The impact of the lead on the physicochemical and optical properties of the fluorophosphate glasses doped by Nd$^{3+}$ ions

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Abstract. Fluorophosphate glasses of the composition 5Ba (PO$_3$)$_2$ - (38-x) AlF$_3$ - 57RF$_2$ - xNdF$_3$ were obtained, where R = Ba, Ca, Sr, Mg, Pb; x = 0.5, 3, 5 mol%. It was found that the introduction of lead fluoride reduces the glass transition and crystallization temperatures. It has been shown that for all systems containing MgF$_2$, the formation of a uovite phase is characteristic. The UV-cutoff has shifted from 200 nm to 250 nm.

1. Introduction
Interest in fluorine-containing systems is due to the possibility of creating glasses based on them that have lower refractive indices and high values of the dispersion coefficient, increased relative dispersion in the blue part of the spectrum, special thermo-optical characteristics, and a wide range of spectral transparency [1]. Due to these properties, as well as a low level of phonon energy, fluorine-containing systems can be used in fiber optic and laser technology [2, 3] Fluorophosphate glasses have high crystallization ability, and are characterized by a small difference between the glass transition temperature and crystallization temperature [4, 5, 6] . Glasses of this system are characterized by surface crystallization [6], which negatively affects the drawing processes of the optical fiber. The introduction of lead fluoride into fluorophosphate glasses leads to an increase in the density ρ, refractive index nD, coefficient of linear thermal expansion α, and a decrease in the thermo-optical constant W. Lead is also an effective glass former, and its introduction into fluorophosphate glass is also expected to reduce the tendency of glass to crystallize. A study of the temperature dependences of fluorophosphate glass and its crystallization ability is necessary to determine the technological conditions for the production of glasses of optical quality and the subsequent drawing of the optical fiber from this material.

2. Materials and methods
Glass melting was carried out in an argon atmosphere at a temperature of 1050 ° C in a glass-carbon crucible according to the “crucible to crucible” scheme. This synthesis method was chosen in order to prevent fluoride from volatilization during melting in a furnace with silicon carbide heaters. Melting time was 45 minutes. Glass melt was produced by casting on a glassy carbon plate. After production, the glass was annealed in a furnace at temperatures close to Tg.
Table 1. Glass compositions (mol.%)

| Compositions | \( \text{Ba} (\text{PO}_3)_2 \) | \( \text{BaF}_2 \) | \( \text{AlF}_3 \) | \( \text{CaF}_2 \) | \( \text{MgF}_2 \) | \( \text{SrF}_2 \) | \( \text{PbF}_2 \) | \( \text{NdF}_3 \) |
|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Initial      | 5               | 10              | 38-x            | 18.5            | 10              | 18.5            | 0               | \( x=0.5, 3, 5 \) |
| B            | 5               | 0               | 38-x            | 18.5            | 10              | 18.5            | 10              | \( x=0.5, 3, 5 \) |
| S            | 5               | 10              | 38-x            | 18.5            | 10              | 8.5             | 10              | \( x=0.5, 3, 5 \) |
| M            | 5               | 10              | 38-x            | 18.5            | 0               | 18.5            | 10              | \( x=0.5, 3, 5 \) |

The characteristic temperatures for determining the temperature-time regime of heat treatment of glasses were determined on the basis of data obtained by analyzing the differential scanning calorimetry (DSC) curve. Measurements and mathematical processing of data were carried out on a Nietzsche STA 449F1 Jupiter differential scanning calorimeter; the heating rate of the samples was 10 K / min.

3. Results and discussion

The DSC results are presented in Figure 1. The DSC of the original glass 1 (a) shows one complex peak. The introduction of lead due to the complete or partial replacement of one of the modifiers leads to the separation of crystallization peaks. Particular attention in this work is given to the composition of the phases formed during crystallization. For the original glass, the peak corresponds to the Usovite crystalline phase (\( \text{MgCaSrBaAl}_2\text{F}_{14} \)) [10,11].

![Figure 1](image-url)
**Figure 1.** DSC curves for glasses: a), b) initial glass NdF$_3$ = 0.1 (a) 2 (b), mol.%; c) glass B, NdF$_3$ = 3 mol%; d) glass S, NdF$_3$ = 3 mol.% e), e) glass M, NdF$_3$ = 0.5 (d), 3 (e), mol%.

