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GLASS FORMATION AND SOME PHYSICAL PROPERTIES IN $NaPO_3$ – LiF AND $NaPO_3$ – (0.4 AlF_3 – 0.6 CaF_2) SYSTEMS

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Abstract. The area of glass formation in $NaPO_3$–LiF–(0.4AlF_3 – 0.6CaF_2) system was determined. The glasses were synthesized using standard melt-quenching techniques. The concentration dependencies of the glass transition temperature, refractive index, density, molar volume, microhardness, and crystallization products were obtained. In $(NaPO_3)_{100-x}$–$(LiF)_x$ glass the linear decrease of noted parameters was observed. The LiF additives to the phosphate network caused the formation of a "friable" glass network. In $(NaPO_3)_{100-x}$ –$(0.4AlF_3 – 0.6CaF_2)_x$ system the concentration dependencies were more complex due to the formation of a mixed fluorophosphate network. It was assumed that the structural groups changed from metaphosphate $(PO_3^-)_n$ in the initial composition to the combinations of $P(O,F)_4$+$[MeF_6]$+$[MeF_4]$ in the final stage. The microhardness values (>360 kg/mm^2) of $NaPO_3$– (0.4AlF_3 – 0.6CaF_2) glasses with high fluoride content were comparable to lead silicate glasses, which indicates the possibility of their practical application in optical instrumentation and devices.

Keywords: $NaPO_3$ – LiF**,** fluorophosphate glass, calcium fluoroaluminate glass, refractive index, density, microhardness

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1. Introduction

The development of advanced science and technology is closely related to the creation and study of new materials, including research in the field of optical materials. Alkaline fluorophosphate glasses have found application in laser technology, photonics, gradient optics, and dosimetry [1].

Phosphate and fluorophosphate glasses attract the attention of researchers, first of all, by their unusual optical constants and high light transmission in the ultraviolet region of the spectrum. Glasses containing phosphates and fluorides have extraordinary optical properties as applied to the creation of optical devices due to the anomalous behavior of the dispersion coefficient and deviation from the Abbe diagram. The fluoride-containing phosphate glasses are of special interest as a glass matrix for rare-earth ions, they combine the favorable optical properties of fluoride glasses and the high mechanical and thermal stability of phosphate glasses [2]. On the basis of systems $Al(PO_3)_2$-BaF_2 [3], a group of "crowns" characterized by low dispersion and an increase in relative dispersion in the blue part of the spectrum was obtained. Flint glasses have also been developed on a fluorophosphate basis [4]. The importance for the practical application of alkaline fluorophosphate glasses is a relatively low glass transition temperature, a large value of the linear expansion coefficient, and also high radiation resistance.

From the point of view of developing glasses with improved mechanical properties, phosphate glasses with high content of fluorides are also of great interest. The fracture strength and Young's modulus increase with increasing anisotropy. Earlier, it was shown that some compositions of alkaline and alkaline metaphosphate glasses, unlike most types of glasses, exhibit birefringence (significant anisotropy) after applying uniaxial tensile stress at temperatures above the glass transition temperature (T_g) [5-7].

Glasses based on fluoride systems have a high tendency to crystallize; however, it is known that the addition of phosphates can significantly increase the glass-forming ability [8]. The glasses of the system $(NaPO_3)_{1-x}$-$(AlF_3)_x$ (0<x<40) is a well-known model fluorophosphate glass [9]. However, other fluorine-containing metaphosphate alkaline glasses are very poorly covered in the literature. It is well known that calcium and aluminum fluorides have high glass formation ability. The ratio of AlF_3/CaF_2=0.4/0.6 was selected based on the phase diagram which is close to the eutectic and has a high glass-forming ability.

Thus, in this work, the objects of study were $NaPO_3$–LiF and $NaPO_3$–($0.4AlF_3$ – $0.6CaF_2$) systems. The regions of glass formation, as well as the concentration dependences of the glass transition temperature, density, refractive index, molar volume, microhardness, and glass crystallization products, were studied.

2. Experimental techniques and objects of the study

The synthesis of glass samples was carried out in an electric furnace at a temperature of 900-1000°C for 30 minutes. The glass preparation was carried out in glassy-carbon crucibles in an argon atmosphere. The gas flow rate was controlled by an electronic flow meter. Reagents with a purity of at least 99.5% were used as raw materials for glass synthesis. Sodium metaphosphate was prepared by thermal decomposition of sodium dihydrogen phosphate at a temperature of about 240°C.

