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**Citation style:** Pisarska Joanna, Lisiecki R., Dominiak-Dzik G., Ryba-Romanowski W., Goryczka Tomasz, Grobelny L., Pisarski Wojciech A. (2010). Influence of PbX<sub>2</sub> (X = F, Cl, Br) content and thermal treatment on structure and optical properties of lead borate glasses doped with rare earth ions. "Optica Applicata" (2010, iss. 2, s. 351-358).



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# **Influence of $\text{PbX}_2$ ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) content and thermal treatment on structure and optical properties of lead borate glasses doped with rare earth ions**

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Oxyhalide lead borate glasses doped with rare earth ions have been studied before and after thermal treatment. The rare earths as optically active ions were limited to the  $\text{Er}^{3+}$  ions. Near-infrared luminescence due to the main  ${}^4I_{13/2} - {}^4I_{15/2}$  laser transition of  $\text{Er}^{3+}$  was registered. The introduction of  $\text{PbX}_2$  to the borate glass results in a reduction of spectral linewidth and an increase of luminescence lifetime of  ${}^4I_{13/2}$  state of  $\text{Er}^{3+}$  ions. The unusual large spectral linewidth for  ${}^4I_{13/2} - {}^4I_{15/2}$  transition of  $\text{Er}^{3+}$  in the oxide glass host was obtained, whereas the luminescence decay from  ${}^4I_{13/2}$  state is longer for a sample with  $\text{PbF}_2$  than  $\text{PbCl}_2$  and  $\text{PbBr}_2$ . Heat treatment introduces transformation from a glass to transparent glass-ceramic (TGC). The coordination sphere around  $\text{Er}^{3+}$  ions is changed, giving important contribution to the luminescence characteristics. The spectroscopic consequence of this transformation is the increase of luminescence lifetime and the narrowing of spectral lines of  $\text{Er}^{3+}$ .

Keywords: lead borate glasses, rare earth ions, thermal treatment, luminescence, up-conversion.

## **1. Introduction**

$\text{B}_2\text{O}_3$  is one of the most important forming oxides from the point view of physics and chemistry of glasses. It was incorporated into the various kinds of glass systems. Glasses containing  $\text{B}_2\text{O}_3$  usually exhibit very good broadband properties, but their luminescence characteristics are rather not satisfied in comparison to low-phonon heavy metal oxide and fluoride based glasses. Incorporation of  $\text{PbO}$  and/or  $\text{PbF}_2$  to the conventional borate glasses leads to an increase of radiative parameters for  $\text{Ln}^{3+}$

ions. From this point of view, Ln-doped borate glasses with relatively high PbO/PbF<sub>2</sub> and low B<sub>2</sub>O<sub>3</sub> concentration are of particular interest for optical investigation. They belong to glass systems, which are promising luminescent materials in relation to practical applications as solid-state laser active media, near-infrared tunable lasers, NIR-to-visible up-converters and broadband optical amplifiers.

Several oxide and oxyfluoride lead borate glasses were prepared and extensively studied by GRESSLER and SHELBY [1, 2] and TAWANSI *et al.* [3, 4] twenty years ago. The Ln-doped mixed oxyhalide glasses with B<sub>2</sub>O<sub>3</sub> and PbX<sub>2</sub> (where X = Cl, Br) have yet not been examined, to the best of our knowledge. From the literature data it can be gathered that oxyhalide systems such as the undoped alkali haloborate B<sub>2</sub>O<sub>3</sub>–BaF<sub>2</sub>–LiX glasses [5] or erbium-doped heavy metal lead halotellurite PbX<sub>2</sub>–TeO<sub>2</sub> glasses [6], where X denotes F, Cl or Br, were successfully prepared and present interesting optical properties.

The present paper is divided into two parts. The first part contains results for erbium-doped borate glasses with PbX<sub>2</sub> content (X = F, Cl, Br). The luminescence spectra at 1.5 μm due to the main <sup>4</sup>I<sub>13/2</sub>–<sup>4</sup>I<sub>15/2</sub> laser transition of Er<sup>3+</sup> ions and luminescence decay curves from the <sup>4</sup>I<sub>13/2</sub> state have been examined.

