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Photoluminescence properties of Er-doped Ge–In(Ga)–S glasses modified by caesium halides

Zoya G. Ivanova*,1, Jiri Zavadil,2,3, Petr Kostka3, Torkia Djouama4, and Mara Reinfelde5**

1 Institute of Solid State Physics, Bulgarian Academy of Sciences, Tzarigradsko Chaussee 72, 1784 Sofia, Bulgaria
2 Institute of Photonics and Electronics CAS, Chaberska 57, 182 51 Prague 8, Czech Republic
3 Laboratory of Inorganic Materials, Joint Workplace of the University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, and the Institute of Rock Structure and Mechanics of the CAS, v.v.i., V Holešovičkách 41, 182 09 Prague 8, Czech Republic
4 Laboratoire d'Electronique Quantique, USTHB Bab-Ezzouar, 16111 Alger, Algeria
5 Institute of Solid State Physics, University of Latvia, Kengaraga 8, 1063 Riga, Latvia

Chalcohalide Ge–In–S and Ge–Ga–S glasses modified by CsX (X = Cl, Br, and I), and doped with Er in the range from 0.1 to 0.5 at.%, have been prepared and investigated. The influence of CsX addition on their optical properties has been studied by transmission and photoluminescence spectroscopy. Nominal compositions of $[Ge_{25}In(Ga)_{10}S_{65})_{90}(CsX)_{10}$ have been selected as host materials. The shift of the absorption edge as a function of caesium halides is observed in GeInS (CsX) system with maximum band gap observed for CsI. The low-temperature photoluminescence reveals the broad band luminescence of the host glass centered at around the half of the band gap energy with superimposed $4f$–$4f$ radiative transitions of Er^{3+} ions. The position of the broad luminescence band is considerably shifted to higher energy in the case of CsI as compared to CsCl and CsBr. In the case of Er-doped chalcohalide $(Ge_{25}Ga_{10}S_{65})_{90}(CsBr)_{10}$ system, a considerable narrowing of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ radiative transitions of Er^{3+} ions accompanied by the pronounced splitting of the emission sub-bands clearly documents the increasing ceramics-like nature in the host material due to the admixture of CsBr. The influence of CsBr concentration on the shape of the broad-band luminescence of Ge–Ga–S–CsBr host is also reported.

1 Introduction An increasing research has recently been reported in rare-earth (RE) doped sulfide glasses for active optical devices such as fiber-optic amplifiers, infrared light sources, and sensors [1–3]. The photoluminescence (PL) efficiency of RE^{3+} ions in these glasses is quite high due to their unique optical properties such as low phonon energy (300–400 cm^{-1}), high refractive index ($\sim$2.5), extended infrared transparency (from $\sim$0.5 to $\sim$20 μm). RE^{3+} ions embedded into the glass host are characterized by an incomplete $4f$ electronic shell that is shielded by closed $5s$ and $5p$ ones. Consequently, relatively sharp radiative $4f$–$4f$ electronic transitions could be achieved from RE-doped materials. In particular, erbium (Er) has a strong emission band at $\sim$1530 nm corresponding to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ electronic transition which is an important telecommunication wavelength [4].

There are different ways to increase the RE-related radiation efficiency in chalcogenide glasses. Modification of the local structure in the glass network resulting in higher solubility of RE ions is one of them. It has been shown that addition of gallium (Ga) into chalcogenide glasses has this effect [5–8] and in particular, the erbium solubility in Ge–S glass increases significantly with the addition of Ga_2S_3 [9].

Another way to improve the radiation lifetime and emission intensity of embedded RE^{3+} ions in chalcogenide glasses is the addition of suitable modifier, such as alkaline halide [10]. A feature of great interest in such chalcohalide

glasses is their ability to crystallize homogeneously and so to prepare designed glass ceramics. Indeed, mixing covalent chalcogenide compounds and ionic alkaline halides in a glass matrix allows a better control of crystallization.