The estimation of the weight loss during glass synthesis did not exceed 5%. After synthesis, the samples were cut and polished.

The values of the glass transition temperature T_g were determined by differential thermal analysis method by "Termoscan-2" device (Analitpribor) with an accuracy of ±2°C. Al_2O_3 powders were used as standard.

The density ρ was determined by the hydrostatic method in toluene on polished glass samples. The error did not exceed 0.003 g/cm^3.

The crystallization ability of glasses was determined visually by the polythermal method when they were kept in corundum boats in a gradient furnace for 30 minutes.

X-ray structural analysis was carried out on a D8-Advance diffractometer (Bruker).

The refractive index n_D was measured on an IRF-23 (LOMO) optical refractometer. The error did not exceed 0.0005.

The values of molar volume V were calculated by the following expression:

$$V = M / \rho , \tag{1}$$

where M is the average molar weight and ρ is the density of glass sample in g/cm^3.

Microhardness by the method of indentation of a diamond pyramid (according to Vickers) was measured by PMT-3M device (LOMO). The instrument was calibrated against a sodium chloride crystal. The microhardness H was calculated according to the well-known formula:

$$H = \frac{1854 \cdot p}{< d >^2} , \tag{2}$$

where *p* is the normal load applied to the diamond tip, <*d*> is the arithmetic mean of the length of the diagonal of the indentation in eyepiece divisions in mkm, d=0.31·T, where T is number of micrometer object divisions. As a load, a mass of 40 g was used at which there was no distortion of prints on the glass as a result of its destruction. The holding time was 30 sec. For each sample, the measurement was carried out at least 25 times, which made it possible to obtain the value of the hardware error of ±5 kg/mm^2.

3. Results and discussion

Glass formation and crystallization products. Widely known optical materials, sodium metaphosphate, lithium, aluminum, and calcium fluoride, were chosen as the basis of the fluorophosphate system under study. Figure 1 shows the region of glass formation in the system $NaPO_3$–LiF–($0.4AlF_3 – 0.6CaF_2$) built on the basis of experimental data.

In $NaPO_3$–LiF system the glasses were obtained up to 40 mol. % of LiF. At higher content of LiF, glass samples could not be obtained and partial crystallization was observed. We carried out controllable crystallization of glasses by keeping them at the crystallization temperature, which, according to the result of X-ray structural analysis, showed that the crystallization product at a LiF content from 0 to 30 mol. % was of crystalline $NaPO_3$, and at 30 – 40 mol. % was LiF (table 1).

As can be seen from the figure, in the $NaPO_3$ – ($0.4AlF_3$ – $0.6CaF_2$) pseudobinary system, the glass formation region was quite wide up to 80 mol. % of ($0.4AlF_3$ – $0.6CaF_2$). The obtained area of glass formation significantly exceeds the glass formation region in binary $NaPO_3$ – AlF_3 system (up to 40 mol. %) [10] and $NaPO_3$ – CaF_2 (up to 25 mol. %) [11]. The region of glass formation ends with the precipitation of a crystalline phase from the melt, whose composition is represented in Table 1.

Table 1. Glass crystallization products in system $NaPO_3$–LiF–($0.4AlF_3 – 0.6CaF_2$)

System	**Composition area, mol. %**	**Crystallization products**
$NaPO_3$–LiF	LiF 0 – 30	$(NaPO_3)_3$
	LiF 30 – 40	LiF
$NaPO_3$–($0.4AlF_3 – 0.6CaF_2$)	($0.4AlF_3 – 0.6CaF_2$) 0 – 20	$(NaPO_3)_3$
	($0.4AlF_3 – 0.6CaF_2$) 20 – 50	$(NaPO_3)_3$, γ - $Ca_2P_2O_7$
	($0.4AlF_3 – 0.6CaF_2$) 50 – 70	CaF_2, γ - $Ca_2P_2O_7$
	($0.4AlF_3 – 0.6CaF_2$) 70 – 80	CaF_2
$NaPO_3$–LiF–($0.4AlF_3$ – $0.6CaF_2$)	$NaPO_3$ 50 – 70	$(NaPO_3)_3$
	$NaPO_3$ 70 – 100	$(NaPO_3)_3$, $Ca_3(PO_4)_2$

