Study of the influence of fluorine containing compounds on the physical and chemical and optical properties of glasses of new fluorophosphate systems.

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1. Investigation strategy

A phosphate system of $Ba(PO_3)_2$-$Al(PO_3)_3$-$Ln(PO_3)_3$ (Ln = Ln,Y) has been chosen as a basis for following introduction of fluorides. To produce glasses of fluorophosphate crown glass type the following fluorides were introduced in the glass of the chosen system: BaF_2, ZnF_2, GaF_3, AlF_3, InF_3, ScF_3, YF_3, LaF_3.

The synthesis of the glasses was carried out in laboratory furnaces equipped with silit heaters.

The glasses containing the fluorides were melt in platinum crucibles at a temperature of 1200-1250^oC for 1.5 hours at vigorous stirring.

Reagents of "extremely pure", "chemically pure" and "analytically pure" grade were used for the synthesis. Fluorides of gallium and indium were introduced via GaF_3*3H_2O and InF_3*3H_2O. All samples were subjected to fine annealing.

The optical constants of the glasses were measured on a GS-5 tone meter and a refractometer IRF-23, the instrument error was plus-minus $1*10^{-5}$ and plus-minus $1*10^{-4}$ respectively.

The density of the glasses was measured by a method of hydrostatic weighing in toluene to within plus-minus 0.001g/cm^3.

The crystallization ability of the glasses was determined by a method of forced crystallization in a gradient furnace.

The IR spectra were recorded on a IKS-29 instrument (samples as tablets with KBr) within a range of 1400-400cm^{-1}.

The transmission spectra in UV and visible spectrum were recorded on a SPECORD-UV-VIS instrument.

2.Study of the glasses of $Ba(PO_3)_2$-$Al(PO_3)_3$-$La(PO_3)_3$-$Y(PO_3)_3$-RFx system.

To study the influence of fluorine - containing compounds into glasses - bases such as $Ba(PO_3)_2$- 56, $Al(PO_3)_3$ - 14, $La(PO_3)_3$ - 20, $Y(PO_3)_3$ - 10 the following fluorides were introduced: BaF_2, ZnF_2, GaF_3, AlF_3, InF_3, ScF_3, YF_3, LaF_3. We managed to introduce 30 mol.% of BaF_2, ZnF_2, GaF_3, InF_3, 20mol.% of ScF_3, YF_3, AlF_3 and 10mol.% of LaF_3. A further increase in the content of fluorides brings to crystallization at glass-making. The crystallization ability of the glasses synthesized is represented in **Fig.1.** Introduction of 10mol% of the mentioned fluorides results in insufficient improvement of crystallization stability. A further increase in the content of fluorides brings to a dramatic growth of crystallization tendency.

The index of refraction and average dispersion of the investigated glasses are increasing with increasing the content of the fluorides.**(Fig.3)**.Only the introduction of 10% of AlF_3 does not change the index of refraction at a simultaneous increase in the average dispersion. The density of the glasses also is increasing at the introduction of the fluorides **(Fig.4).** The least increase in the density occurs when AlF_3 and ScF_3 are introduced. The greatest increase in the density takes place when BaF_2 and InF_3 are introduced.

Such a change in the index of refraction and density may witness that a considerable amount of fluorine is evaporated during the synthesis. This conclusion was made on the basis of a comparison with the data of influence of fluorides on fluorophosphate bases. A chemical analysis of the glasses synthesized was carried out. Due to a high temperature of the synthesis (t= 1200^{o} -1500^{o}C) a considerable part of fluorine vaporized that was confirmed by the variation of the density and optical constants on the content of the fluorides. The results of the chemical analysis are given in **Table 1**. The greatest amount of fluorine is in the glasses with scandium fluoride, a little less amount of fluorine is contained in the glasses with fluorides of aluminum, yttrium, barium.

Table 1. *Results of chemical analysis of the glasses $Ba(PO_3)_2$-$Al(PO_3)_3$-$La(PO_3)_3$-$Y(PO_3)_3$-RFx system.*

Glass number	Content of components, mol.%					Fluorine content in synthesis, wt.%	Analytical fluorine content, wt.%
	$Ba(PO_3)_2$	$Al(PO_3)_3$	$La(PO_3)_3$	$Y(PO_3)_3$	RFx		
52	50,4	12,6	18	9	BaF_2-10	1,28	0,31

