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$PbWO_4$ formation during controlled crystallization of lead borate glasses

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Abstract

Lead borate glasses were prepared and then heat treated in order to obtain transparent glass-ceramics. Controlled crystallization of precursor lead borate glass at appropriate annealing temperature and time led to formation of the $PbWO_4$ crystallites. The observed broad blue emission band is related to the $PbWO_4$ crystallites. The influence of PbX_2 content (X = F, Cl, Br), PbF_2 concentration and lanthanide doping (Eu, Dy) on the excitation and emission spectra of lead borate glass-ceramics containing $PbWO_4$ phase was examined. The relationship between Pb–X bond and spectral line width of the blue emission can be successfully observed, when halogen X ions (X = F, Cl or Br) are also present in the distorted $PbWO_4$ crystallites.

Keywords: Lead borate glasses; Crystallization; $PbWO_4$; Structure; Luminescence

1. Introduction

Oxide [1–3] and oxyhalide [4–6] lead borate glasses belong to a wide family of heavy metal glasses [7–11]. They find practical applications in laser technology, when trivalent lanthanide ions are built in a lead borate glass [12]. Various spectroscopic techniques such as FT-IR [13], NMR [14] and EPR [15] were successfully used to characterize lead borate glass. Thanks to this, the local structure of lead borate glass after gamma irradiation [15] or heat treatment [16] was clarified. The latter process, i.e. heat treatment of precursor glasses, done under specific conditions of time and annealing temperature, is very useful to obtain transparent glass-ceramics (TGC).

Controlled crystallization leads to transformation from a glassy state to a glass-ceramic. During heat treatment of precursor glasses (called also devitrification or ceramming process) glass-ceramic materials can be obtained, in which, crystallites are formed in micrometric or nanometric scale. Previously published results indicated that crystallization process appeared to be an effective way for inducing thermoluminescence in lead borate glass [17]. Thus, lead borate glass-ceramics are promising materials for thermoluminescence dosimetric applications. The presence of several crystalline phases in lead borate glass after heat treatment gives important contribution to luminescence characteristics of the Pr^{3+} ions [18]. Also, in the multicomponent B_2O_3–PbO–Al_2O_3–WO_3 glass system [19] crystallites of the lead tungstate phase are produced. It has been proved in our previously published results that the $PbWO_4$ phase can be obtained from controlled crystallization process. However concentration of lead and tungsten oxide should be at the appropriate level [20]. Also, the role of WO_3 phase in structural and optical properties of multicomponent WO_3–Al_2O_3–PbO–B_2O_3 glasses was explained [21]. From literature data it has been known that crystallites of the $PbWO_4$ phase are successfully formed in lead borate glass after laser irradiation [22]. They were synthesized using sonochemical methods [23]. The crystalline phase of $PbWO_4$ revealed the ABO_4-type of structure with

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tetragonal crystal lattice. However, phase transformation from tetragonal to monoclinic structure is also possible [24].

In the present work, formation of the $PbWO_4$ phase during controlled crystallization of lead borate glasses is examined using X-ray diffraction, excitation and emission spectroscopy. New results, which reveal the influence of the PbX_2 content (X=F, Cl, Br) and lead fluoride concentration ($yPbF_2=9$, 36, 72 wt%) as well as a type of lanthanide doping on optical properties of the lead borate systems, are discussed. These phenomena had not been observed for lead borate glasses before heat treatment. It can be due to the absence of the crystalline $PbWO_4$ phase.

