Praseodymium in heavy metal oxyfluoride glass systems

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A new thermally stable glasses based on P2O5 – InF3 and PbF2 – B2O3 containing Pr3+ ions were prepared, which belong to wide family of heavy metal oxyfluoride systems. Influence of P2O5 content on thermal, structural and optical behavior of multicomponent InF3 – based glass has been investigated, whereas the second oxyfluoride system in the case of total substitution PbO by PbF2 has been analyzed. A large value of stability parameter ΔT close to 157°C was obtained for Pr – doped oxyfluoride glass with 8% of P2O5 content. With further increasing P2O5 content stability parameter ΔT decreased and several crystalline peaks related to InOF phase appeared, what was stated by X-ray diffraction. Shift of luminescence lines has been observed for both heavy metal oxyfluoride glass systems. However, shift direction depends on kind of additives (oxide or fluoride components) to the basic matrix. Incorporation of P2O5 results in shift of red luminescence due to lines has been observed for both heavy metal oxyfluoride glass systems. However, shift direction depends on kind of additives (oxide or fluoride components) to the basic matrix. Incorporation of P2O5 results in shift of red luminescence due to PbF2 – B2O3 emitting reddish–orange light. Substitution PbO by PbF2 leads to shift of luminescence band in direction to shorter wavelengths.

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1. Introduction

Heavy metal oxyfluoride glasses containing rare earth ions are the most important class of the modern advanced materials for application in optoelectronics, which have been extensively studied in recent years. The main disadvantages of fluoride glasses are poor chemical and mechanical stability and easy crystallization. In contrast to simple oxide or fluoride glasses, some advantages have been observed in mixed oxyfluoride systems, which combined the excellent optical properties of rare earth ions in fluoride host with simultaneously large chemical stability and mechanical property of oxide glasses. Several reports on the oxyfluoride glass systems in different chemical compositions have been known in literature. One of them is phosphate fluoride glass containing P2O5 and CaF2 [1] as well as lead fluoroborate glass [2], which have been investigated using spectroscopic methods.

Praseodymium – doped crystals and glasses have proved to be effective for several applications in optical devices as blue up-converters (1P5 – 1H4) and solid-state lasers emitting visible (1D2 – 1H4) or near-infrared light (1G4 – 1H4), respectively. The latter plays the role as efficient amplifier working around 1.3μm requested for optical telecommunication systems. Especially, Pr3+ ions in a great number of optical materials like crystalline compounds [3] as well as heavy metal oxide and fluoride glasses [4] exhibit a prominent red luminescence from the 1D2 excited state. In contrast to them, more intensive visible luminescence due to 3P0 – 3F2 transition than 1D2 – 3H4 one is observed for Pr3+ ions in polymeric (PMMA) materials [5]. Recently, chalcogenide glass – polymer composite materials containing Pr3+ ions were prepared [6], which can be interesting from the optical point of view.

Recently, rare earth doped fluoride and oxide glasses based on InF3 [7-11] and PbO – B2O3 [12-16] were investigated. Presented work deals with thermal, structural and optical investigations of Pr3+ ions in two different heavy metal oxyfluoride glassy matrices based on P2O5 – InF3 and PbF2 – B2O3. Both optical systems have been investigated using DSC, XRD, FT-IR and photoluminescence spectroscopy.

2. Experimental details

Oxyfluoride glasses in (72–x)PbO–xPbF2–18B2O3–6Al2O3–3WO3–1Pr2O3 (x = 0 – 72 wt%) system referred as xPbF2 – PBAW:Pr and 44InF3–14ZnF2–(19-x)BaF2–xP2O5–17SrF2–3GaF3–2LaF3–1PrF3 (x = 0 – 16 wt%) system referred as xP2O5–IZBSGL:Pr were prepared. For both systems, anhydrous oxides and fluorides (99.99% purity, Aldrich) were used as a starting materials and a homogeneous mixture was heated in a protective atmosphere of dried argon. Glasses were melted at 850°C in Pt crucibles, then poured into preheated copper moulds andannealed below the glass transition temperature. After this procedure, the samples were slowly cooled to the room temperature.

