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Compositional-dependent europium-doped lead phosphate glasses and their spectroscopic properties

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ABSTRACT

New multicomponent europium-doped lead phosphate based glasses with various $PbO:P_2O_5$ molar ratios were prepared and next studied using optical spectroscopy. Based on excitation and luminescence spectra measurements, some spectroscopic parameters like the phonon energy of the glass host and the fluorescence intensity ratio R of the $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} ions were determined. Luminescence lifetimes (τ_m) for the $^5D_0$ state of Eu^{3+} ions were also evaluated. Optical properties of Eu^{3+} ions have been investigated in lead phosphate based systems, in which $PbO:P_2O_5$ molar ratio were changed from 1:5 to 5:1 in glass composition. The value of the phonon energy of the host decreases with increasing PbO concentration. In addition, the spectral lines are shifted toward higher wavelengths. Non-monotonic dependence of fluorescence intensity ratio R (Eu^{3+}) upon $PbO:P_2O_5$ content has been observed. Influence of $PbO:P_2O_5$ molar ratio on spectroscopic parameters for Eu^{3+} are presented and discussed.

1. Introduction

In recent years, the rare earth-doped glasses have been interested to many scientists due to their application as optical fibers and amplifiers, visible and infrared solid state lasers, generators of light, glass scintillators and semiconductor LEDs [1–11]. Among glasses with rare earth ions the most interesting is trivalent europium ions in view of spectroscopic properties [12–17]. Furthermore, the Eu-doped glass systems have been important for application in optical materials for example europium is used in new industrial nuclear glass [18]. Many glass systems demonstrate intense and efficient red emission at 611 nm related to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. Index characterizing the spectral changes in the glasses containing Eu^{3+} ions is the red-to-orange fluorescence intensity ratio R/O (usually referred as R factor). It is the ratio of the intensity of the $^5D_0 \rightarrow {}^7F_2$ (red) to $^5D_0 \rightarrow {}^7F_1$ (orange) transition and allows to determine the degree of asymmetry in the environment of Eu^{3+} ions in the matrix. Moreover, this factor is a convenient measure of covalency or relatively ionicity between trivalent europium ions and the surrounding ligands [19,20].

Literature on luminescence of trivalent europium ions in same oxide and oxyfluoride phosphate based glasses is well documented [21]. These systems have unique benefits, for example low melting point, low refractive index and low dispersion. On the other hand, disadvantages are hygroscopic properties of P_2O_5 because contribute to the lower luminescence for RE-doped phosphate glasses [22]. Furthermore, among oxide glasses, the system based on P_2O_5 have large phonon energy of the host matrices. The stretching vibrations of network affect the spectroscopic parameters of glasses. The glass systems $PbO–P_2O_5$ are able to accommodate higher content of rare earth ions and still remain amorphous in comparison to other host matrices. Additionally, the introduction PbO to the glass network is the cause of some properties of glasses. The example of this is the use of lead oxide for shielding against high-energy radiations, including nuclear radiation. As with the adding of the third metal-oxide component to the host matrices [23], the presence of PbO in the phosphate glass may also result in the formation of P–O–Pb bonds and lead to an improvement of the chemical durability of glass systems [24].

Thermal properties of lead phosphate glasses doped with rare-earth were successfully characterized [25,26]. Also, structure of lead-phosphate glasses were studied by using different spectroscopic methods such as nuclear magnetic resonance (^{31}P, ^{27}Al, ^{207}Pb NMR), electron paramagnetic resonance (EPR), Raman, Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) [27–34]. These spectroscopic techniques enable detecting structural modifications due to adding a third metal-oxide component to the glass network [35] or changes induced by gamma irradiation [36,37] and also heat treatment process [38]. The local structure of $PbO–P_2O_5$ based system

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depends strongly on the content both PbO and P_2O_5 in glass. Particularly, PbO is known to play a dual role in many glassy matrices, as both a glass modifier and a glass former [39]. In another case, the optical properties of glasses depend on the local structure host matrices [40,41]. From this point of view, it is interesting to find out, how spectroscopic properties of Eu^{3+} ions in lead phosphate glasses are changed with different PbO:P_2O_5 ratio in chemical composition.

In this paper, we present results for new multicomponent Eu-doped lead phosphate glasses. Optical properties of Eu^{3+} ions was analyzed as a function of PbO:P_2O_5 molar ratio (from 1:5 to 5:1). Especially, the phonon energy of the glass host and the fluorescence intensity ratio R related to $^5D_0 \rightarrow {}^7F_2$ (red) and $^5D_0 \rightarrow {}^7F_1$ (orange) transition of Eu^{3+} were examined with PbO content. Also, luminescence lifetimes for the $^5D_0$ state of Eu^{3+} ions were evaluated and discussed in relation to PbO:P_2O_5 molar ratio.