2. Experimental techniques and materials

The chemical composition of multicomponent lead borate glasses ($yPbX_2$–PBAW:Ln) was as follows: $yPbX_2$–$(72-y)$ PbO–$18B_2O_3$–$6Al_2O_3$–$3WO_3$–$1Ln_2O_3$; X=F, Cl or Br; $y=9$, 36 or 72 wt%; Ln=Dy or Eu. Anhydrous oxides as well as the lead halides PbX_2 (99.99% purity, Aldrich) were used as the starting materials. In order to prepare samples, appropriate amounts of components were weighted and homogeneously mixed and annealed in an atmosphere of dry argon. The mixed reagents were capsulated in Pt crucible, melted at 850 °C and kept there for 1 h. Then they were poured into a preheated copper mold and annealed at temperature below the temperature of the glass transition. After that, the samples were slowly cooled down to room temperature. Thermal behavior of the as-received glasses was characterized with use of a Perkin-Elmer calorimeter (DSC-7). Measurements were done only in the heating mode with the rate of 10 °C/min. The glass transition temperature T_g was determined with accuracy of ± 1 °C. In order to obtain glass-ceramics the samples were annealed at 450 °C for 10 h. The X-ray diffraction patterns were carried out using an X′Pert Pro diffractometer with $Cu_{K\alpha}$ radiation. The luminescence spectra of glass-ceramic samples were excited at UV with filtered radiation provided by a Xenon lamp. Luminescence was dispersed by a 1-m double grating monochromator. The bandwidth of the monochromator was set at 0.1 nm. A photomultiplier with S-20 spectral response was applied to detect the emission of samples. Signals were averaged using the Stanford SRS 250 boxcar integrator and registered with a computer program. The resolution for all spectral measurements was ± 0.1 nm.

3. Results and discussion

Multicomponent mixed oxyhalide lead borate glasses containing PbX_2 components referred to as $yPbX_2$–PBAW:Ln (where X denotes F, Cl or Br; $y=9$, 36 or 72 wt%; Ln=Dy or Eu) were prepared. From the DSC heating curves, the glass transition temperature T_g was determined for the studied glass systems. Depending on the X element ~~of~~ in the PbX_2 phase, the glass transition temperature T_g was close to 340 °C (X=F), 375 °C (X=Cl) and 390 °C (X=Br). It can be noted that their values increased in F→Cl→Br direction [20]. Obtained results were in good agreement with that received for the oxide (PBAW:Er) and the oxyfluoride (PbF_2–PbAW:Er) lead borate glasses. For these, value of the glass transition temperature T_g varied from 310 to 475 °C, depending on the B_2O_3:PbO ratio and concentration of the PbF_2 component [25]. In order to obtain transparent glass-ceramics, the precursor glasses were heat-treated at temperature above the glass transition temperature (450 °C/10 h). All studied glass-ceramic samples were fabricated under the same experimental conditions.

X-ray diffraction was used for phase identification and verification of the crystallization progress induced by isothermal annealing in the precursor lead borate glasses. The X-ray diffraction patterns measured for the studied glass systems with PbX_2 content (X=F, Cl, Br) and various PbF_2 concentrations before and after heat treatment are shown in Figs. 1 and 2, respectively. Independent of concentration of the PbX_2 or PbF_2 component, several narrow diffraction lines were identified. In general, diffraction lines were identified as belonging to the $PbWO_4$ phase with tetragonal unit cell (PDF-2 card no. 19-0708).

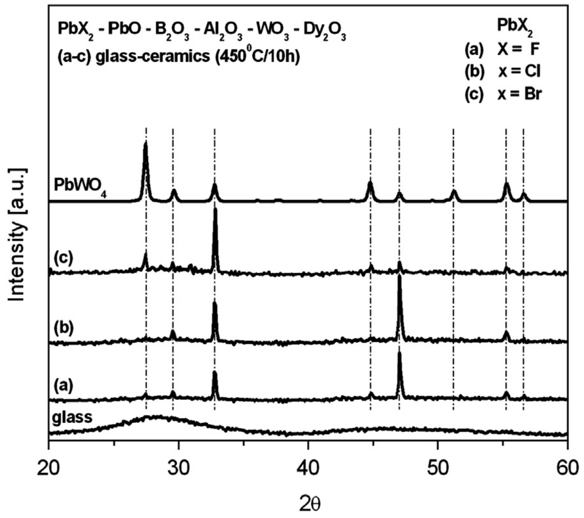

Fig. 1. X-ray diffraction patterns measured for lead borate glasses containing PbX_2 (X=F, Cl, Br) after heat treatment.