Ga-containing chalcohalide glasses have also been studied by ^{71}Ga solid state nuclear magnetic resonance [11]. The obtained results highlight the evolution of local surroundings of Ga atoms in the glass network as a function of the halide concentration. In particular for Ge–Ga–S–CsBr system, it has been proposed [12] that new structural units of $[GaS_{3/2}Br]^-$ type are formed with the preferred coordination of Br ions around RE^{3+} ions. EXAFS studies have proved that RE^{3+} ions are surrounded by approximately seven S ions in $Ge_{25}Ga_{10}S_{65}$ glass but are coordinated by $\sim$6 Br ions with the addition of 10 mol.% CsBr. At this composition the number of Br ions is approximately the same as that of Ga ions. All Ga ions can make bonds with Br and form $[GaS_{3/2}Br]^-$ structural units and RE^{3+} ions can be surrounded solely by Br ions without participation of S ions. The coordination environment of RE^{3+} ions gradually changes until they are surrounded mainly by Br ions in the case of addition of 10 mol.% CsBr into $Ge_{25}Ga_{10}S_{65}$ glass [12]. As a result, the electron-phonon coupling strength between RE ions and the host matrix decreases which in turn results in the enhancement of the excited-state lifetime. Such changes in the local structure surrounding of RE^{3+} ions are considered to be responsible for reported improvement of the radiative properties [13].

In the previously reported work [14], the influence of the addition of CsBr on the optical and thermal properties of GeGaS glass doped with Er has been investigated. These glasses exhibit an enhanced radiative lifetimes and strong photoluminescence for $^4I_{13/2} \rightarrow ^4I_{15/2}$ and $^2H_{11/2} \rightarrow ^4I_{15/2}$ transitions in Er^{3+} ions. The addition of CsBr into Ge–Ga–S glass, keeping the ratio between CsBr and Ga close to one, has been found favorable for the incorporation of larger amount of Er. In this work, we investigate the role of caesium halides CsX (X = Cl, Br, and I) on the optical properties of Ge–In–S glasses by using the transmission and photoluminescence spectroscopy. In particular, the influence of CsX addition on the position of the host glass fundamental absorption edge and emission spectra of studied glasses has been investigated. The influence of temperature on the PL emission has also been considered. In addition, the influence of CsBr admixture on the broad-band luminescence and on the absorption and emission bands of Er^{3+} ions at 1530 nm has been studied in detail for the Ge–Ge–S and Ge–Ga–S–CsBr systems.

2 Experimental Bulk chalcohalide glasses with starting compositions of $[Ge_{25}In(Ga)_{10}S_{65}]_{90}(CsX)_{10}$ doped with Er in the range of 0.1–0.5 at.%, were synthesized by heating the initial elements ($\sim$5N purity) up to 950 $^\circ$C for 12 h in a rocking furnace with consequent quenching in ice water and annealing for 1 h at the temperature near glass transition (the procedure details are given in Ref. [14]). Er-doped chalcogenide $Ge_{25}Ga_{10}S_{65}$ glass was also

prepared for comparison. Optical transmittance spectra in the 450–3000 nm region were measured using the Perkin Elmer Lambda 900 spectrophotometer, and by using the Specord 210 Analytic Jena in the range of 190–1100 nm. Room-temperature photoluminescence (RTPL) spectra of Ge–Ga–S–CsBr glass doped with Er were measured under excitation with a laser diode operating at 532 nm using an ORIEL Cornerstone 1/8 m monochromator and a cooled ORIEL InGaAs photodiode. Low-temperature photoluminescence (LTPL) spectra were collected at various levels of excitation by He-Ne laser (632.8 nm) in an optical He closed cycle cryostat enabling measurements in the range of 3.5–300 K. The 1 m focal length monochromator Jobin-Yvon coupled with a cooled high purity Ge detection system enables sensitive and high resolution measurement in the spectral range of 800–1700 nm by using the lock-in technique and computer controlled data collection. Typical spectral resolution in reported experiments was in the range of 0.04–0.08 nm and 20 measurements were collected for each wavelength of the spectrum.