The analysis of the crystallization ability of $NaPO_3$–LiF–($0.4AlF_3$ – $0.6CaF_2$) glasses showed that the introduction of LiF (up to 30 mol. %) into $NaPO_3$ increases the resistance of glasses to crystallization. Further, as LiF increases, the resistance to crystallization decreases. At first glance, this seems to contradict the available data that the introduction of alkali metal fluoride shortens long phosphate chains and thus creates favorable conditions for crystallization. However, if we consider the state diagram of systems of type $MePO_3$-MeF, and assume an analogy between them and $NaPO_3$–LiF, then the increase in resistance to crystallization is explained as the composition approaches the eutectic.

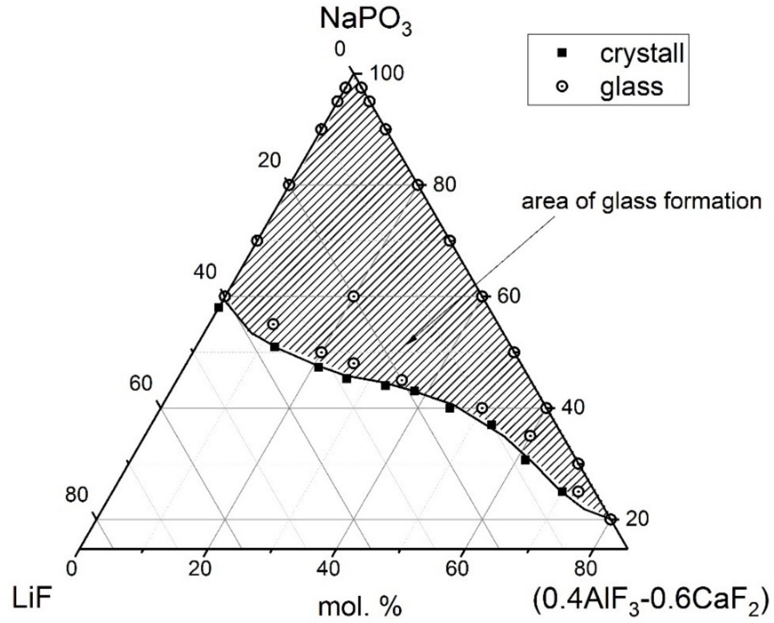

Fig. 1. The area of glass formation in $NaPO_3$–LiF–($0.4AlF_3$ – $0.6CaF_2$) system

In pseudobinary system $NaPO_3$–($0.4AlF_3$ – $0.6CaF_2$), the introduction of $0.4AlF_3$ – $0.6CaF_2$ up to 20 mol. % increased the tendency to glass formation, then in the range from 20 to 50 mol. % the tendency to crystallization increased, and in the range of 50-70 mol. % tendency to glass formation increased again.

Figure 2, *a* and *b* shows the concentration dependences of T_g value in $NaPO_3$-LiF and $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$) glass systems, correspondingly.