Figure 1 shows that the introduction of lead leads to the formation of two peaks and a decrease in the glass transition temperature $T_g$. It should be noted that glasses B and S are characterized by a large difference in the glass transition temperatures and the onset of phase crystallization. On the contrary, the composition of M is characterized by a lower temperature of the onset of the formation of the first (low-temperature) peak. Also, the peaks of glasses B and S have a wider width than the peaks of glasses without magnesium fluoride (glass M). Characteristic temperatures are presented in table No. 2. Substitution of lead for strontium and barium in glass leads to a slight increase in the interval between the glass transition temperature and crystallization temperature. Overall, peak peaks of all compositions can be estimated as narrow, and, accordingly, it can be argued that volume crystallization is characteristic of all glasses. An increase in the concentration of neodymium leads to a decrease in the interval between the glass transition temperature and crystallization temperature.

![Figure 2. Comparison of diffraction patterns of crystallized source glass and B, M glasses at temperatures corresponding to low-temperature peaks. The bar diagram shows the phase of the usovit Ba$_2$CaMgAl$_2$F$_{14}$.](image)

**Table 2.** Glass transition temperatures $T_g$, crystallization temperatures $T_{cr}$

| Glass compositions | $T_g$, °C | $T_{cr}$, °C | $T_{cr}$-$T_g$, °C |
|--------------------|----------|-------------|-------------------|
| Initial, 0.1% NdF$_3$ | 440      | 545         | 105               |
| Initial, 2% NdF$_3$ | 445      | 535         | 90                |
| B, 3% NdF$_3$      | 409      | 503, 563    | 94                |
| S, 3% NdF$_3$      | 421      | 528, 602    | 107               |
| M, 0.5% NdF$_3$    | 412      | 485, 567    | 73                |
| M, 3% NdF$_3$      | 405      | 486, 573    | 81                |

In order to study the crystallization process for all glasses, X-ray diffraction patterns were obtained (Figure 2). All glasses were crystallized in the temperature range corresponding to the first exothermic peak. An analysis of the obtained data shows that, for glasses B, S and the initial first crystalline phase the Usovit monoclinic crystal (map No. 010722129). Glass M is characterized by phase separation, which also has low symmetry, data on which are not yet available in the catalog.
Optical characteristics were obtained for glasses of all compositions — the refractive index and absorption spectra. A logical increase in the density $\rho$, refractive index $n_D$, and with the introduction of lead for all glasses was shown (Table 3).

| Glass compositions | $n_D$       | $\rho$, г/см$^3$ |
|-------------------|------------|-----------------|
| Initial, 3 mol. % NdF$_3$ | 1.4535 | 3.725           |
| B, 5 mol. % NdF$_3$      | 1.4800 | 4.178           |
| S, 3 mol. % NdF$_3$      | 1.4826 | 4.257           |
| M, 3 mol. % NdF$_3$      | 1.4842 | 4.310           |

The absorption was measured in the UV region and the near infrared region (3–7 $\mu$m). The measurement results are presented in Fig. 3. As you can see, the introduction of lead into the glass shifts the UV absorption limit of the glasses (Figure 3.a) to the long-wavelength region from 180 nm (initial glass) to 245 (glass B and S) and 250 nm (glass M). The infrared transmission limit for all compositions is determined by the composite frequencies of the natural vibrations of the phosphate groups (4.5 $\mu$m). In this part of the spectrum, one can also observe a shift of the absorption bands of phosphate groups by 60 nm to the region of large wavelengths.

The glass structure was analyzed based on the analysis of the Raman spectrum (Figure 4). In the spectra, vibration bands of $P - O - P$ bridges are observed, the presence of which indicates the presence in glass structure of not only isolated tetrahedra (PO$_4$), but also dimers (P$_2$O$_7$). Also a band corresponding to vibrations of the fluorine-aluminate network (580 cm$^{-1}$) is observed.
Figure 4. Raman spectra of light for two concentrations of neodymium: 1) 0.5 mol.% NdF$_3$; 2) 2 mol.% NdF$_3$.

4. Conclusion
The introduction of PbF2 leads to lower glass transition and crystallization temperatures in all glasses. In glasses with lead, a separation of DSC curves is observed and the formation of two exothermic peaks is observed. The content of neodymium fluoride in all glasses leads to an increase in the temperature of crystallization and glass transition. During the heat treatment in the region of the first peak, it was found that for all glasses B and S, the formation of a phase similar to usovite is characteristic. Glass M is characterized by the formation of a different phase, but also has low symmetry. The refractive index increases with the introduction of PbF2. The Fourier spectroscopy data did not show a change in the transparency of the glasses in the region from 2.5 to 4 μm. Measurement of the UV and IR absorption boundaries showed that with the addition of lead, these boundaries shift in the region of higher wavelengths. Despite the introduction of lead, these glasses still retain their high transparency in a wide spectral region, and can be considered as a promising photonic material.

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