3 Results

3.1 Ge–In–S system Transmission spectra of Er doped Ge–In–S–CsX glasses with the addition of CsCl, CsBr, and CsI are shown in Fig. 1. The assignment of respective curves to samples is given in the inset. The fundamental absorption edge due to inter-band transitions is located around 450 nm and sharp $4f$–$4f$ up-transitions due to absorption in inner shells of Er^{3+} ions are clearly seen. The structure at 1430 nm is an artifact of the experimental setup.

Optical band gaps could be estimated from the intersection of the linear part of the absorption edge with the abscissa. It follows from measured transmittance that the fundamental absorption edge is shifted to shorter wavelength for CsI in contrast to its almost constant position for CsCl and CsBr. Accordingly, the highest band gap is observed for glasses prepared with the admixture of CsI.
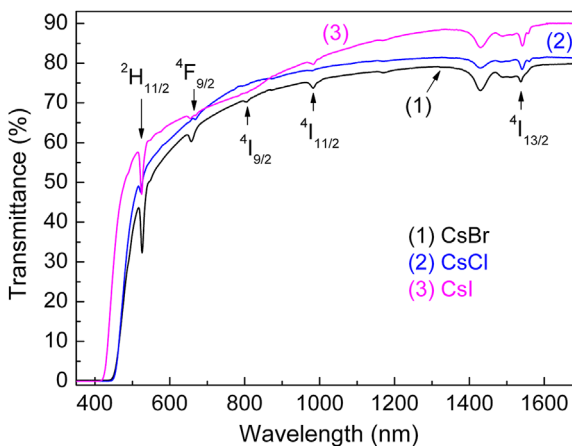

Figure 1 Transmission spectra of $(Ge_{25}In_{10}S_{65})_{90}(CsX)_{10}$ glasses doped with 0.1 at.% Er are shown for CsBr, CsCl, and CsI addition by curves (1), (2), and (3), respectively.

Low-temperature photoluminescence spectra in the spectral range of 900–1700 nm are shown in Figs. 2 and 3. The dominant LTPL feature of the host glass is a broad band centered at around half the band gap. The difference between the observed position of PL maximum and the optical band gap is the indication that deep states are involved in the recombination. It has been suggested [15, 16] that such transitions are from band tails to states near the middle of the gap. The host glass luminescence is observed in glass materials usually at low temperatures, and is attributed to deep states within the band-gap which are due to native defects [15–20]. These states could be optically excited in the host glass Urbach absorption edge [20]. He-Ne (632.8 nm line) laser was used for excitation in this study, which implies that Er^{3+} ions are excited via the electronic structure of the host glass [21, 22] or directly by Ground State Absorption (GSA) and Excited State Absorption (ESA) channels [23].

LTPL spectra of Er doped glasses prepared with the admixture of the three halides are shown in Fig. 2. Relatively narrow 4f–4f transitions of Er^{3+} ions, super-imposed on the broad band luminescence of the host glass, are shown in the figure. The strong emission due to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is observed on all samples. The $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition at about 980 nm was observed only on sample prepared with the admixture of CsBr. The non-radiative transitions from $^4F_{3/2}$ state to $^4I_{11/2}$ level, that are behind the population of $^4I_{11/2}$ under He-Ne excitation, seem to be sensitive to the neighborhood of Er^{3+} ions, in our case on particular CsX addition.

The host glass luminescence is centered at around 1300 nm for CsBr and CsCl admixtures. However, the maximum of the host glass luminescence is shifted to higher energy (maximum around 1050 nm) for the admixture of CsI. It has been stated above that there is a correlation between the position of the broad host glass luminescence
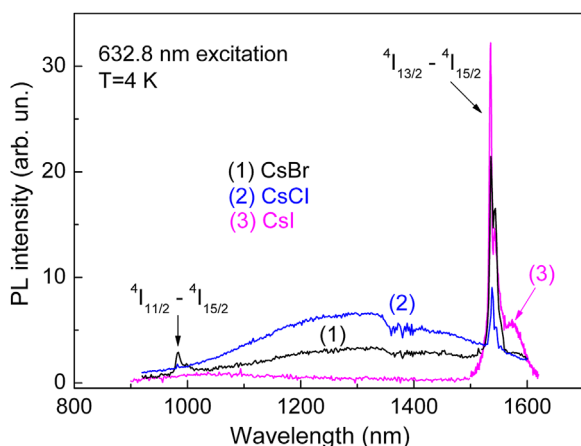
Figure 3 LTPL spectra of $(Ge_{25}In_{10}S_{65})_{90}(CsX)_{10}$ doped with 0.5 at.% Er are shown by curves (1), (2), and (3) that correspond to CsBr, CsCl, and CsI, respectively. The inner shell $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions is well expressed on the host glass luminescence in case of CsBr admixture.