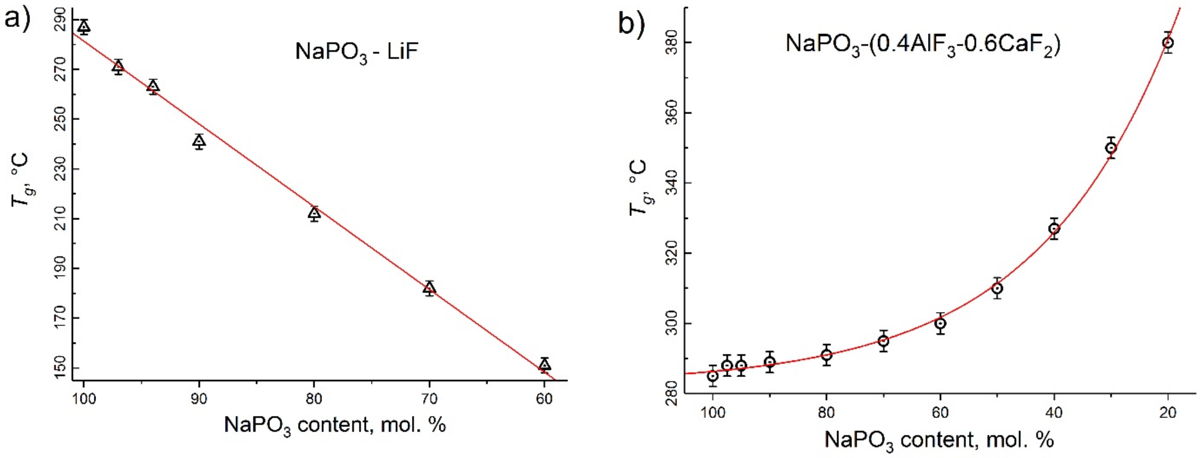

Fig. 2. Concentration dependences of glass transition temperature (T_g) in $NaPO_3$-LiF (a) and $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$) (b) glass systems

Consider the experimental dependence for the lithium-containing system. It can be seen from Fig. 2, *a* that an increase in the fraction of fluorides significantly reduced the T_g value. A decrease in the T_g value can be explained by the following: the lithium fluoride introduction leads to the rupture of certain metaphosphate chains and the formation of chains with a shorter length; as a result, the bond strength weakens and causes an increase in the amplitude of thermal vibrations of weakly bound structural groups.

The dependence shown in Fig. 2, *b* has a completely different form – firstly, a significant increase in the glass transition temperature is observed with a decrease in the proportion of the phosphate component, and secondly, the dependence has an exponential form.

An increase in the T_g values indicates that less bound structural groups in the glass were replaced by more bound ones, which leads to an increase in the energy of the structural network of the glassy matrix. It should be noted that the formation of shorter meta- and pyrophosphate groups as a result of breaking long phosphate chains with fluorine atoms is also possible. The last one was confirmed by the presence of $(NaPO_3)_3$, and γ – $Ca_2P_2O_7$ in crystallization products.

Physical properties. Figure 3 shows the dependencies of density and molar volume in both glass systems.

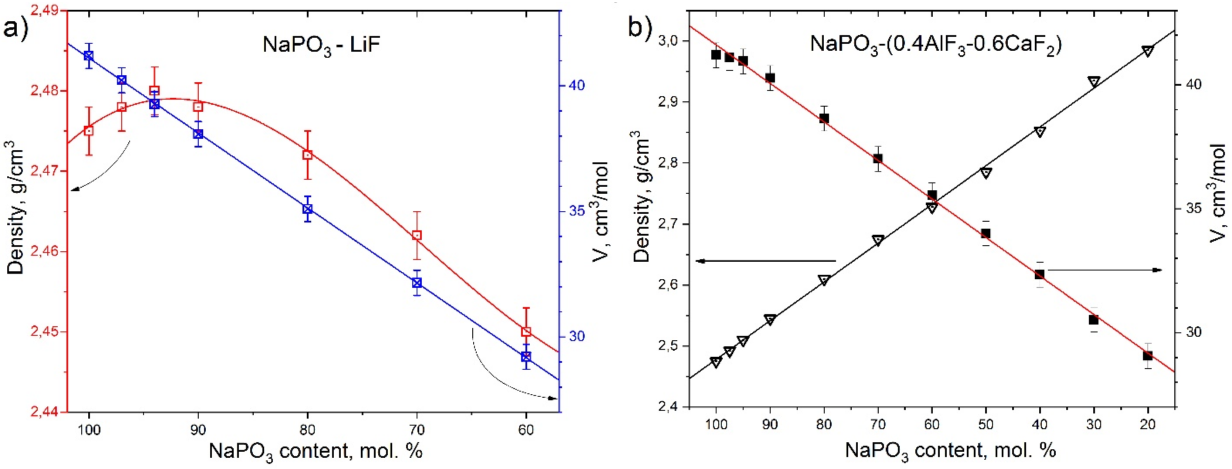

Fig. 3. Dependences of ρ and V versus $NaPO_3$ content in studied glassy systems

The dependence of ρ shown in Fig. 3, *a* ($NaPO_3$-LiF) is more complex than for pseudo-binary system. The density of lithium fluorophosphate glasses initially slightly increased (up to 5 mol. % of LiF), and then a monotonic decrease was observed. The increase in density up to 5 mol. % can be explained by the incorporation of lithium fluoride into microvoids of PO_4 tetrahedra of phosphate glass. This possibility is due to the small size of lithium ions, as well as its high mobility in glass. The transition from an increase in density to its decrease after 5 mol. % is associated with the exhaustion of noted microvoids and the beginning of the formation of fluoride structural fragments along with the existence of phosphate groups. The reason for the subsequent monotonic decrease of density is the replacing of the heavier component $NaPO_3$ (M_{NaPO3}=101.96 g/mol) with a lighter one – LiF (M_{LiF}=25.94 g/mol) and the formation of a "friable" glass structure due to the appearance of a mixed fluorophosphate matrix.

