. 3 shows transmittance spectra in the region of short-wavelength edge, which were used to calculate the optical band gap. It can be clearly seen that the increase in the Er content in the glass matrix results in a decrease of its transmittance and that the short-wavelength edge is shifted towards higher wavelengths. The calculated values of the absorption coefficient, based on the transmittances registered for the thinnest samples (without reflection correction) are shown in Fig. 4. It can be noticed that the values of absorption coefficients do not follow the observed decrease of glass transmittance with increase in the Er content in the composition, which is a direct consequence of the different thicknesses of samples on which experiment was performed. The extrapolation of the linear parts of the graph showing the dependence α=f(hν), where samples behave in accordance with the Urbach rule [11, 12], served to determine the values of optical band gaps for the investigated samples. The obtained values are shown in Table 2.

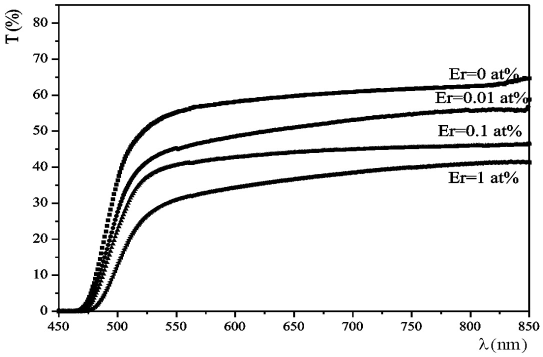

Fig. 3. Transmittance of the investigated glasses in the region of the Urbach edge.

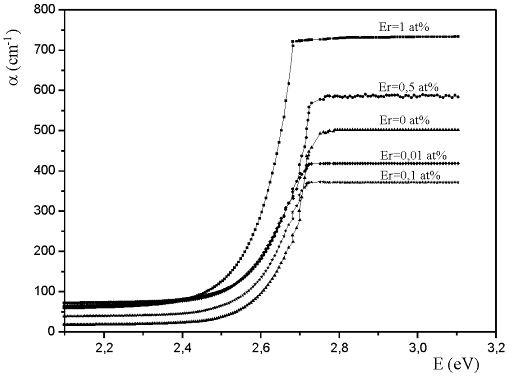

Fig. 4. Absorption spectra of the thinnest samples from the $[(As_2S_3)_{30} (GeS_2)_{70}]_{1-y}(Er_2S_3)_y$ system.

Table 2. Valuses of the optical band gap of the samples .

x (at % Er)	E_g^{opt} (eV)
0	2.582 (7)
0.1	2.576 (9)
0.01	2.546 (9)
0.5	2.510 (1)
1	2.423 (8)

It can be noticed that the optical band gap decreases with increase in the Er concentration, which is a consequence of the induction of localized states in the band tails caused by doping [12]. The dependence of the optical band gap on the Er content in the investigated system is shown in Fig. 5, and it can be satisfactorily represented by a linear function in the observed Er concentration interval.

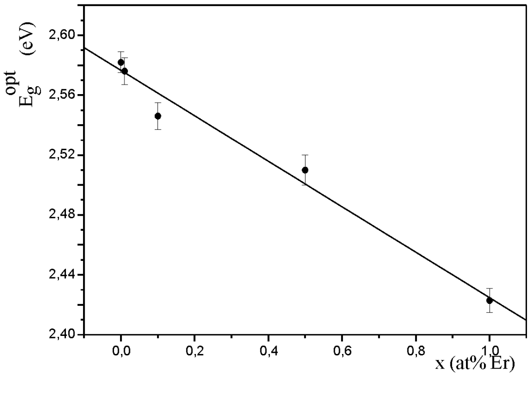

Fig. 5. Dependence of the optical band gap on the Er content in the system

Analytic form of the function obtained by least-squares method is:

$$E_g^{opt} = 2.577(5) - 0.15(1)x$$

where x is the Er concentratio expressed in atomic percents.

The fluorescence spectra of the samples are presented in Fig. 6. It is evident that fluoresence bands are missing from the spectra of the samples with 0.01 and 0.1 at% Er, which may indicate that these concentrations are not sufficient to exhibit fluoresence properties in the chosen matrix. The fluorescence band for the samples with 0.5 and 1 at% Er is detected at about 1550 nm, and it corresponds to the electron transition from $^4I_{13/2}$ to $^4I_{15/2}$ level in the 4f shell of Er^{3+}, Fig. 1.

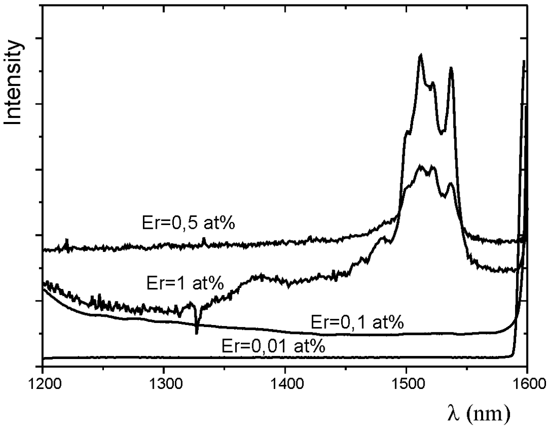

Fig. 6. Fluorescence spectra of glasses of the As-S-Ge system doped with Er^{3+}. These spectra are not normalized.

By comparing the intensities of fluoresence bands for the samples with 0.5 and 1 at% Er it can be concluded that the increase in the Er concentration yields an increased intensity of the fluorescence band, which indicates that in the selected glass matrix there is no quenching effect that has been detected in some other matixes [13]. This is an especially important result, which indicates that the Er^{3+} concentration in the interval from 0.5 to 1 at% in the given matrix is optimal. Namely, previous investigations [4, 8] showed that higher contents of rare earths in similar matrixes of chalcogenide glasses yielded mechanical strains and occurrence of clusters and cracks.

4. Conclusion

Transmission spectra of the chalcogenide glasses from the As-S-Ge system doped with 0.1; 0.01; 0.5 and 1 at% Er indicate that the increase in the Er content results in a decrease of glass transparency and shifting of the short-wavelength edge towards higher wavelengths. Calculations showed that all the glasses from this system have large values of optical band gap, about 2.5 eV. In this range of concentrations, the increase in Er content yielded a decrease in the optical band gap of 0.16 eV.

The fluorescene spectra of the glasses are characterized by a 50-nm broad band (1500-1550 nm) of the Er^{3+} transition corresponding to the electron transition from $^4I_{13/2}$ to $^4I_{15/2}$ level within the 4f shell of the Er^{3+}, for the samples with 0.5 and 1 at% Er. The increase in the Er^{3+} content yields an increase in the intensity of the fluorescence band, indicating that in the given glass matrix no quenching effect takes place.

Acknowledgement

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