band and the band-gap of the host glass. Having this in mind we propose that the shift of the fundamental absorption edge observed in case of CsI addition (Fig. 1) is behind the shift of the broad host glass luminescence to higher energy. This effect is better documented in Fig. 3, where spectra were taken at higher excitation power and were collected only to 1500 nm. Thus the strong luminescence band due to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in Er^{3+} ions does not compete with less strong host glass luminescence, and the shift of the broad luminescence band of the host glass due to CsI addition is better seen. The structure seen in Figs. 2 and 3 at about 1350 nm corresponds to the absorption due to water vapor in the air.

In order to evaluate the influence of temperature on the shape of the emission-cross section, the strongest emission band at 1530 nm due to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in sample with CsI addition is plotted in Fig. 4 for two temperatures

Figure 2 LTPL spectra of $(Ge_{25}In_{10}S_{65})_{90}(CsX)_{10}$ doped with 0.5 at.% Er are shown. The curves (1), (2), and (3) correspond to CsBr, CsCl, and CsI, respectively. The inner shell transitions of Er^{3+} ions at 980 and 1530 nm are shown together with the broad band luminescence of the host.
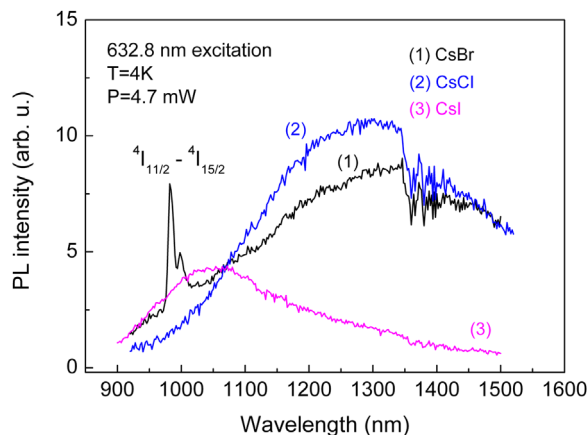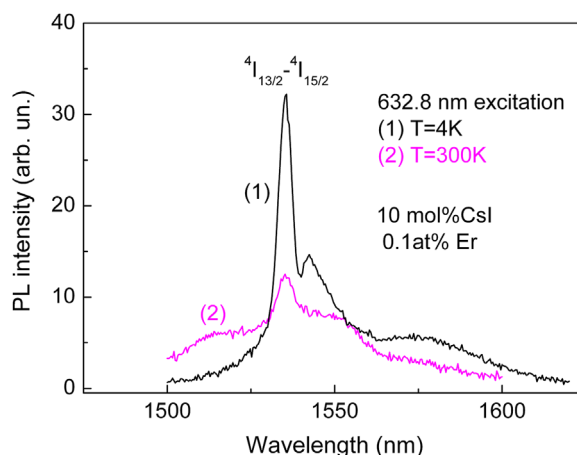
Figure 4 The $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in photoluminescence spectra of $(Ge_{25}In_{10}S_{65})_{90}(CsI)_{10}$ glass doped with 0.1 at.% Er and measured at 300 and 4 K is shown.

(4 and 300 K) by curves (1) and (2), respectively. The spectra were collected with higher resolution in order to reveal their fine structure due to energy splitting in manifolds involved.