The glass samples were characterized by a Perkin Elmer differential scanning calorimeter (DSC) and INEL diffractometer (XRD). The DSC curves were measured with a heating rate of 10deg/min. The X-ray diffraction analysis was carried out with Cu Kα radiation in 20 range 0° to 120°. The IR transmission spectra in range of 400 - 4000 cm⁻¹ were taken on BIO-RAD FT-IR spectrometer using the standard KBr pellet disc technique. The samples has been excited by a Continuum Surelite Optical Parametric Oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser. The luminescence was dispersed by a 1-meter double grating monochromator and detected with a photomultiplier with S-20 spectral response. The luminescence 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.

3. Results and discussion

3.1 P$_2$O$_5$–InF$_3$–ZnF$_2$–BaF$_2$–SrF$_2$–GaF$_3$–LaF$_3$–PrF$_3$ glasses

Thermal properties of xP$_2$O$_5$ – IZBSGL:Pr oxyfluoride glasses containing different concentration of P$_2$O$_5$ have been examined. Fig. 1 shows DSC curves recorded for glasses based on P$_2$O$_5$ – InF$_3$ containing Pr$^{3+}$ ions. From DSC curves characteristic temperatures such as glass transition temperature T$_g$, crystallization onset T$_x$ and maximum of the crystallization peak T$_p$ were obtained, from which stability factor $\Delta T$ defined as difference between glass transition temperature T$_g$ and crystallization onset T$_x$, was calculated. This parameter plays an important role in manufacturing of the optical fibers.

![Fig. 1. DSC curves recorded for Pr – doped glasses based on P$_2$O$_5$ – InF$_3$.](image)

Rare earth – doped fluoride glass has been formed in many elements systems, but only a few numbers of them can be considered as stable and suitable for optical devices. Unfortunately, one of the main disadvantages to application is relatively low thermal stability and easy crystallization during melting and forming. From literature concerning data about preparation of fluoride glass fibers it is known, that fiber drawing is possible when value of $\Delta T$ is higher than 100°C. This parameter usually does not exceed 100°C in ternary InF$_3$–ZnF$_2$–BaF$_2$–SrF$_2$ (IZBS) fluoride glasses. However, further optimization was achieved in IZBS basic system using different fluorides as stabilizing additives to decrease devitrification rate. Increasing the number of components may enhance glass-forming ability. Thus, it is possible to obtain thermally stable fluoride glasses with relatively high $\Delta T$ factors in the multicomponent InF$_3$ – based systems. The values of $\Delta T$ close to 108 °C with GaF$_3$ [17], 117 °C with LiF [18] and 118 °C with GaF$_3$ and LaF$_3$ [19] components in the InF$_3$ – based glasses were obtained. The addition of new components to the base glass is still under the test because of changes of the glass composition as well as the relative ratios of the existing components drastically influence on thermal and optical properties. For that reason, P$_2$O$_5$ as a well-known glass-former and stabilizing component was added to the fluoride matrix. For Pr-doped fluoroindate glass without P$_2$O$_5$ thermal stability parameter $\Delta T$ is found to be 116 °C. The best value of $\Delta T$ close to 157 °C was obtained for mixed oxyfluoride system with 8% of P$_2$O$_5$ content. Further addition of P$_2$O$_5$ leads to decrease $\Delta T$ factor and partial crystallization of the investigated oxyfluoride glass system. It results in an additional second exothermic peak observed for mixed oxyfluoride glass with 16% of P$_2$O$_5$ content and suggests that crystallization process takes place. It is consistent with XRD results.

![Fig. 2. X-ray diffraction patterns for Pr – doped glasses based on P$_2$O$_5$ – InF$_3$.](image)

Fig. 2 shows the X-ray diffraction patterns obtained for samples without and with 16% of P$_2$O$_5$ content, respectively. The XRD patterns of samples without and with P$_2$O$_5$ (up to 12%) display two broad peaks corresponding to remaining amorphous phases. Glass tendency towards crystallization increases with further increasing oxide component and several diffraction lines due to the crystalline phases are observed for sample with 16% of P$_2$O$_5$ content. Phase identification reveals, that crystalline peaks can be related to the InOF phase.