The second part is concerned with erbium-doped transparent glass-ceramics. Thermal treatment introduces transformation from a glass to transparent glass-ceramic (TGC). The coordination sphere around Er<sup>3+</sup> ions is changed, giving important contribution to the luminescence characteristics. The spectroscopic consequence of this transformation is the increase of luminescence lifetime and the narrowing of spectral lines of Er<sup>3+</sup>. These aspects are presented and discussed in relation to the previously published results [7].

## 2. Experiment

Multicomponent mixed oxyhalide glasses with the following composition given in wt%: 9PbX<sub>2</sub>–63PbO–18B<sub>2</sub>O<sub>3</sub>–6Al<sub>2</sub>O<sub>3</sub>–3WO<sub>3</sub>–1Er<sub>2</sub>O<sub>3</sub> (X = F, Cl, Br) were prepared by mixing and melting appropriate amounts of metal oxides and lead halide of high purity (99.99%, Aldrich Chemical Co.). A homogeneous mixture was heated in a protective atmosphere of dried argon. Mixed reagents were melted at 900 °C. Then, they were quenched and annealed below *T<sub>g</sub>* in order to eliminate internal mechanical stresses. NIR luminescence spectra were measured with a Continuum Model Surelite I optical parametric oscillator pumped by a third harmonic of a Nd:YAG laser. Luminescence was dispersed by a 1-meter double grating monochromator and detected with a photomultiplier with S-20 spectral response. Up-conversion luminescence spectra were recorded under excitation by diode laser at 980 nm. Both luminescence and up-conversion spectra were recorded using a Stanford SRS 250 boxcar integrator controlled by a computer. Luminescence decay curves were recorded and stored by a Tektronix TDS 3052 oscilloscope. All measurements were carried out at room temperature. The spectral resolution was equal to 0.1 nm. Luminescence decay curves were detected with accuracy of ±1 μs.

### 3. Results and discussion

It is interesting to see that glass modification strongly influenced the surroundings of  $Ln^{3+}$  ions, bringing about an important contribution to their luminescence characteristics. Substitution of  $PbO$  by  $PbX_2$  ( $X$  denotes  $F, Cl$  or  $Br$ ) and/or thermal treatment of precursor glasses results in the structural changes of the local environment of  $Ln^{3+}$  ions. These phenomena are correlated with the optical changes.

#### 3.1. Influence of $PbX_2$ content ( $X = F, Cl, Br$ )

Our preliminary investigations indicate that erbium-doped oxide and oxyhalide lead borate glasses are promising materials for NIR solid-state laser and broadband optical amplifiers [8]. An introduction of lead halide  $PbX_2$  (where  $X = F, Cl$  or  $Br$ ) to the borate glass changes coordination sphere around  $Er^{3+}$ . The anion electronegativities ( $Br - 2.8, Cl - 3.0, F - 4.0$ ) and ionic-type bond character increase in  $Br \rightarrow Cl \rightarrow F$  direction, which results in reduction of spectral linewidth and the increase of luminescence lifetime for  $Ln^{3+}$  ions. Figure 1 presents NIR luminescence spectra at  $1.5 \mu m$  due to the main  ${}^4I_{13/2} - {}^4I_{15/2}$  laser transition of  $Er^{3+}$  ions in oxide and oxyhalide lead borate glasses. Figure 2 shows luminescence decay curves from the  ${}^4I_{13/2}$  state of  $Er^{3+}$  ions. Spectroscopic parameters for  $Er^{3+}$  ions strongly depend on  $PbX_2$  content. The unusual large spectral linewidth ( $\Delta\lambda = 100.5 \text{ nm}$ ) for the  ${}^4I_{13/2} - {}^4I_{15/2}$  transition of  $Er^{3+}$  in the glass sample without  $PbX_2$  is useful for potential broadband optical applications. The linewidths for glass samples with  $PbX_2$  are close to  $52.5 \text{ nm}$  ( $X = F$ ),  $60 \text{ nm}$  ( $X = Cl$ ) and  $80 \text{ nm}$  ( $X = Br$ ). Their values are reduced in  $Br \rightarrow Cl \rightarrow F$  direction. They are considerably smaller than that obtained for glass sample without