The temperature decrease from 300 down to 4 K leads, besides intensity enhancement, to narrowing of this PL band, and better resolution of the fine structure due to crystal field splitting of electronic manifolds involved. It should be noted that the narrowing takes place predominantly on the high energy side of Er^{3+} related PL band [24]. In fact, the degeneracy of energy states of RE ions depends on their neighborhood symmetry. Thermal vibrations of this neighborhood, which quench with decreasing temperature, are responsible for widening of spectral bands. This means that at low temperature the higher energy sub-levels of the excited upper manifolds are not occupied, and only transitions from the lowest sub-level take place. Thus, in case of Er^{3+} ions in studied glasses only transitions from the lowest sub-level of $^4I_{13/2}$ manifold to eight sub-levels of the ground state manifold $^4I_{15/2}$ [24, 25] are realized. At 300 K we can expect that higher sub-levels of the upper manifold $^4I_{13/2}$ are thermally occupied, and consequently are responsible for the broadening of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ PL band at its high energy side.

As seen from Fig. 4, the fine structure of the ground state manifold $^4I_{15/2}$ is not fully resolved even at 4 K in case of studied Ge–In–S–CsX samples.

3.2 Ge–Ga–S system In addition to previously reported [14, 23], optical properties of Ge–Ga–S–CsBr glass we present a more detailed study of the influence of CsBr addition on the absorption and PL cross-sections of Er^{3+} related emission band at 1530 nm. The comparison of absorption and photoluminescence cross-sections of Er-doped $Ge_{25}Ga_{10}S_{65}$ and those corresponding to Ge–Ga–S–CsBr glass measured at room temperature under excitation by 532 nm is shown in Fig. 5. The base glass of $Ge_{25}Ga_{10}S_{65}$ composition is chosen from the stoichiometric tie-line between GeS_2 and Ga_2S_3 (GeS_2:Ga_2S_3 = 5:1).

It has been reported that under similar experimental conditions the Er^{3+} related PL intensity in chalcohalide Ge–Ga–S–CsBr host is about two times higher than in Ge–Ga–S one [14]. The overall width of corresponding PL bands in both materials is about the same. However, considerable narrowing and better resolution of the fine structure of the bands is observed in photoluminescence and absorption spectra in CsBr-containing glass compared to samples without CsBr. The observed narrowing of $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ transitions in Er^{3+} ions due to the admixture of CsBr into the Ge–Ga–S glasses (Fig. 5) indicates smaller dispersion of crystal field values, that is, it demonstrates the increasing degree of ordering in the vicinity of RE^{3+} ions.

To estimate the role of caesium halides on the host electronic structure and consequently on the host glass luminescence, we investigated the low-temperature PL spectra of un-doped samples prepared with various admixtures of CsBr. LTPL spectra of three samples
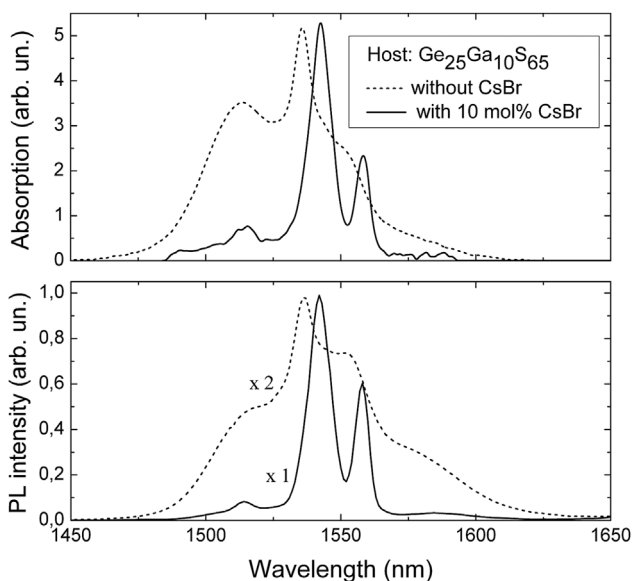

Figure 5 Absorption and photoluminescence bands at ∼1530 nm of $(Ge_{25}Ga_{10}S_{65})_{90}(CsBr)_{10}$ (solid lines) and $Ge_{25}Ga_{10}S_{65}$ (dash lines), both doped with 0.15 at.% Er.

prepared by introduction of 10, 20, and 25 mol.% CsBr into $Ge_{25}Ga_{10}S_{65}$ glass are presented in Fig. 6 by curves (1), (2), and (3), respectively. The structure seen at about 1350 nm corresponds to the absorption due to vapor in the air.

