

Synthesis and optical properties of phosphate-borate-fluoride glasses doped with rare earth elements

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A method for $Li_2O–P_2O_5–B_2O_3–CaF_2–Ln$ glasses (Ln = Ce, Er, Eu, Lu, Nd, Pr, Gd and Tb) synthesis is presented as well the optical properties study results of the glasses. The homogeneity of the elemental composition and absence of significant mechanical stresses in the samples obtained have been demonstrated. The obtained absorption and photoluminescence spectra of glasses synthesized have been compared with literature data. The dependences of photoluminescence intensivity on Ce, Eu, and Pr concentrations have been obtained.

Представлены результаты разработки технологии получения и исследования оптических свойств стекол состава $Li_2O–P_2O_5–B_2O_3–CaF_2–Ln$ (где Ln = Ce, Er, Eu, Lu, Nd, Pr, Gd и Tb). Продемонстрирована однородность элементного состава и отсутствие существенных механических напряжений в полученных образцах. Выполнено сравнение полученных данных о полосах поглощения и фотолюминесценции с имеющимися в литературе. Получены зависимости интенсивности фотолюминесценции от содержания церия, европия и празеодима в стеклах.

1. Introduction

The glass-forming materials are used widely in many fields of science and engineering. Those are a prospective alternative for single crystals scintillation materials. The glasses show numerous advantages such as a low synthesis cost and manufacturing simplicity of arbitrary shaped large-size articles. The oxide glasses are promising materials to provide an efficient luminescence of rare earth ions. Due to this feature, they are widely used in information display and transfer technologies (plasma display panels, optical fibers and amplifiers), as laser materials, in radiation spectrometry and dosimetry [1–4].

Glasses doped with high concentrations of lithium, boron, gadolinium reveal an effective luminescence. Those are prospective materials for the development of detectors as well as photo- and thermoluminescence dosimeters for thermal neutrons [5–8]. The multicomponent phosphate-borate-fluoride glasses are very attractive for these purposes. Such glasses are characterized by low melting temperature, high solvability of rare earth compounds, transparency and moisture resistance.

This work is aimed at development of preparation method for new materials with high luminescence efficiency - multicomponent glasses of general composition $Li_2O–P_2O_5–B_2O_3–CaF_2–RE$ (RE = Ce, Er, Eu, Lu, Nd, Pr and Tb).

2. Experimental

To synthesize the glasses, $LiPO_3$, H_3BO_3, CaF_2, CeO_2, $Er(NO_3)_3 \cdot 5H_2O$, Eu_2O_3, $Lu(NO_3)_3 \cdot 4H_2O$, $NdCl_3$, Pr_2O_3, Gd_2O_3, Tb_2O_3 were used. All chemicals were of extra pure grade and were used without further purification. $LiPO_3$ was prepared by melting LiH_2PO_4 in a platinum crucible at 900°C for 40 min. The compositions of synthesized glassy materials are presented in the Table below. The required amounts of reagents were calculated for per 10 g of the initial mixture.

The glass samples were prepared by melting the required amounts of compounds in a platinum crucible and annealing in glass-carbon crucible using a SNOL 7.2/1300 muffle furnace. The platinum crucible with the fusion mixture was placed in a muffler heated to ca. 800°C. Then the temperature was raised up to 900–1100°C (depending on the glass composition) and the melt was hold at this temperature for 90 min being mixed every 20 min for homogenization. To prevent the glass devitrification, the obtained homogenious melt was poured in a glass-carbon crucible heated to 200°C, and cooled down to room temperature spontaneously. The glass samples were annealed at 300°C during 5 h.

The elemental composition of obtained glasses was controlled using a Jeol JSM-6390LV scanning microscope with X-ray detector INCA 350 (Jeol, Japan). The glass phase composition was studied by the X-ray structure analysis using a Siemens D500 powder diffractometer. To study the internal stresses, the optical polarization method was used (a PKR-125 unit).

To study the glass optical properties, the samples were cut and polished with ACM-5-3 diamond powder. The sample thickness was 3 mm. The absorption spectra were recorded between 195 and 1000 nm on a SF-2000 spectrophotometer ("Spektr" corporation, St. Petersburg). The luminescence spectra of the glasses were recorded using a Varian Cary Eclypse (USA) spectrofluorimeter at 20°C.

