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Influence of PbF_2 concentration on thermal, structural and spectroscopic properties of Eu^{3+}-doped lead phosphate glasses ☆

Lidia Żur [a,*], Marta Sołtys [a], Tomasz Goryczka [b], Joanna Pisarska [a], Wojciech A. Pisarski [a]

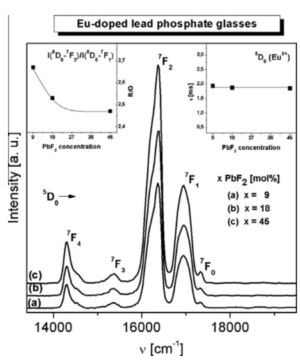
[a] Institute of Chemistry, University of Silesia, Szkolna 9, 40-007 Katowice, Poland
[b] Institute of Materials Science, University of Silesia, Bankowa 12, 40-007 Katowice, Poland

HIGHLIGHTS

- Effects of PbF_2 concentration on Eu^{3+} ions in $PbO–P_2O_5$ glasses have been studied.
- The local structure and thermal stability of investigated glasses were examined.
- Luminescence spectra of Eu^{3+} ions in lead phosphate glasses were registered.
- Luminescence intensity ratios (R/O) and measured lifetimes of Eu were determined.

GRAPHICAL ABSTRACT

Luminescence spectra of mixed oxyfluoride lead phosphate glasses doped with Eu ions, with dependence of selected spectroscopic parameters of Eu^{3+} in function of PbF_2 concentration, such as R/O factor and $^5D_0$ measured lifetimes.



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ABSTRACT

Effects of PbF_2 content on the local structure, thermal and spectroscopic properties of Eu^{3+} ions in lead phosphate glass systems have been studied. The glass samples, where PbO was partially or totally replaced by PbF_2, were examined using X-ray diffraction (XRD), differential scanning calorimetry (DSC) and luminescence spectroscopy. Based on DSC curves, characteristic temperatures and the thermal stability parameters useful for glass fiber drawing were determined. In order to confirm glass structure, XRD measurements were used. Luminescence spectra and their decays were analyzed in details. Especially, the changes of red-to-orange luminescence intensity ratios R/O (Eu^{3+}) and measured lifetimes for $^5D_0$ excited state of Eu^{3+} are presented and discussed as a function of PbF_2 concentration.

Introduction

Optical properties of glasses doped with rare earth ions (RE^{3+}) are widely investigated for potential applications in optical devices such as fiber lasers, up-conversion lasers, hole burning high-density memory, laser-induced holographic gratings and amplifiers for optical communication [1–9]. To all these applications, the knowledge of the local structure of the rare earth in glass matrices

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* Corresponding author. Tel.: +48 32 359 1732.
E-mail address: lidia.zur@us.edu.pl (L. Żur).

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is significant. Rare earth ions have been playing a significant role in modern lighting and display fields due to the abundant emission colors based on their 4f–4f or 5d–4f transitions [10]. Among the RE^{3+} ions, Eu^{3+} is found to be an excellent probe to investigate local structure around the RE^{3+} ions in different hosts. This useful information about the local structure around Eu^{3+} ions can be obtained quite easily from its f–f transition spectra [11,12].

Amongst glass hosts capable to accept Eu^{3+}, phosphate glasses deserve special attention. Due to their properties, such as high thermal expansion coefficients, low melting and softening temperatures as well as ultra-violet transmission [13–15], phosphate glasses seemed to be better than conventional silicate or borate glasses. However, other properties of this matrix – the poor chemical durability, high hydroscopic and volatile nature prevented them from replacing the conventional glasses in a wide range of applications [16,17]. Through the modification of the glass host composition, aluminophosphate, phosphate-tellurate, lead-phosphate, lead fluorophosphate matrices were obtained, which properties are competitive to other glass systems [18–20]. Mixed, oxyfluoride glasses with PbO partially replaced PbF_2 improve anion conductivity throughout fluorine ions as the conducting anions. Thus, electrical conductivity considerably increases due to fluorine migration, which is useful in the development of advanced batteries and other electrochemical devices [21]. To the best of our knowledge, the optical properties of rare earth ions in lead phosphate glasses are less documented in the literature. These systems containing rare-earth ions are applied in optoelectronics, and they are suitable for the fabrication of optical fibers, have a great importance in optical data transmission, detection, sensing and laser technologies [22]. Based on thermal and spectroscopic parameters obtained for rare earth ions it can be concluded that $PbO–P_2O_5$ based glasses present interesting thermo-optical [23,24] and non-linear optical [25] properties.

In this work we present some structural, thermal and luminescence properties of Eu^{3+} ions in mixed oxyfluoride lead phosphate glasses in function of PbF_2 concentration. Based on luminescence spectra and their decays several parameters such as R/O factor and measured lifetimes were determined.