The spectrum corresponding to the lowest admixture of CsBr is characterized by a broad band with one maximum at about 1250 nm. It should be noted that the $Ge_{25}Ga_{10}S_{65}$ host glass is characterized by a simple broad band luminescence centered at about 1250 nm [18]. When the amount of CsBr is increasing the weak shoulder at about 1100 nm, corresponding to another emission channel, starts to develop. We propose that the introduction of CsBr into the $Ge_{25}Ga_{10}S_{65}$

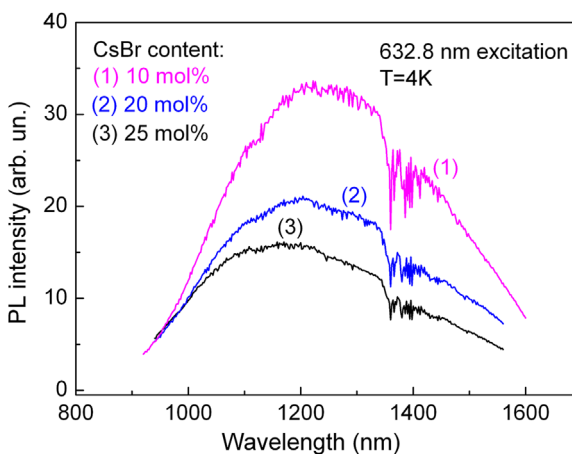**Figure 6** Low-temperature PL spectra of the $(Ge_{25}Ga_{10}S_{65})_{100-x}$ $(CsBr)_x$ ($x = 10, 20, 25$) series of glasses at 0.6 mW excitation intensity are shown and represented by curves (1), (2), and (3), respectively.

glass matrix leads to the appearance of less deep electronic states that are behind the observed structure in the host glass luminescence for CsBr concentrations exceeding 20 mol.%.

4 Discussion The role of alkaline halides addition on two series of chalcogenide systems—namely CsCl, CsBr, CsI in Ge–In–S and CsBr in Ge–Ga–S glasses—doped with Er^{3+} ions has been investigated by transmission and low-temperature photoluminescence spectroscopy. In addition also un-doped Ge–Ga–S–CsBr samples were investigated by low-temperature PL spectroscopy. The short wavelength electronic absorption edge of studied Ge–In–S glasses has been found to be located in the range of 420–450 nm. The fundamental absorption edge is shifted to shorter wavelength in case of CsI admixture, that is, the highest band gap is observed for glasses prepared with the admixture of CsI. Among the studied alkaline halides the CsI has the lowest ionic character. Thus it could be expected that CsI is more easily incorporated into covalent network of the Ge–In–S host as compared to more ionic halides CsBr and CsCl. These are incorporated in the glass matrix in the form of crystalline inclusions and a similar shift of absorption edge is not observed. The sharp absorption bands detected in the transmission spectra of investigated glasses are attributed to transitions from the ground state $^4I_{15/2}$ to the following excited states $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ of Er^{3+} ions.

The low-temperature PL spectroscopy used for the investigation of Er-doped glasses enabled a simultaneous observation of both the broad band luminescence due to electronic transitions in the host and also narrow PL bands due to electronic transitions within $4f$–$4f$ states of Er^{3+} ions doped into the glass host. The luminescence that originates from the electronic structure of the host glass (like in crystalline semiconductors) depends considerably on temperature—the lower the temperature the higher PL signal. This inverse proportionality is due to the fact that the efficiency of all competing non-radiative recombination mechanisms is decreasing with decreasing temperature—thus the radiative recombination that contributes to the observed PL signal becomes more intense. Consequently, the broad band luminescence that originates from electron recombination processes in the host is usually much easily observed at low temperature as compared to room temperature.