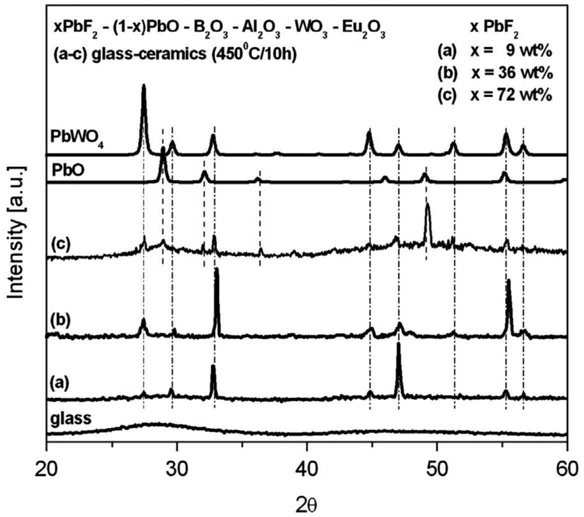

Fig. 2. X-ray diffraction patterns measured for lead borate glasses with various PbF_2 concentrations after heat treatment.

However, in the glass-ceramic sample containing a high concentration of fluoride component (72 wt% PbF_2) additional diffraction peaks appeared. These peaks were identified as belonging to the PbO crystalline phase (PDF-2 card no. 35-1482).

It is worth noticing that measured position of diffraction lines for the $PbWO_4$ phase showed the same value as the pattern 19-0708 (PDF-2). However, measured intensities of diffraction lines differed in their intensities in comparison to that from the PDF pattern. Especially, the diffraction line 112 of the $PbWO_4$ phase, which is considered to be the most intense, appeared as a weak one. This can be due to two reasons. First, growth of the crystallites could be directional. This means that differences in intensities of diffraction originated from texture. However, measured pole figures did not show significant differences in pole densities. Second, halogen X ions (X=F, Cl or Br) can substitute one of the elements in the $PbWO_4$ phase. In the light of the results obtained from the excitation and emission measurements (discussed in the next sections) this reason seems to be more probable.

3.1. Influence of the element in PbX_2 (X=F, Cl, Br) component on optical properties

Fig. 3 presents the excitation spectra measured for the PbX_2–PBAW:Dy glasses after heat treatment, which were monitored at $\lambda_{em}=430$ nm. The concentration of the PbX_2 (X=F, Cl, Br) component was equal to 9 wt%. Independent of the PbX_2 component, two excitation bands, located at 310 nm and 360 nm, were observed. The main strong excitation peak, at 310 nm, is characteristic for the presence of the crystalline $PbWO_4$ phase [26,27]. It corresponds to an exciton excitation [26] and can be shifted to shorter wavelengths [27]. These spectral lines at 310 nm and 360 nm were not identified for the studied glass systems before the annealing process. It is worth noticing that the excitation spectra for the PbX_2–PBAW:Dy heat treated glasses were slightly shifted toward the direction of longer wavelengths following components: Br→Cl→F.

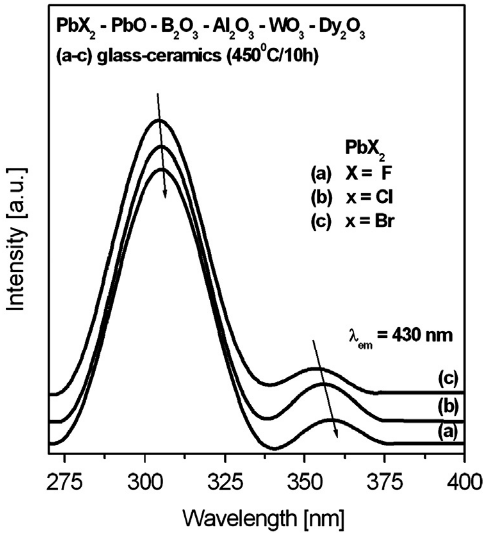

Fig. 3. Excitation spectra for lead borate glasses containing PbX_2 (X=F, Cl, Br) after heat treatment.