![Fig. 3. FT-IR transmission spectra recorded for Pr – doped glasses based on P$_2$O$_5$ – InF$_3$.](image)

It also corroborates results obtained from FT-IR transmission measurements (Fig. 3), where lines
associated with non-bridging P-O vibrations are shifted in direction of lower frequencies with increasing P2O5 content (red shift). It indicates that phosphate group was able to bridge octahedral \([\text{InF}_6]\) group. At consequence, InOF phase is formed, which was evidenced using X-ray diffraction analysis for sample with 16% of P2O5. Two intense bands associated with In-F and P-O vibrations are observed for Pr - doped oxyfluoride glasses in the IR transmission spectra. The first band existing at 468 cm\(^{-1}\) is assigned to the \(\nu_1 (A_{1g})\) symmetric vibration of the octahedral \([\text{InF}_6]\) group. The second broad band consists of four lines appearing at 957, 1021, 1061 and 103 cm\(^{-1}\), which are assigned to the P-O symmetric (\(\nu_s\)) and asymmetric (\(\nu_a\)) stretching vibrations. The intensity of these lines increases with increasing of P2O5 content. Detailed information about assignment of infrared bands associated with P-O vibrations can be found in [1, 20].

Fig. 4 shows luminescence registered for Pr\(^{3+}\) ions in fluoride and oxyfluoride InF\(_3\) - based glass. Luminescence from both \(^3\)P\(_0\) and \(^1\)D\(_2\) excited levels are observed for fluoride and oxyfluoride systems under excitation of \(^3\)P\(_2\) level of Pr\(^{3+}\) ions. Energy gap between \(^3\)P\(_0\) level and the next lower \(^1\)D\(_2\) level is found to be 3900cm\(^{-1}\). Using the measured and calculated radiative lifetimes for the \(^3\)P\(_0\) level in case of low Pr\(^{3+}\) concentration and phonon energy of the host (hv\(\sim\)500 cm\(^{-1}\)), the non-radiative transition rate \(W_{nr}\) can be calculated. The \(W_{nr}\) value due to multiphonon relaxation process determined in [21] for InF\(_3\) - based glass is close to 2.47x10\(^4\) s\(^{-1}\), which indicates that radiative and non-radiative transitions from the \(^3\)P\(_0\) level take place. The \(^3\)P\(_0\) level can populate quite efficiently \(^1\)D\(_2\) level. From this point of view it is possible to observe emission from \(^3\)P\(_0\) and \(^1\)D\(_2\) levels in this spectral range. Thus two strong asymmetric and less intense emission bands were recorded at 603, 616 and 636 nm, which correspond to the \(^3\)D\(_2\) - \(^3\)H\(_6\), \(^3\)P\(_0\) - \(^3\)H\(_6\), and \(^3\)P\(_0\) - \(^1\)F\(_2\) transitions, respectively. These luminescence lines are shifted to longer wavelengths, when P2O5 was introduced to the InF\(_3\) - based fluoride glass.

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\text{Fig. 4. Luminescence spectra recorded for Pr}^{3+}\text{ ions in fluoride and oxyfluoride InF}_3\text{ - based glasses.}
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### 3.2 PbF\(_2\)–PbO–B\(_2\)O\(_3\)–Al\(_2\)O\(_3\)–WO\(_3\)–Pr\(_2\)O\(_3\) glasses

Thermal properties of glasses based on PbF\(_2\) – B\(_2\)O\(_3\) containing Pr\(^{3+}\) ions have been analyzed. Influence of PbF\(_2\) on thermal behavior has been investigated using differential scanning calorimetry (DSC). Figure 5 presents DSC curves for oxyfluoride glasses with low (9%), middle (36%) and high (72%) PbF\(_2\) concentrations. The glass transition temperature was evaluated, but no obvious crystallization peak was detected in the limited range of DSC – 600 °C. Inset shows evolution of glass transition temperature \(T_g\) as a function of PbF\(_2\) concentration (0 - 72% wt). It is clearly seen, that glass transition temperature slightly decreases with increasing PbF\(_2\) concentration in glass composition.