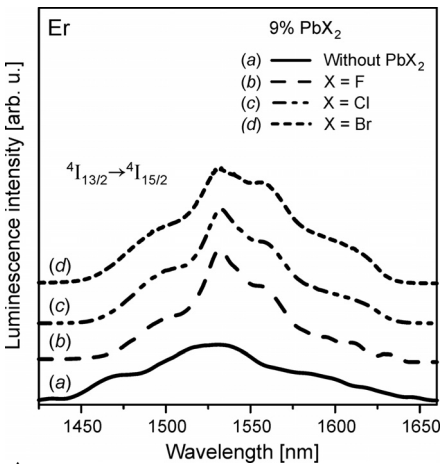


Fig. 1. NIR luminescence spectra for  $Er^{3+}$  ions in lead borate glasses without and with  $PbX_2$  ( $X = F, Cl, Br$ ).

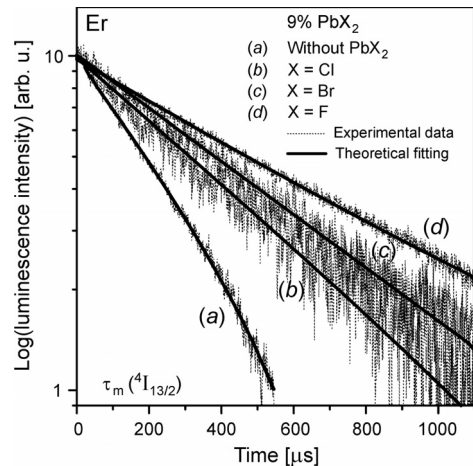


Fig. 2. Luminescence decay curves for  $Er^{3+}$  ions in lead borate glasses without and with  $PbX_2$  ( $X = F, Cl, Br$ ).

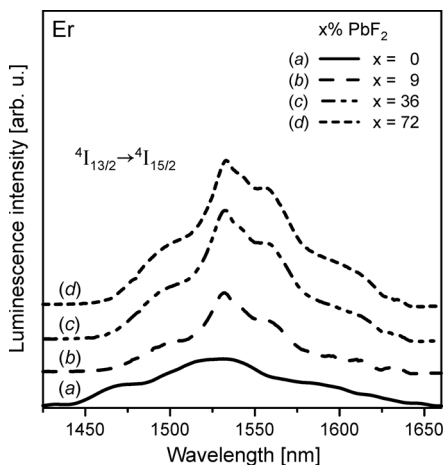


Fig. 3. NIR luminescence spectra for  $\text{Er}^{3+}$  ions in lead borate glasses without and with  $\text{PbF}_2$ .

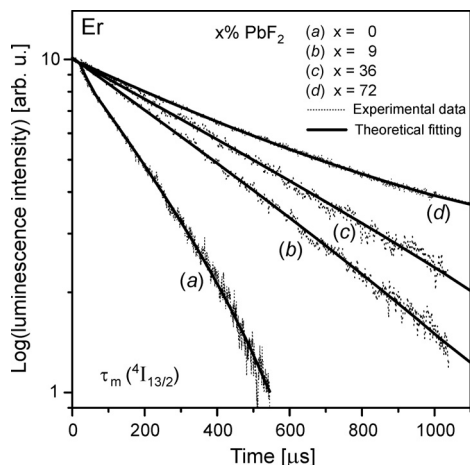


Fig. 4. Luminescence decay curves for  $\text{Er}^{3+}$  ions in lead borate glasses without and with  $\text{PbF}_2$ .

$\text{PbX}_2$ . This indicates that part of X ions ( $X = \text{F}, \text{Cl}$  or  $\text{Br}$ ) is successfully bridged with  $\text{Er}^{3+}$ .