54	39,2	9,3	14	7	BaF_2-30	4,22	0,76
71	50,4	12,6	18	9	GaF_3-10	1,96	0,27
73	39,2	9,8	14	7	GaF_3-30	6,71	0,48
75	50,4	12,6	18	9	InF_3-10	1,93	0,22
78	39,2	9,8	14	7	InF_3-30	6,37	0,62
81	50,4	12,6	18	9	ScF_3-10	1,97	0,62
82	44,3	11,2	16	8	ScF_3-20	4,24	1,04
84	50,4	12,6	18	9	AlF_3-10	1,98	0,37
85	44,3	11,2	16	8	AlF_3-20	4,29	0,65
87	50,4	12,6	18	9	YF_3-10	1,94	0,51
88	44,3	11,2	16	8	YF_3-20	4,11	0,76
90	50,4	12,6	18	9	LaF_3-10	1,91	0,59
95	50,4	12,6	18	9	ZnF_2-10	1,31	0,28
97	39,2	9,3	14	7	ZnF_2-20	4,59	0,57

The transmission in UV and visible spectrum was measure λ_{50} was measured from 270 to 340 nm **(Fig.5).** A shift of the transmission cut-off to the long-wave region at introduction of the fluorides can be due to interaction of the melt with air.

The greatest deviation from a "normal straight line" is observed for the glasses containing fluorides of scandium, yttrium, bariun $\Delta\nu_{eg\text{-}F}$ =+6 - +8.

A study of a possibility to introduce greater amount of fluorides into glasses has shown that the introduction in the glass-base of 55mol% of BaF_2 resulted in formation of a glassy phase with crystal inclusions during glass-making.

To reduce the crystallization rate, MgF_2 was introduced into the glasses of $Ba(PO_3)_2$-$Al(PO_3)_3$-$La(PO_3)_3$-$Y(PO_3)_3$-BaF_2 system. During the glass –making on a cold plate it was managed to produce a glass. The replacement of BaF_2 and $Ba(PO_3)_2$ with BaO allowed to obtain volume samples of glasses and to measure their optical characteristics.

The compositions of the synthesized glasses and their optical characteristics are given in **Table 2**. The crystallization ability of the synthesized glasses is presented in **Fig.6.** The experimental results have shown that the replacement of $Ba(PO_3)_2$ with BaO results in a reduction in the index of refraction and average dispersion. A negligible improvement of the crystallization stability was observed at the replacement of BaF_2 with SrF_2 and/or BaO. The replacement of BaF_2 with BaO led to a growth of the index of refraction and average dispersion. To reduce the crystallization ability, the content of MgF_2 in the composition of glass was increased up to 30 mol.% and 1mol.% of AlF_3 was added (glass N^o157).That resulted in a considerable improvement in resistance to crystallization **(Fig.6)**.The optical constants of the glasses were: n_e= 1,583 ν_e =68, $\Delta\nu_{eg\text{-}F}$ = +11.

Table 2. *Composition of the glasses and their optical constants.*

Glass number	Content of components, mol. %									n_e	$(n_{F'} - n_{C'})$	ν_e
	$Ba(PO_3)_2$	$Al(PO_3)_3$	$La(PO_3)_3$	$Y(PO_3)_3$	BaF_2	MgF_2	SrF_2	AlF_3	BaO			
110	22,4	5,6	8	4	50	10	-	-	-			
111	16,8	4,2	6	3	50	20	-	-	-			
112	11,8	4,2	6	3	50	20	-	-	5	1,5889	885	66,5
115	6,8	4,2	6	3	50	20	-	-	10	1,5793	844	69
119	4,3	4,2	6	3	50	20	-	-	12,5	1,5767	836	69
117	1,8	4,2	6	3	50	20	-	-	15	1,5747	830	69
121	4,3	4,2	6	3	45	20	-	-	17,5	1,5813	848	68,5
128	11,8	4,2	6	3	40	20	10	-	5	1,5868	879	66,8
131	11,8	4,2	6	3	30	20	10	-	15	1,5902	891	66,2
157	6,8	4,2	6	3	20	30	10	1	25	1,5835	855	68,2

The transmission in UV and visible spectrum was determined for all synthesized glasse λ_{50} for 10mm thickness of a sample was within a range of 335-340nm **(Fig.7)**. Possible ways to improve the transmission are synthesis in controllable atmosphere or a change of temperature-time parameters of glass-making.