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\text{Fig. 5. DSC curves recorded for Pr} – \text{doped glasses based on PbF}_2 – B_2O_3.
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Dependently on PbF\(_2\) concentration, the glass transition temperatures are located in 350–375°C ranges, which is in a good agreement with results obtained for similar Sm\(^{3+}\) or Dy\(^{3+}\) doped glasses in B\(_2\)O\(_3\) – ZnO – PbO system [22].

The value of \(T_g\) strongly depends on O/F ratio in glass composition. Introduction of the oxide component such as P\(_2\)O\(_5\) to the InF\(_3\) - based fluoride matrix induces an increase of glass transition temperature, which is attributed to the formation of stronger chemical bonds (see chapter 3.1, Fig. 1). The opposite effect has been observed for glass based on PbF\(_2\) – B\(_2\)O\(_3\). Firstly, as the PbF\(_2\) content increases the \(T_g\) values decrease rapidly suggesting that the PbF\(_2\) content acts as a network modifier. Secondly, the covalency of the Pb – F bond is smaller than that of the Pb – O bond because of the larger difference of electronegativity between cation and anion ions. It is expected that the influence of the Pb – F bond on the local ligand environments around Pr\(^{3+}\) ions increase with increasing of PbF\(_2\) concentration. Consequently, the covalency of the Pr – O/F bond decreases. Therefore, it suggests based on the observed evolution of \(T_g\) that the introduction of fluoride component decreases the strength of the average chemical bond and/or produces a less linked or interconnected glass network.

Fig. 6 presents FT-IR transmission spectra recorded for Pb\(_2\)O containing Pr\(^{3+}\) ions have been analyzed. Influence of PbF\(_2\) on thermal behavior has been investigated using differential scanning calorimetry (DSC). Figure 5 presents DSC curves for oxyfluoride glasses with low (9%), middle (36%) and high (72%) PbF\(_2\) concentrations. The glass transition temperature was evaluated, but no obvious crystallization peak was detected in the limited range of DSC – 600 °C. Inset shows evolution of glass transition temperature \(T_g\) as a function of PbF\(_2\) concentration (0 - 72% wt). It is clearly seen, that glass transition temperature slightly decreases with increasing PbF\(_2\) concentration in glass composition.

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The infrared bands due to the B–O vibrations have been observed in 1500–600 cm⁻¹ spectral ranges. Three characteristic groups of bands are due to BO₃ bending (650–700 cm⁻¹) and stretching vibrations of tetrahedral BO₄ (850–1050 cm⁻¹) and trigonal BO₃ (∼1300 cm⁻¹) units, respectively. Two important effects associated with total substitution of PbO by PbF₂ can be observed. Firstly, these bands are shifted to the lower frequency region (longer wavelengths). Secondly, the intensity of the infrared band related to the BO₄ units decreases, when PbO was replaced by PbF₂ in glass composition. The PbO₄ units bridge preferentially rather to BO₃ groups than BO₄ ones. The fluorine atoms added to the glass network start to reduce BO₄ units. Thus, the intensity of infrared band associated with BO₄ group decreases as clearly seen in Fig. 6. The opposite effect was observed for Sm – doped lead borate glass in the case of BO₄ unit formation, when the oxygen atoms added to the oxyfluoride glassy network reduces the effect of fluorine ions in the PbO₄ units [23].

In contrast to glass based on P₂O₅ – InF₃, quite intense luminescence from the ¹D₂ state was registered for glass based on PbF₂ – B₂O₃ under excitation of the ³P₂ level of Pr⁢⁺⁺ (Fig. 7). Blue shift of luminescence band related to the ¹D₂ – ³H₄ transition of Pr⁢⁺⁺ ions in oxyfluoride glass is observed in comparison to the oxide one. Excitation energy transfers very fast from ³P₂ level via ³P₁ level to the ³P₀ level by nonradiative relaxation. Energy gap between ³P₀ level and the next lower lying ¹D₂ level is found to be 3800 cm⁻¹. Thus, only three phonons (hν = 1260 cm⁻¹) are needed to bridge energy gap. Thus, the ¹D₂ level is populated quite efficiently by ³P₀ level of Pr⁢⁺⁺ ions.