2. Experimental

Multicomponent europium-doped lead phosphate based glasses with various PbO:P_2O_5 molar ratios were synthesized. The glass composition are presented in Table 1. To prepare samples metal oxides of high purity (99.99%, Aldrich Chemical Co.) as starting materials were used. The appropriate amounts of all components were weighed and mixed homogeneously together in a glove box in a protective atmosphere of dried argon. The glass samples were melted for 0.5 h at 1100 °C. Local structure of lead phosphate glasses were investigated using FT-IR spectroscopy. The infrared spectra were carried out using standard KBr disc techniques and were measured with a Fourier-transform FT-IR Bruker spectrometer. Optical measurements were performed on a PTI QuantaMaster QM40 coupled with tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD). The luminescence was dispersed by double 200 mm monochromators. The luminescence spectra were registered using a multimode UVVIS PMT (R928) detector controlled by a computer. The excitation correction for real time correction was applied for excitation spectra. Luminescence decay curves were recorded and stored by a PTI ASOC-10 [USB-2500] oscilloscope with an accuracy of ± 1 μs. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Optical properties of Eu^{3+} ions in lead phosphate glasses

Fig. 1 presents the excitation spectra of Eu-doped glasses with various PbO:P_2O_5 molar ratios. These spectra were monitored at λ_{em} = 611 nm. The narrow and well resolved bands were registered and were assigned to transition originating from the $^7F_0$ ground state to higher-lying states. Furthermore, among different excitation bands the most intense band correspond to $^7F_0 \rightarrow {}^5L_6$ (393 nm) and $^7F_0 \rightarrow {}^5D_2$ (464 nm) transitions. The spectral range between 430 nm and 450 nm is important from the structural point of view. In this spectra range the phonon sideband (PSB) is located, which is associated with the pure electronic transition (PET) of $^7F_0 \rightarrow {}^5D_2$ at 464 nm. The important parameter, which is the phonon energy of the glass host *hv*, was determined based on excitation spectra. The difference between PSB and PET specifies the value of phonon energy of the glass host. The spectral range denoted as (*), where PSB is situated, clearly shows that the spectral lines are shifted toward higher wavelengths with increasing PbO concentration. Hence, the value of the phonon energy decreases, when PbO:P_2O_5 molar ratio increases from 1:5 to 5:1 (Fig. 4).

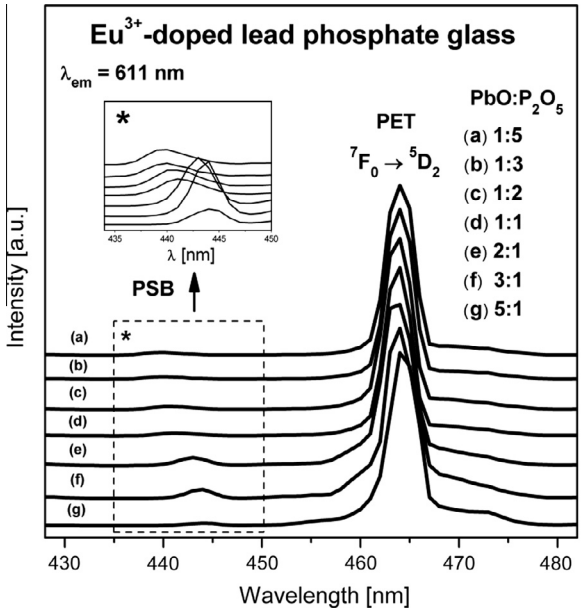

Fig. 1. Excitation spectra for Eu^{3+}-doped lead phosphate glasses.

Luminescence spectra of Eu^{3+} ions in lead phosphate glasses were registered under excitation of $^5L_6$ level (λ_{exc} = 393 nm). Because of small energy gaps between $^5L_6$, $^5D_3$, $^5D_2$, and $^5D_1$ states, the excitation energy was transferred nonradiatively to the $^5D_0$ level, and then visible luminescence was observed due to $^5D_0 \rightarrow {}^7F_J$ (where J = 0–4) transitions. Two characteristic emission bands corresponding to $^5D_0 \rightarrow {}^7F_J$ (where J = 2, 1) transition of Eu^{3+} are presented as a function of PbO:P_2O_5 molar ratio (Fig. 2). For better comparison, registered spectra were normalized to the $^5D_0 \rightarrow {}^7F_1$ transitions (590 nm). The factor of integrated emission intensity of the $^5D_0 \rightarrow {}^7F_2$ (red) to $^5D_0 \rightarrow {}^7F_1$ (orange) transition, is defined as red-to-orange fluorescence intensity ratio *R*/*O* (simply *R*). This factor is a measure of the strength of covalent/ionic bonding between the Eu^{3+} ions and the surrounding ligands. It is also known that the $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition and is independent of local symmetry, while the $^5D_0 \rightarrow {}^7F_2$ transition has electric dipole character and it is said to be hypersensitive transition because is strongly influenced by the environment of Eu^{3+} ions. For that reason, the ratio of the $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition informs us about local asymmetry around the Eu^{3+} ions. Small *R* value is usually assigned to higher local symmetry for Eu^{3+} ions, whereas the increase *R* value is due to increasing asymmetry. Our results clearly shown that increasing concentration of lead oxide in these systems change the ratio of integrated emission intensity of the red line to the orange line. The value of fluorescence intensity ratio *R* (Eu^{3+}) decreases from 3.1 to 2.62, when PbO:P_2O_5 molar ratio is changed from 1:5 to 1:1. Meanwhile, an

Table 1
Composition for Eu-doped lead phosphate glasses.

Glass composition (mol%)				PbO:P_2O_5 ratio
PbO	P_2O_5	Ga_2O_3	Eu_2O_3	
15	75	9	1	1:5
22.5	67.5	9	1	1:3
30	60	9	1	1:2
45	45	9	1	1:1
60	30	9	1	2:1
67.5	22.5	9	1	3:1
75	15	9	1	5:1