The molar volume characterizes the packing density of structural groups in glass. The LiF additives to the phosphate network reduced the molar volume and caused the shrinkage of the network. Li-ions at small content are a glass network modifier, which means the presence of it the glass network must form around these ions. Therefore, a decrease in both the density and the molar volume indicates an increase in the size of the interstitials in the phosphate network of the glass.

Figure 3, *b* shows the concentration dependencies in $NaPO_3$–($0.4AlF_3$ – $0.6CaF_2$) system. It can be seen that dependencies of density and molar volume had an opposite linear character – with the introduction of fluorides, the density of glasses increases, and the molar volume decreases. In contrast to the $NaPO_3$–LiF system, the increase in the density value was observed with an increase in the proportion of the fluoride component.

The opposite dependences of ρ and V, indicate that despite the decrease in the average molar volume (through the addition of fluoride component with lower than $NaPO_3$ M_{NaPO3}=101.96 g/mol molar weight M_{AlF3}=83.98 g/mol, M_{CaF2}=78.07 g/mol), there is an increase in density. The increase in glass density is probably due to the fact that aluminum and calcium fluoride has a higher density than $NaPO_3$.

From the point of view of glass formation, it is known that calcium and aluminum fluorides have a significantly greater tendency to form a glass network and fluorides have a higher electronegativity than oxides, so the distance between atoms is smaller. Therefore, the observed increase in the density of glasses is associated with a decrease in the average distance between the structural groups of glass – fluoride, and phosphate leading to the formation of a more tightly coupled glass network. The latter is confirmed by the results obtained for multicomponent fluorophosphate glasses, in which the formation of a mixed fluorophosphate glass framework was also found even at low content of phosphates [8].

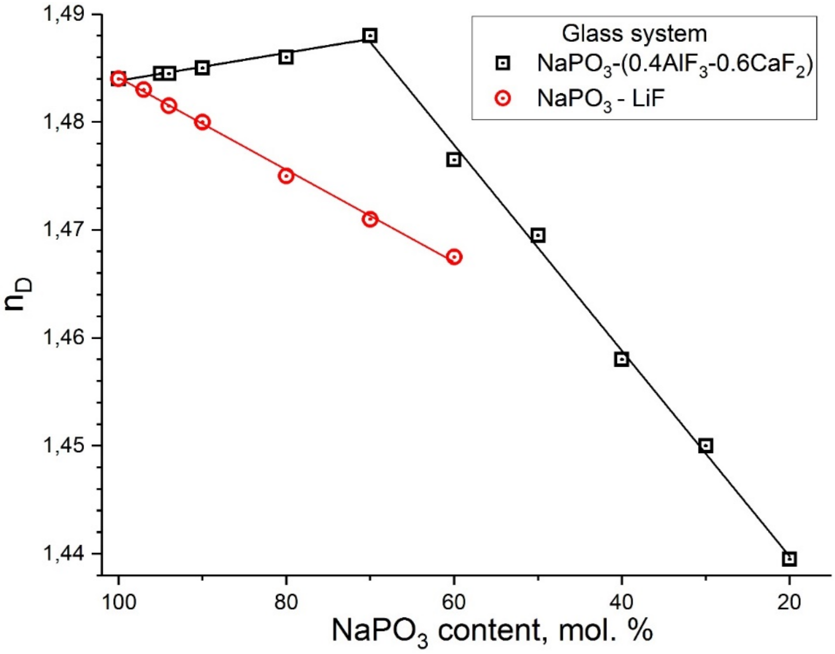

Fig. 4. Concentration dependences of refractive index n_D in $NaPO_3$-LiF and $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$) glassy systems

Figure 4 shows the dependence of n_D in both series of studied glass samples. It is seen from the dependence of $NaPO_3$-LiF system a linear decrease of glass refractive index with fluoride content growth. This corresponds to the well-known fact that the refractive index of fluoride materials, in general, is lower than that of oxide materials, for example, n_D(LiF)=1.392, n_D(CaF_2)=1.434 [12], and n_D($NaPO_3$)=1.484. The value of n_D changed in the studied area of compositions from 1.484 to 1.467. The n_D value for pure $NaPO_3$ coincides with that described in the literature [7], while the values for lithium fluorophosphate glasses are not found in the literature.