From the exponential dependence of the multiphonon relaxation rates for rare earth ions in various glasses on the energy gap to the next-lower level, it is clearly seen that Wₘₜ value for borate glass is approximately 10⁵ times larger than that of fluoride system [24]. Thus, the ¹D₂ state is populated more efficiently in oxide or oxyfluoride lead borate glasses than fluoroindate ones with or without P₂O₅. At consequence, only luminescence from ¹D₂ excited state is observed, which corresponds to the ¹D₂ – ³H₄ transition of Pr⁢⁺⁺ ions. The luminescence band in 570 – 640 nm spectral range due to the ¹D₂ – ³H₄ transition of Pr⁢⁺⁺ ions is shifted in direction to the shorter wavelengths, when PbO was totally substituted by PbF₂.

Measured (τₘ) and calculated (τₐₐ₃) radiative lifetimes of ¹D₂ excited state of Pr⁢⁺⁺ ions in oxide and oxyfluoride lead borate glasses have been schematized in Figure 8. Luminescence lifetimes are compared to that ones obtained for fluoride and oxyfluoride InF₃ – based systems. Radiative lifetimes for ¹D₂ excited state of Pr⁺⁺ ions in fluoroindate glass [25] and lead borate glass [26] were calculated using Judd-Ofelt theory [27, 28]. Quantum efficiency (η) defined as τₘ / τₐₐ₃ was calculated. The η value of ¹D₂ excited state for lead borate glass (η = 14%) is much smaller than that obtained for fluoroindate matrix (η = 88%). It indicates that contribution of nonradiative processes to the excited state relaxation of Pr⁢⁺⁺ ions in lead borate glasses is significantly higher than fluoroindate ones. At consequence, the mechanism of ¹D₂ excited state relaxation is quite different in InF₃ – based glass [25] than PbO-B₂O₃ based system [26]. Both heavy metal systems have been analyzed as a function of PbF₂ and P₂O₅ content, respectively.

Fig. 6. FT-IR transmission spectra recorded for Pr – doped glasses based on PbF₂ – B₂O₃.

Fig. 7. Luminescence spectra recorded for Pr⁢⁺⁺ ions in oxide and oxyfluoride lead borate glasses.

Fig. 8. Influence of PbF₂ and P₂O₅ on luminescence lifetimes for Pr⁢⁺⁺ ions in oxyfluoride glasses.
It should be noticed that luminescence lifetime for $^1D_2$ state ($\tau_{\text{m}} = 16.5$ µs) of Pr$^{3+}$ ions in highly PbF$_2$ – concentrated sample (72%) is slightly longer than that one in case of absence PbF$_2$ (13.5 µs). Both values are similar to that ones obtained for Pr–doped borate crystals [29]. However, the discrepancy between the $^1D_2$ lifetimes of Pr$^{3+}$ ions in fluoroindate glasses without (400 µs) and with (35 µs) P$_2$O$_5$ is significant.

4. Conclusions

Thermal, structural and optical properties of Pr$^{3+}$ ions in multicomponent oxyfluoride glass matrices have been investigated. Several transparent oxyfluoride Pr–doped samples were prepared in wide range of PbF$_2$ concentrations, which indicates that large glass-forming region exists in lead fluoroborate systems. Quite different situation is observed for Pr–doped glasses based on P$_2$O$_5$ – InF$_3$, which relatively quickly and easy crystallized. It results in occurrence of crystalline InOF phase identified using by X-ray diffraction analysis for oxyfluoride sample with 16% of P$_2$O$_5$ content. However, it is possible to obtain transparent and thermally stable oxyfluoride glassy samples in narrow range of P$_2$O$_5$ concentrations. A large value of stability parameter $\Delta T$ close to 157 °C was obtained for sample with 8% of P$_2$O$_5$ content.

Luminescence properties of Pr$^{3+}$ ions in both heavy metal oxyfluoride glasses have been compared. Red luminescence corresponding to the $^1D_2 \rightarrow ^3H_4$ transition of Pr$^{3+}$ ions in glass based on P$_2$O$_5$ – InF$_3$, emitting reddish-orange light, where luminescence band is shifted to shorter wavelengths.

References