Table. Initial mixtures composition for synthesis of glasses

Series No.	Precursor, mass. %				
	$LiPO_3$	H_3BO_3	CaF_2	Ce, Eu, Pr	Er, Lu, Nd, Tb
1	100	–	–	–	–
2	90	10	–	–	–
3	80	20	–	–	–
4	80	10	10	–	–
5	70	20	10	–	–
6	78	10	10	1	1
7	79–79.8	10	10	0.2–1.0	–

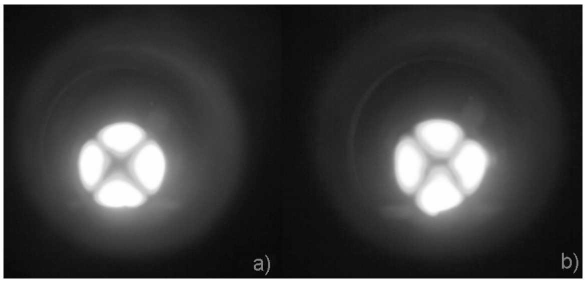

Fig. 1. Photo of glass sample (Series 4) in polarized light: *a*, unannealed; *b*, annealed.

3. Results and discussion

The parameters to be optimized are the synthesis temperature, the duration of melting and the melt homogenization stages. It has been shown that the intimate mixing of all initial reagents was attained at 900–1100°C, depending on the rare earth element concentration in the mixture. The synthesis temperature of 900°C allows the maximal concentration of lanthanides in a glass of 2 wt. % to be added. Increasing the synthesis temperature up to 1100°C, the maximal concentration of rare earth elements of 6 wt. % was reached. The thorough stirring of compounds was carried out every 20 min for homogenization. In all cases, the melting was continued during 90 min that was enough to obtain a visually homogeneous melt.

Varying the initial temperature of the glass-carbon crucible where the glass is formed, the optimal cooling condition for the fused mixture has been determined. It has been found that to prevent the glass devitrification, the fused mixture should be poured into the crucible heated up to 200°C. Then the fused mixture is to be allowed to cool spontaneously down to room temperature.

The homogeneity of the glass composition was verified by the "point-to-point" elemental analysis using an electron scanning microscope. Perfection of the obtained glasses was monitored by the optical polarization method. It has been shown that the synthesized glasses are characterized by low internal stress values (Fig.1, a). The glass annealing at 300°C results in a deteriora-

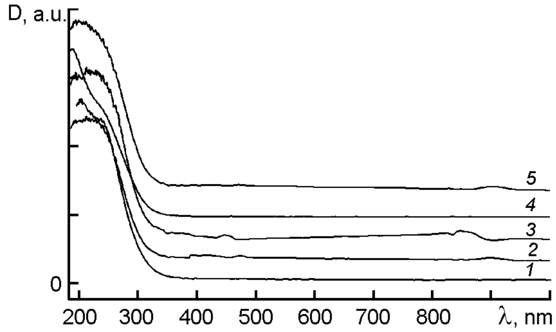

Fig. 2. Absorption spectra of glasses (Series 1–5).

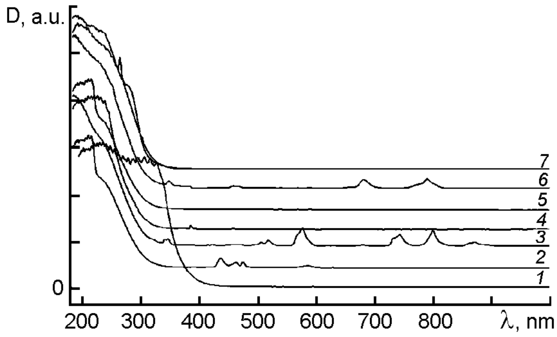

Fig. 3. Absorption spectra of glasses doped with rare earth elements (Series 6): *1* – Ce, *2* – Pr, *3* – Nd, *4* – Em, *5* – Tb, *6* – Er, *7* – Lu.

tion of the glass properties (Fig. 1, b). The glass sample structure was studied by the X-ray structure analysis that has shown that the annealed glass samples do not contain any crystal phase.

The absorption spectra of obtained glasses (see Table) are presented in Fig. 2. All the spectra exhibit a wide band in the near UV spectral region with maximum at 240–250 nm. That can be ascribed to the intrinsic absorption of phosphate matrix predominant in the glasses. When the glasses contain calcium fluoride, a higher optical transmission in UV region was obtained. When the initial mixture was formed by 20 wt. % of H_3BO_3, the obtained glasses revealed a large amount of different defects, which impair the glass transparence. The optimal content of H_3BO_3 for further synthesis was found to be of 10 wt. %.

In the glasses doped with rare earth elements (Fig. 3), the following absorbance bands are obsreved agreeing well with the data [9–14]: Ce(III), — 300–340 nm; Pr(III) — 445, 470, 482, and 592 nm; Nd(III), 350–356, 513–526, 583, 747, 804, and 875 nm; Er(III), 358, 466–474, 687, and 793 nm; Eu(III), 395 nm.