In a pseudo-binary system, the refractive index curve has an extremum in the region of 30 mol. % fluorides. A similar character of the n_D dependence was observed for other fluorophosphate glasses system, which was additionally studied by IR, Raman, and NMR spectroscopy [13,14]. However, in work [14], an extremum on the n_D dependence was observed at a fluoride content of about 36 mol. % in glass composition $64Ba(PO_3)_2 \cdot 4MgF_2 \cdot 19CaF_2 \cdot 13AlF_3$. The difference in the position of the maximum is associated both with the difference in the chemical composition of the glasses and in the significantly larger step in fluoride concentration, which in [14] was 18 mol. %.

The probable cause of the observed maximum is the formation of glass consisting of fluoride and phosphate groups: in the inflection region (around 30 mol. % of fluorides), the prevailing but weak pyrophosphate chains collapsed and formed stronger fluoride chains. By analogy with the one proposed in work [14] and assuming a similar nature of the glass formation of phosphate and fluoride groups in studied compositions, it can be assumed that the structural groups forming the glass network changed from metaphosphate $(PO_3^-)_n$ in the initial composition to the combinations of $P(O,F)_4$+$[MeF_6]$+$[MeF_4]$ (where Me was Al or Ca) in the final stage.

Glass microhardness. The widespread use of miniature glass displays in modern mobile communications determines the relevance of considering the microhardness of glasses, and their resistance to abrasion. In addition, the dependences on microhardness make it possible to identify changes in the structure of glasses, which is certainly useful in the context of our study. The concentration dependences of the microhardness in both glass systems are shown in Fig. 5.

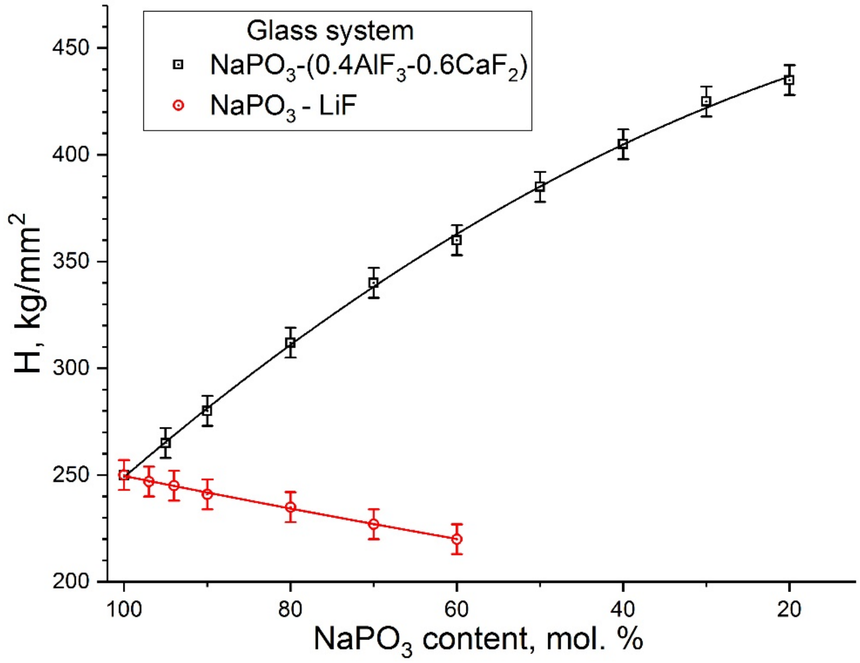

Fig. 5. Dependence of the microhardness in $NaPO_3$-LiF and $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$) glassy systems

For original phosphate glass, the value of the microhardness was 250 kg/mm^2. The introduction of lithium fluoride reduces the microhardness up to 220 kg/mm^2. This is apparently due to the destruction of strong bonds formed by phosphate groups in the glass and their replacement by short bonds of lithium fluoride.