On the other hand, the luminescence decay analysis indicates that the  ${}^4I_{13/2}$  lifetime of  $\text{Er}^{3+}$  ions increases in the glass samples where  $\text{PbO}$  was partially replaced by  $\text{PbX}_2$ . The relatively long lifetime of the upper  ${}^4I_{13/2}$  state of  $\text{Er}^{3+}$  is demanded for solid-state laser active media and optical amplifiers (EDFA). The  ${}^4I_{13/2}$  lifetimes for glass samples with  $\text{PbX}_2$  are close to  $610 \mu\text{s}$  ( $X = \text{F}$ ),  $500 \mu\text{s}$  ( $X = \text{Cl}$ ) and  $555 \mu\text{s}$  ( $X = \text{Br}$ ). The luminescence decays are longer in comparison with the one obtained for the oxide sample ( $\tau_m = 400 \mu\text{s}$ ). The highest value of  $\tau_m$  was obtained for sample with  $\text{PbF}_2$ . This is in good agreement with the results of lead halotellurite glasses doped with  $\text{Er}^{3+}$  [6]. Further substitution of  $\text{PbO}$  by  $\text{PbF}_2$  in borate glass enhanced significantly luminescence intensities (Fig. 3) and lifetimes (Fig. 4) of  $\text{Er}^{3+}$ . The total replacement of  $\text{PbO}$  by  $\text{PbF}_2$  results in a two-fold increase of the  ${}^4I_{13/2}$  lifetime of  $\text{Er}^{3+}$  ions from  $400 \mu\text{s}$  to  $820 \mu\text{s}$ , which is advantageous from the optical point of view [9].

### 3.2. Influence of thermal treatment

The influence of thermal treatment on the optical properties of  $\text{Er}^{3+}$  ions in oxyfluoride lead borate glass was analyzed in detail [10]. During temperature-controlled crystallization, crystalline domains embedded in the glass matrix are formed. These new advanced materials with their general properties between crystals and glasses [11] are known in the literature as transparent glass-ceramics (TGC). Transformation from glasses to glass-ceramics causes changes in spectroscopic properties of  $\text{Ln}^{3+}$ . Spectral lines are more intense and narrowed. Luminescence decays from excited states of  $\text{Ln}^{3+}$  ions in glass-ceramics are relatively longer in comparison to precursor glasses. This behavior can be explained by changes in the environment around  $\text{Ln}^{3+}$  ions.

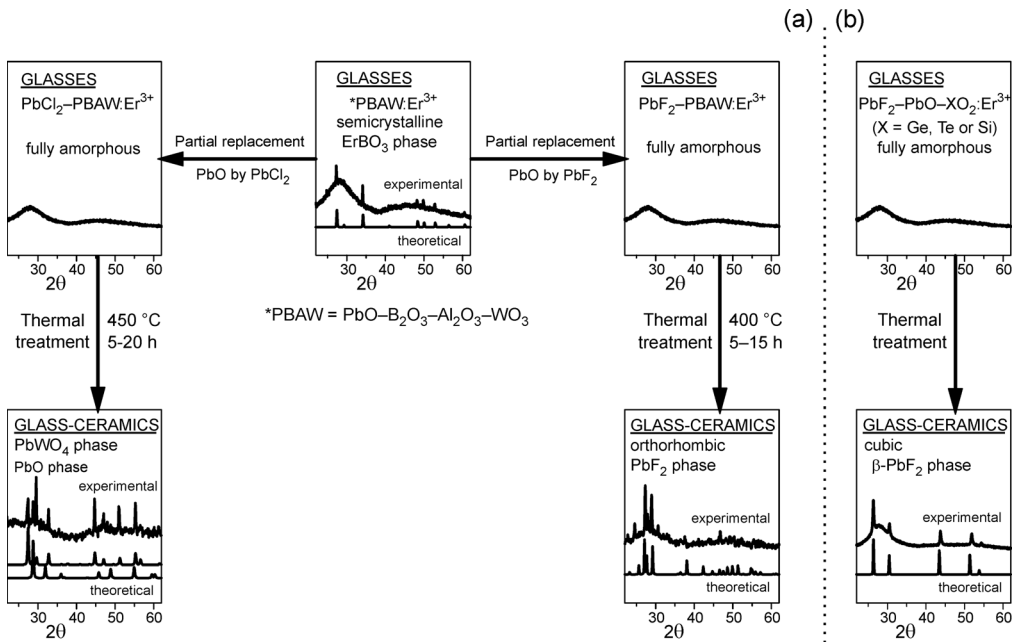


Fig. 5. Thermal treatment of precursor glasses.