On the other hand, the radiative recombination due to transitions within screened $4f$ electronic shell in rare-earths ions is not so much sensitive to external temperature because the $4f$–$4f$ transitions are shielded from external influence by $5s$ and $5p$ electrons of RE ions. The only competing mechanism is the non-radiative phonon assisted recombination. Thus RE emission is more easily observed in glass hosts characterized by low phonon energy. Consequently, $4f$–$4f$ emission processes are usually well observed also at room temperature. At low temperature their PL intensity is also increased but the fine structure of emission bands is much better

resolved because the thermal motion of electrons is not smearing the PL curves.

In the case of Ge–In–S system, the low-temperature PL spectra are dominated by a broad PL band of the host glass centered at around the mid-gap energy. The large energy difference between the PL maximum of each host glass and its optical band gap is an indication that deep states, in the gap, are involved in the recombination. It has been reported [16, 20] that such transitions are from band tails to deep states near the middle of the gap. In studied Ge–In–S–CsX system, the PL maxima were located at 1050 and/or 1300 nm for respective CsX admixtures. The host glass luminescence is centered at around 1300 nm for CsBr and CsCl admixtures. In case of CsI admixture, the maximum of the host glass luminescence is shifted to higher energy (around 1050 nm). This observation correlates well with the corresponding shift of the fundamental absorption edge when going from CsBr to CsI addition to the host composition. We propose that the less ionic CsI is more easily incorporated into the covalent network of the Ge–In–S host as compared to CsBr and CsCl that tend to form crystalline inclusions in the glass matrix. This difference in CsX admixtures is manifested in varied position of the fundamental absorption edge. Another aspect of different ionicity of CsX admixtures is manifested in Fig. 2. The band at 1530 nm is the narrowest in case of the most ionic CsCl admixture and the broadest when the least ionic CsI is used for glass modification.

In the case of Ge–Ga–S system, the addition of CsBr seems to induce some crystallinity (ionic and rigid structure). This conclusion is supported by narrowing of the obtained both absorption and emission $^4I_{13/2} \rightarrow {}^4I_{15/2}$ bands as shown in the Fig. 5. In Ge–Ga–S glass this band is rather smooth similarly to other disordered materials, and in contrast to crystalline materials where more pronounced sub-peaks are typical [14, 26]. The addition of CsBr also influences the shape of the broad-band luminescence of the host glass. The PL spectrum of samples with the lowest admixture of CsBr exhibits the broad band with one maximum at about 1250 nm. When the admixture of CsBr is increasing a second peak at about 1100 nm, corresponding to the second emission channel, starts to develop. We propose that the introduction of CsBr into the $Ge_{25}Ga_{10}S_{65}$ glass matrix leads to the appearance of less deep electronic states that are manifested by a shoulder on the host glass luminescence at about 1100 nm for CsBr concentrations exceeding 20 mol.%.

5 Summary In summary, the obtained results from the transmission and photoluminescence spectra of Er-doped chalcohalide $(Ge_{25}In(Ga)_{10}S_{65})_{90}(CsX)_{10}$ ($X = Cl$, Br, and I) glasses have shown that:

(i) The addition of CsX into the studied Ge–In–S–CsX glasses changes the position of the fundamental absorption edge which is shifted to shorter wavelength for CsI in contrast to CsCl and CsBr. In a similar way is

shifted the maximum of the broad band luminescence of the host glass.

(ii) The well pronounced narrowing effect of Er-related PL bands for these glasses by temperature decrease from 300 down to 4 K is accompanied by intensity enhancement and better resolution of the fine structure due to crystal field splitting of electronic manifolds involved. It was demonstrated that the narrowing takes place predominantly on the high energy side of Er^{3+} related PL bands.

(iii) The line-shape and the radiative efficiency of $4f$–$4f$ transitions of Er ions in Ge–Ga–S–CsBr glasses depend markedly on the admixture of CsBr in the host composition.

(iv) The line-shape of the broad-band luminescence of the host Ge–Ga–S–CsBr glass is characterized by broad band with maximum at about 1250 nm and depends on the concentration of CsBr. When the admixture of CsBr is exceeding 20 mol.% the structure at about 1100 nm, corresponding to the second emission channel, starts to develop.

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