The glass-ceramic samples also contain Dy^{3+} ions, which as optically active ions give yellow/blue luminescence well observed in the lead borate glasses [6] and glass-ceramics [28]. For this reason, our thermally treated samples were excited in the spectral range ($\lambda_{ext}=310$ nm), where bands due to 4f–4f electronic transitions of Dy^{3+} ions are not observed. Fig. 4 shows emission spectra for the PbX_2–PBAW:Dy glasses after heat treatment measured under 310 nm excitation. The spectra consisted of broad blue emission bands, which are typical for the crystalline $PbWO_4$ phase [27,29]. This effect was not observed for lead borate glasses doped with Dy before thermal treatment. It can be due to the absence of the crystalline $PbWO_4$ phase. From the literature, it has been known that the emission of $PbWO_4$ can be composed of several sub-bands, but the origin of blue, green and red bands is still under discussion [26]. It was suggested that the blue emission coming from the $PbWO_4$ crystals, centered at about 430 nm, is based on the radiative transition within the tetrahedral $[WO_4^{2-}]$ group [29]. The green one at 500 nm was due to a WO_3 defect center [30]. It is also worth noticing that the spectral width of blue band in the PbX_2–PBAW:Dy system reduced from $\Delta\lambda=74.4$ nm (X=Br) to 64.4 nm (X=Cl) and 60 nm (X=F) in Br→Cl→F direction (Table 1). The anion electronegativities for the elements: F, Cl, Br were 4.0, 3.0 and 2.8, respectively. Considering these facts, it can be concluded that the Pb^{2+} ions form more ionic chemical bonds with their nearest neighboring of the X^- anions in the Br→Cl→F direction. This results in decrease of the spectral line widths. It is impossible to detect

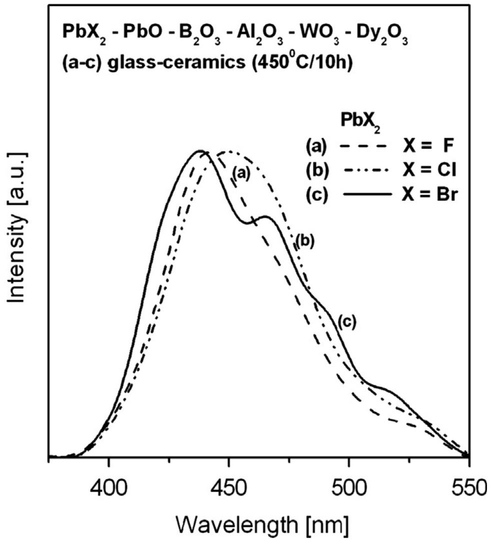

Fig. 4. Emission spectra for lead borate glasses containing PbX_2 (X=F, Cl, Br) after heat treatment.

Table 1
Emission linewidth for Dy-doped oxyhalide glass-ceramics containing $PbWO_4$.

$yPbX_2$–PBAW:Dy	λ_p [nm]	$\Delta\lambda$ [nm]
X=F	441.5	60.0
X=Cl	450.0	64.5
X=Br	438.0	74.5

$y=9$ wt%.

such phenomena in crystallites of the pure $PbWO_4$ phase. It can be proved that halogen ions are present in the distorted crystal unit of the $PbWO_4$ phase influencing on their excitation and emission properties. Recently, the influence of the F^-, Cl^-, I^- and S^{2-} doping ions on scintillation properties of the $PbWO_4$ crystals was also reported [31].

3.2. Influence of PbF_2 concentration on optical properties

The previously published results for the $PbWO_4$ single crystals indicated, that the presence of lead fluoride strongly influenced their structure, stability and scintillation properties [32]. A mechanism of doping was proposed for Cr^{3+} ions, which, with the help of F^- ions, predominantly occupied the W^{6+} sites in the $PbWO_4$ crystals [33].