Experimental

Series of samples: $(45 - x)PbO–xPbF_2–45P_2O_5–9Ga_2O_3–1Eu_2O_3$ (where $x = 9$, 18, 45 mol%) were prepared by mixing and melting appropriate amounts of metal anhydrous oxides and fluorides of high purity (99.99%, Aldrich Chemical Co.) as starting materials. In order to prepare samples, the appropriate amounts of all components were mixed homogeneously together and heated at the atmosphere of dry argon. Then, they were melted at 1100 °C for 0.5 h. Next, they were quenched and annealed below glass transition temperature T_g in order to eliminate internal mechanical stresses. The DSC curves were acquired with heating rate of 10 °/min using Perkin Elmer differential scanning calorimeter. The emission spectra were performed using the QuantaMaster™ system, Photon Technology International, Inc.; their decays were registered using *Opolette*™ (HE) 355 II + UV system. The spectral measurements were carried out with a resolution of 0.5 nm. Luminescence lifetimes were determined with accuracy of 2 μs. All measurements were carried out at room temperature.

Results and discussion

Thermal and structural properties

Influence of PbF_2 concentration on thermal behavior of Eu^{3+} doped lead phosphate glasses has been investigated using differential scanning calorimetry (DSC). Fig. 1 shows the DSC curves for Eu-doped mixed oxyfluoride lead phosphate glasses recorded under standard heating rate. The DSC curves were measured for glass samples with low (9 and 18 mol%) and high (45 mol%) PbF_2 concentration. From DSC curves glass transition temperatures, T_g were evaluated, and are close 440 °C for investigated samples containing different concentration of PbF_2. It is in a good agreement with thermal data obtained for similar phosphate glass system in $P_2O_5–BaO–Al_2O_3–Li_2O–La_2O_3–Eu_2O_3$ chemical composition [26]. On the DSC curve registered for sample containing medium concentration of PbF_2 (18%, Fig. 1b), the glass transition peak is followed by the crystallization peak, located at about 520 °C. This peak referred as (I) could be probably assigned to the precipitation of cubic β-PbF_2 crystals. Similar results were earlier obtained for silicate [27] and germanate [28–31] glasses modifying by PbF_2, as well as for silicate glasses containing MF_2 (where M = Ca [32], Ba [33] and Sr [34]). The presence or absence of peak associated to the crystallization of PbF_2 strongly depend on kind of erbium compounds (ErF_3, Er_2O_3, ErOF and $ErCl_3$) introduced into germanate glass composition and their molar concentrations [35]. Based on literature data can be seen, that the PbF_2 crystallization peak had completely disappeared after heat treatment of precursor glass, indicating that all the PbF_2 had been crystallized in the glass–ceramics [36]. For that reason, further investigations are necessary to obtain information about crystallization processes in oxyfluoride lead phosphate glasses.

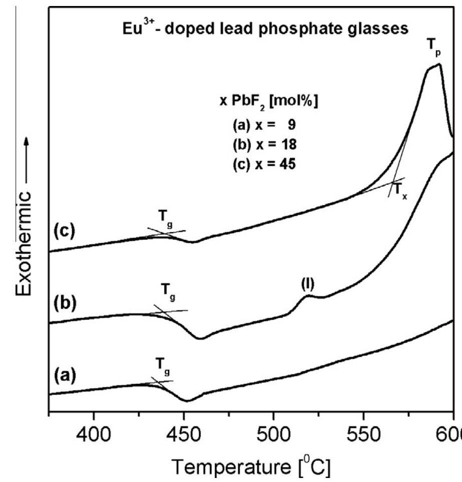

Fig. 1. DSC curves of mixed oxyfluoride lead phosphate glasses doped with Eu^{3+}.

Based on characteristic temperatures obtained for investigated glass samples, the thermal stability parameter ΔT was also determined. In general, the difference between the crystallization onset, T_x and the glass transition temperature, T_g is usually chosen as an approximate measure of glass formation ability. The larger value of ΔT gives a larger working range during operations for fiber drawing [5]. If ΔT is higher than 100 °C, glass can be considered as a glass with relatively good thermal ability [37]. Thus, the ΔT factor was calculated for glass containing high PbF_2 concentration (45 mol%), and was found to be 127 °C. The calculated result is well referred to that obtained for lead fluoroborate glass ($\Delta T = 137$ °C) in which PbO was totally substituted by PbF_2 [38]. On the discussed curve appears exothermic peak, T_p which corresponds to crystallization of the glassy matrix. For samples with lower concentration of PbF_2 this exothermic peak is located probably at higher temperature and consequently the thermal stability parameters seem to be considerably larger. Previously published results for lead fluorogermanate glasses indicate that thermal stability parameters are considerably larger for samples with low PbF_2