The structural changes for borate glasses with  $PbX_2$  ( $X = F$  or  $Cl$ ) induced by thermal treatment and evidenced using X-ray diffraction are well illustrated in Fig. 5. It is interesting to see that the  $Ln^{3+}$ -doped oxide lead borate glasses in the  $PbO$ - $B_2O_3$ - $-Al_2O_3$ - $WO_3$  system, referred to as PBAW, are fully amorphous, except for  $Er^{3+}$ . Lead borate glasses singly doped with  $Er^{3+}$  or doubly doped with  $Er^{3+}$  and  $Yb^{3+}$  are semi-crystalline systems with the presence of  $ErBO_3$  phase. The fully amorphous lead borate glasses doped with  $Er^{3+}$  are possible to obtain in the case of replacement  $PbO$  by  $PbX_2$  ( $X = F, Cl$ ). Thermal treatment introduces the transformation from glass to glass-ceramic material. The X-ray diffraction analysis indicates that the orthorhombic  $PbF_2$  crystals are formed during controlled crystallization of precursor lead borate glass (Fig. 5, part a), in contrast to the other oxyfluoride systems (Fig. 5, part b) containing cubic  $\beta$ - $PbF_2$  phase [12, 13]. Quite a different situation is observed for glasses with  $PbCl_2$  after annealing. The preliminary results suggest larger tendency to crystallize lead tungstate than lead chloride in the lead borate glasses, which are promising in the formation of  $PbXO_4$  ( $X = W, Mo$ ) crystalline phases such as  $PbMoO_4$  crystals in the  $B_2O_3$ - $PbO$ - $MoO_2$  system [14].

Near-infrared luminescence and up-conversion spectra for  $Er^{3+}$  ions in glasses with  $PbX_2$  ( $X = F, Cl$ ) before and after annealing were examined. Figure 6 presents NIR luminescence spectra at 1.5  $\mu m$  measured for oxyfluoride and oxychloride glasses and glass-ceramics, which correspond to the main  $^4I_{13/2}$ - $^4I_{15/2}$  laser transition of  $Er^{3+}$ . The luminescence bands are more intense and narrowed for glass-ceramics than precursor glasses, which suggests that local structure around optically active ions was

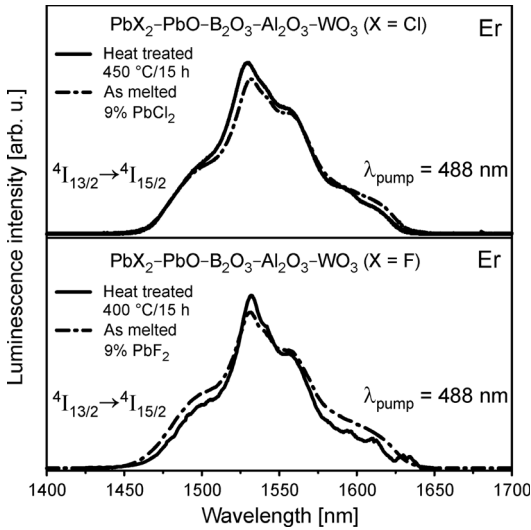


Fig. 6. NIR luminescence spectra for  $\text{Er}^{3+}$  ions in oxyhalide lead borate glasses before and after thermal treatment.