Here, the influence of the PbF_2 concentration on the excitation and emission spectra in lead borate glass-ceramics containing $PbWO_4$ crystalline phase is presented. Fig. 5 shows the excitation spectra detected for the PbF_2–PBAW:Eu glasses after heat treatment. They were monitored at $\lambda_{em} = 430$ nm. The concentration of the PbF_2 component was changed from 9 wt% to 72 wt%. The measured spectra consisted of two characteristic bands for the $PbWO_4$ phase, but they were shifted toward the direction of longer wavelengths in comparison to the one obtained for samples containing PbX_2 (Fig. 3). Moreover, the spectra were shifted to longer wavelengths with increase of the PbF_2 concentration. Fig. 6 presents emission spectra measured under UV excitation for the $yPbF_2$–PBAW:Eu glasses ($y = 9$, 36, 72 wt%) after heat treatment. The thermally treated glass samples were excited in the spectral range, where bands due to 4f–4f electronic transitions of Eu^{3+} are not observed. Similar to those samples containing PbX_2, the spectra consisted of blue emission bands, which are typical for the $PbWO_4$ crystal phase. However, the emission bands for each sample were broadened with an intense tail extending up to nearly 700 nm. The spectral linewidth for the $yPbF_2$–PBAW:Eu system is reduced with increase of the PbF_2 concentration from 117.5 nm ($y = 9$wt%) to 91.5 nm ($y = 72$wt%). The values of spectral linewidth for the $yPbF_2$–PBAW:Eu glass-ceramic system are shown in Table 2. The number of more ionic chemical bonds of the Pb^{2+} ions with their nearest neighboring F^- anions starts to increase with increase of the PbF_2 concentration. It results in reduction of the spectral linewidths. This is in good agreement with the experimental results obtained for glass-ceramic samples containing the PbX_2 component (Section 3.1). It also confirmed the presence of fluorine ions in the distorted crystal unit of the $PbWO_4$ phase.

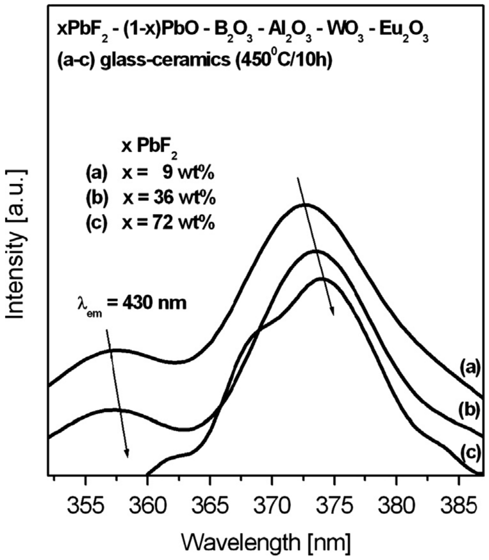

Fig. 5. Excitation spectra for lead borate glasses with various PbF_2 concentrations after heat treatment.

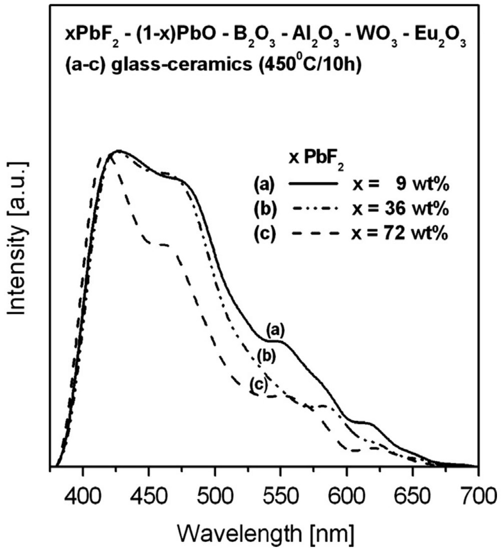

Fig. 6. Emission spectra for lead borate glasses with various PbF_2 concentrations after heat treatment.

Table 2
Emission linewidth for Eu-doped oxyfluoride glass-ceramics containing $PbWO_4$.

$yPbF_2$–PBAW:Eu	λ_p [nm]	$\Delta\lambda$ [nm]
$y = 9$ wt%	427.0	117.5
$y = 36$ wt%	426.5	105.5
$y = 72$ wt%	417.0	91.5

3.3. Influence of lanthanide doping on optical properties

Finally, the influence of type Ln^{3+} ion (Ln = Dy or Eu) doping on the excitation and emission spectra in lead borate glass-ceramics containing the crystalline $PbWO_4$ phase was examined. The previously published results indicate that the trivalent europium and dysprosium ions play a significant role of spectroscopic probes in the lead borate glasses [34].