The dependence on the pseudo-binary system had an increasing character. The introduction of a calcium fluoroaluminate eutectic into $NaPO_3$ led to an increase in the microhardness value up to 435 kg/mm^2. Thus, with an increase in the fluoride content, the microhardness increases by 74% compared to phosphate glass. The latter is due to the greater hardness of glassy aluminum and calcium fluorides as such.

It should be noted that due to the low measurement accuracy (±5 kg/mm^2), the exact course of the dependence and the function that describes it cannot be determined. However, it can be said with certainty that the nature of the change is non-linear with an increase in the fluoride content.

The comparison of the microhardness values with other glass systems showed that microhardness of $NaPO_3$-LiF is 2.5 times lower than for lead silicate glass ≈430 – 600 kg/mm^2 [15] and is comparable to the value for alkali earth silicate 280 kg/mm^2 [16], Sb_2O_3–$ZnBr_2$ ≈200 kg/mm^2 [17] and ZBLAN ≈200 kg/mm^2 [18] glasses. For system $NaPO_3$–($0.4AlF_3$ – $0.6CaF_2$) the microhardness value is comparable to lead silicate glasses ≈430 – 600 kg/mm^2 [15], but still lower than for Li_2O–ZnO–MgO–Al_2O_3–SiO_2 glasses ≈700 kg/mm^2 [19].

4. Conclusions

The paper presents the results of a study of two glass systems based on $NaPO_3$–LiF, and $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$). The glasses were synthesized using standard melt-quenching techniques. The area of glass formation in system $NaPO_3$–LiF was limited by 40 mol. % of lithium fluoride and in $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$) is limited by 80 mol. % of ($0.4AlF_3$ – $0.6CaF_2$).

The concentration dependences of the crystallization products, refractive index, glass transition temperature, microhardness, and density indicated on the formation of a mixed fluorophosphate glass network. The obtained concentration changes in the characteristics of glasses were due to a significant difference in the glass-forming ability, chemical and optical properties of phosphates and fluorides. The introduction of lithium fluoride into the $NaPO_3$–LiF led to the replacement of three-dimensional phosphate chains and the formation of short chains of LiF, which led to both a decrease in the bond strength between structural groups and an increase in the compactness of their arrangement.

The dependence of the density and molar volume on system $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$) had an antibatic character: with an increase in the fluoride content, the glass density increased, while the molar volume decreased. The greater electronegativity of fluorides and the shorter bond length than in sodium metaphosphate causes a decrease in the average distance between the structural groups of glass – fluoride, and phosphate and leadsto the formation of a more tightly coupled glass network.

In the system $NaPO_3$–LiF, the dependence of the refractive index had a linear decreasing form and is consistent with theoretical concepts. In a pseudo-binary system, the dependence of refractive index had extremum around 30 mol. % of fluorides, which is consistent with reported in the literature. The suggested reason for the noted character is that the network structural groups changed from metaphosphate $(PO_3^-)_n$ in the initial composition to the combinations of $P(O,F)_4$+$[MeF_6]$+$[MeF_4]$ (where Me was Al or Ca) in the final composition. However, to confirm this assumption, further studies of the glasses of this series by structurally sensitive methods, such as IR spectroscopy, are required.

The microhardness values for $NaPO_3$–LiF glasses lie in the region 250 – 220 kg/mm^2 which is comparable to fluorozirconate and alkaline earth glassy systems. The values of microhardness in the $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$) system are significantly higher than in lithium system, and it increases from 250 to 435 kg/mm^2 with increasing fluoride content and its maximum value is comparable to lead silicate glasses.

Thus, this study made it possible to clarify the areas of glass formation in fluorophosphate systems $NaPO_3$–LiF and $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$), as well as to establish the regularities in the change of some physical properties of glasses with an increase in the content of fluoride components. For glasses in $NaPO_3$– ($0.4AlF_3$ – $0.6CaF_2$) system the obtained relatively high microhardness values and the possibility of varying the refractive index values in a wide range indicates the possibility of their practical application in optical instrumentation and devices.

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