The luminescence spectra (Series 6, see Table) were recorded in spectral range up to 1000 nm. Intense luminescence bands were obtained only for glasses doped with Ce, Eu, and Pr ions (Fig. 4). The photoluminescence excitation wavelengths were determined from the absorption data: 295 nm for glasses doped with Ce; 445 nm, for Pr doped ones; and 395 nm, for those doped with Eu. The luminescence bands of Ce doped glasses (maximum at 340 nm) are associated with the electron transition from $4f$ to $5d$ shell [10–12]. In luminescence spectra of Eu doped glasses, the bands are located at 580, 590, 620 nm and are conditioned by transitions $^5D_0 \to {}^7F_{0.1.2.3.4}$ in Eu(III) [10, 13]. The luminescence spectra of glasses doped with Pr exhibit two intense bands that correspond to the basic transitions: the band at 490 nm ($^3P_0 \to {}^3H_4$ tran-

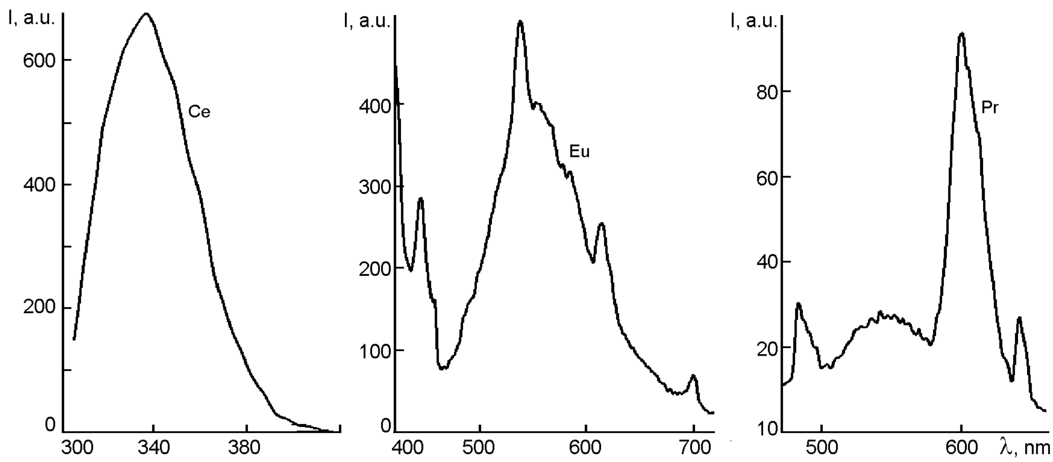

Fig. 4. Photoluminescence spectra of glasses doped with Ce, Eu, Pr (Series 6).

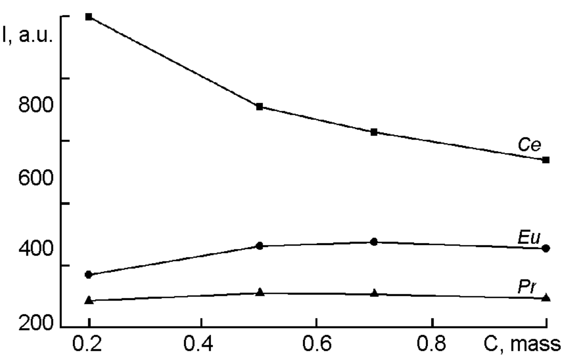

Fig. 5. The photoluminescence bands intensity dependence (relative units) on Ce (340 nm), Eu (580 nm) and Pr (610 nm) content in the glasses (Series 7).

sition) and one centered at 610 nm ($^3P_0 \rightarrow {}^3H_6$ transition) [10, 14].

To study the influence of rare earth element concentration on the main photoluminescence band intensity, the Series 7 samples (see Table) were used. The increase of Ce ion concentration causes a significant decrease of luminescence intensity in the glasses (Fig. 5). It seems to be associated with the effect of luminescence concentration quenching.

4. Conclusions

An efficient technique has been developed to obtain the phosphate-borate-fluoride glasses doped with rare earth elements. The glass samples prepared have homogeneous elemental composition and do not reveal significant mechanical stresses. The optical properties of glasses doped with Ce, Eu, Pr have been studied in the region from 195 to 1000 nm. All absorption bands are typical of the trivalent rare earth elements. For glasses doped with Ce, Eu, and Pr, the intense photoluminescence bands have been obtained. The concentration quenching of luminescence for Ce doped glasses (band 340 nm) has been observed.

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Синтез та оптичні властивості фосфат-борат-фторидних стекол із добавками рідкісноземельних елементів

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Наведено результати розробки технології отримання та дослідження оптичних властивостей стекол складу Li_2O–P_2O_5–B_2O_3–CaF_2–Ln (де Ln = Ce, Er, Eu, Lu, Nd, Pr та Tb). Продемонстровано однорідність елементного складу та відсутність істотних механічних напружень в отриманих зразках. Проведено порівняння отриманих даних щодо смуг поглинання та фотолюмінесценції з наведеними у літературі. Отримано залежності інтенсивності фотолюмінесценції від вмісту церію, європію та празеодиму у стеклах.