Here, two Ln-doped samples (Ln = Dy, Eu) with the same concentration of the PbF_2 component (9 wt%) are compared. In both cases, the Ln^{3+} content is the same and close to 1 wt%. The excitation and emission spectra detected for the $yPbF_2$–

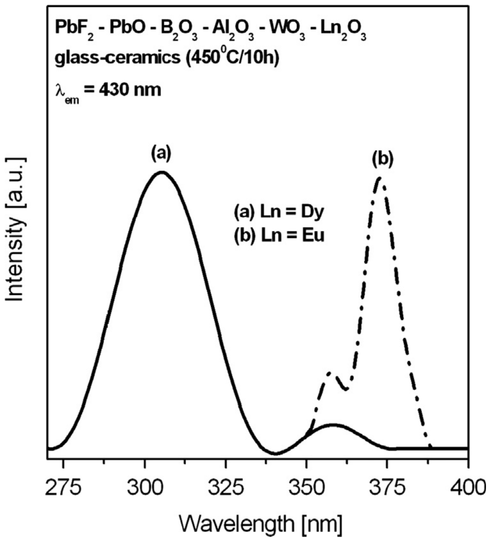

Fig. 7. Excitation spectra for oxyfluoride lead borate glasses doped with Ln^{3+} (Ln = Dy, Eu) after heat treatment.

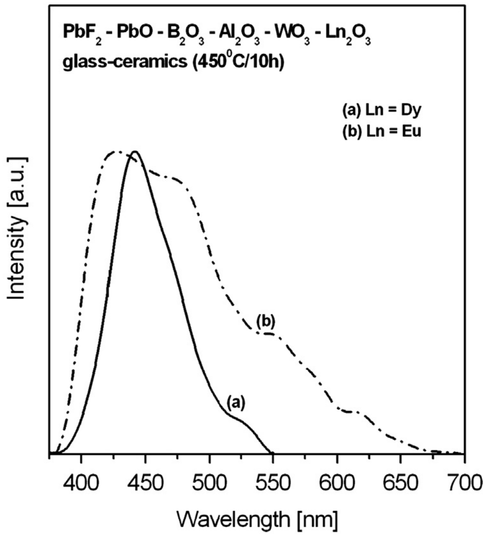

Fig. 8. Emission spectra for oxyfluoride lead borate glasses doped with Ln^{3+} (Ln = Dy, Eu) after heat treatment.

PBAW:Ln ($y = 9$ wt%; Ln = Dy, Eu) glass-ceramic samples are presented in Figs. 7 and 8, respectively.

The excitation and emission spectra measured in the same experimental conditions (450 °C/10 h) for thermally treated glass-ceramic samples consisted of characteristic bands, which were due to the presence of the $PbWO_4$ phase. The excitation and luminescence bands were not observed for the glass samples before heat treatment. The band maxima monitored at λ_{em}=430 nm were located at different excitation wavelengths (Fig. 7), whereas emission linewidths for the oxyfluoride glass-ceramic samples containing Ln^{3+} were close to $\Delta\lambda = 60$ nm (Ln = Dy) and $\Delta\lambda = 117.5$ nm (Ln = Eu) (Table 3). Our investigations clearly proved that the spectral properties of the studied systems also depend on type of lanthanide doping.

Table 3
Emission linewidth for Ln-doped oxyfluoride glass-ceramics containing $PbWO_4$.

$y$$PbF_2$–PBAW:Ln	λ_p [nm]	$\Delta\lambda$ [nm]
Ln = Dy	441.5	60.0
Ln = Eu	427.0	117.5

$y = 9$ wt%.

4. Summary

Multicomponent mixed oxyhalide lead borate glasses were prepared and then heat-treated in order to obtain transparent glass-ceramics. Controlled crystallization of precursor lead borate glass at appropriate annealing temperature ($T = 450$ °C) and time ($t = 10$ h) led to formation of the $PbWO_4$ crystallites. Observed broad blue emission spectra were related to the presence of $PbWO_4$ crystallites. The influence of concentration of PbF_2 and PbX_2 content (X = F, Cl, Br) as well as doping of lanthanide (Eu, Dy) on excitation and emission spectra of the $PbWO_4$ containing transparent lead borate glass-ceramic samples was examined. The relationship between the Pb–X bond and spectral line width of the blue emission can be successfully observed, when halogen X ions (X = F, Cl or Br) are present in the distorted unit cell of the $PbWO_4$ crystallites.

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