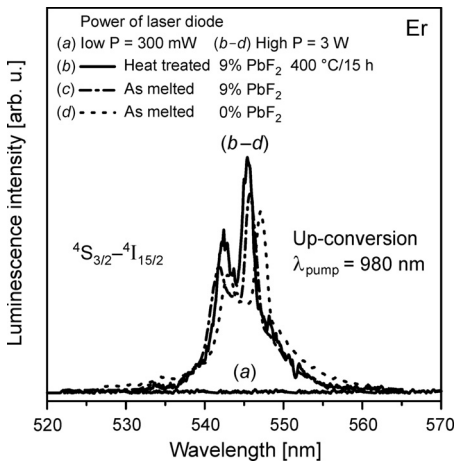


Fig. 7. Green up-conversion spectra for  $\text{Er}^{3+}$  ions in oxyfluoride lead borate glasses before and after thermal treatment.

changed and part of  $\text{Er}^{3+}$  ions are incorporated into crystalline phase. The luminescence decay analysis for oxyfluoride samples indicates that the  ${}^4I_{13/2}$  lifetime of  $\text{Er}^{3+}$  ions is slightly changed from 610  $\mu\text{s}$  (glass) to 670  $\mu\text{s}$  (glass-ceramic). This suggests that small amount of  $\text{Er}^{3+}$  ions is incorporated into the orthorhombic  $\text{PbF}_2$  crystals. The similar phenomena were observed for  $\text{Er}^{3+}$  ions in borate glass with  $\text{PbCl}_2$  before and after annealing.

The green up-conversion luminescence of  $\text{Er}^{3+}$  ions in oxyfluoride lead borate glasses and transparent glass-ceramics was registered under excitation with laser diode at 980 nm (Fig. 7). There were no up-conversion spectra observed for samples with  $\text{PbCl}_2$ . The luminescence band at about 545 nm corresponds to  ${}^4S_{3/2}-{}^4I_{15/2}$  transition of  $\text{Er}^{3+}$  ions. In comparison with the precursor glass the luminescence intensity is considerably higher, whereas the luminescence linewidth slightly decreases in

the oxyfluoride TGC systems under study. This indicates that part of the trivalent erbium is incorporated into  $PbF_2$  crystalline phase.

Two dominant 2-photon mechanisms are involved in the up-conversion process [15], namely the excited state absorption (ESA) and energy transfer up-conversion (ETU). The  $^4I_{11/2}$  level is directly excited by 980 nm line. In the ESA process, the  $Er^{3+}$  ions ( $^4I_{11/2}$  state) absorb photons and then are excited to  $^4F_{7/2}$  state. In the ETU process, two excited  $Er^{3+}$  ions ( $^4I_{11/2}$  state) interact with each other. One of them is de-excited to  $^4I_{15/2}$  ground state, whereas the other is promoted to  $^4F_{7/2}$  state. Both ESA and ETU processes populate the  $^4F_{7/2}$  state, which transfers energy nonradiatively very fast to  $^4S_{3/2}$  state of  $Er^{3+}$ . Finally, the green up-conversion luminescence due to  $^4S_{3/2} - ^4I_{15/2}$  transition of  $Er^{3+}$  ions has been observed.

In our case, the conversion of near-infrared radiation into visible (green) light is observed only in the high limit of laser power. The relatively high power of excitation source was used to register the luminescence spectrum, due to low efficiency of up-conversion process. In the low power limit of diode laser, the up-conversion process was not observed for Er-doped lead borate glasses, in contrast to glass samples doubly doped with  $Yb^{3+}$  and  $Er^{3+}$  ions [16, 17].

## 4. Conclusions

An introduction of  $PbX_2$  ( $X = F, Cl$  or  $Br$ ) to the borate glass changes coordination sphere around  $Er^{3+}$  ions. It results in the reduction of spectral linewidth for the  $^4I_{13/2} - ^4I_{15/2}$  transition in  $Br \rightarrow Cl \rightarrow F$  direction and the increase of luminescence lifetime for the  $^4I_{13/2}$  state of  $Er^{3+}$ . The  $^4I_{13/2}$  lifetime is longer for glass sample with  $PbF_2$  than  $PbCl_2$  and  $PbBr_2$ , which suggests that the F ions might have a special effect on luminescence lifetime among the halides.

Thermal treatment introduces transformation from glasses to transparent glass-ceramics. The spectroscopic consequence of this transformation is the narrowing of spectral lines and the elongation of luminescence lifetimes of  $Er^{3+}$ .

*Acknowledgment* – The Ministry of Science and Higher Education supported this work under the research project N N507 3617 33.

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*Received November 12, 2009  
in revised form March 23, 2010*