Conclusions

1. Glass-making systems to introduce fluorides have been chosen
2. The influence of fluorine-containing compounds on the optical and physical-chemical properties of fluorophosphate systems has been studied.
3. It has been shown that the introduction of fluorides of scandium, yttrium, barium into glasses results in obtaining glasses with a deviation from the "normal straight line": $\Delta\nu_{eg-F} =$ +6 - +8.
4. Introduction of magnesium fluoride and aluminum fluoride into glass results in a decrease of the deviation from the "normal straight line" to $\Delta\nu_{eg-F} =$ +11.
5. Introduction of fluorine-containing compounds into optical glass of the studied systems provides 99% transmission within a range of 365-40 nm.

Fig.1 Crystallization of glasses of Ba(PO3)2-Al(PO3)3-La(PO3)3-Y(PO3)3-RFx system.

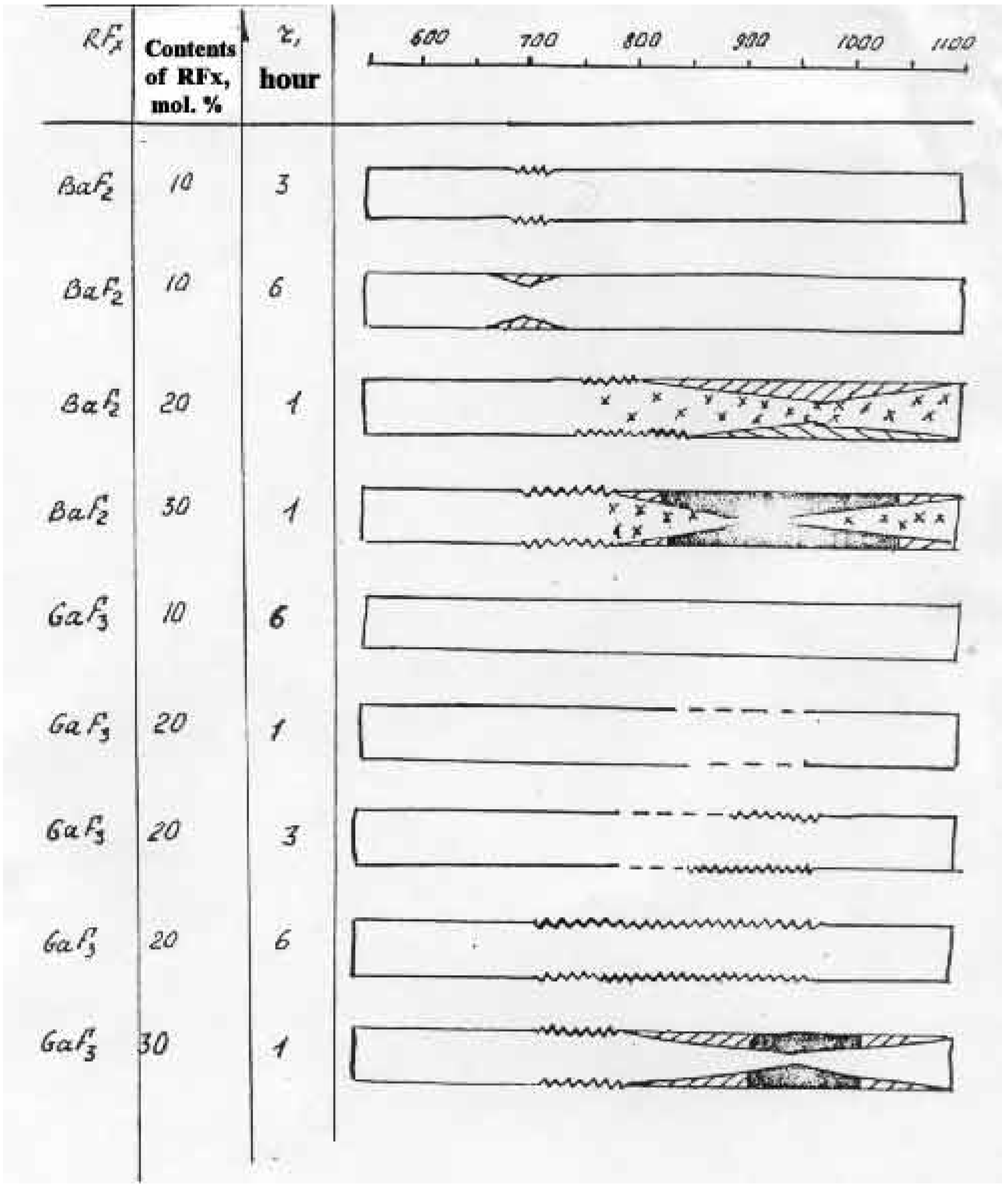

Fig.2 The index of refraction versus the content of fluorides

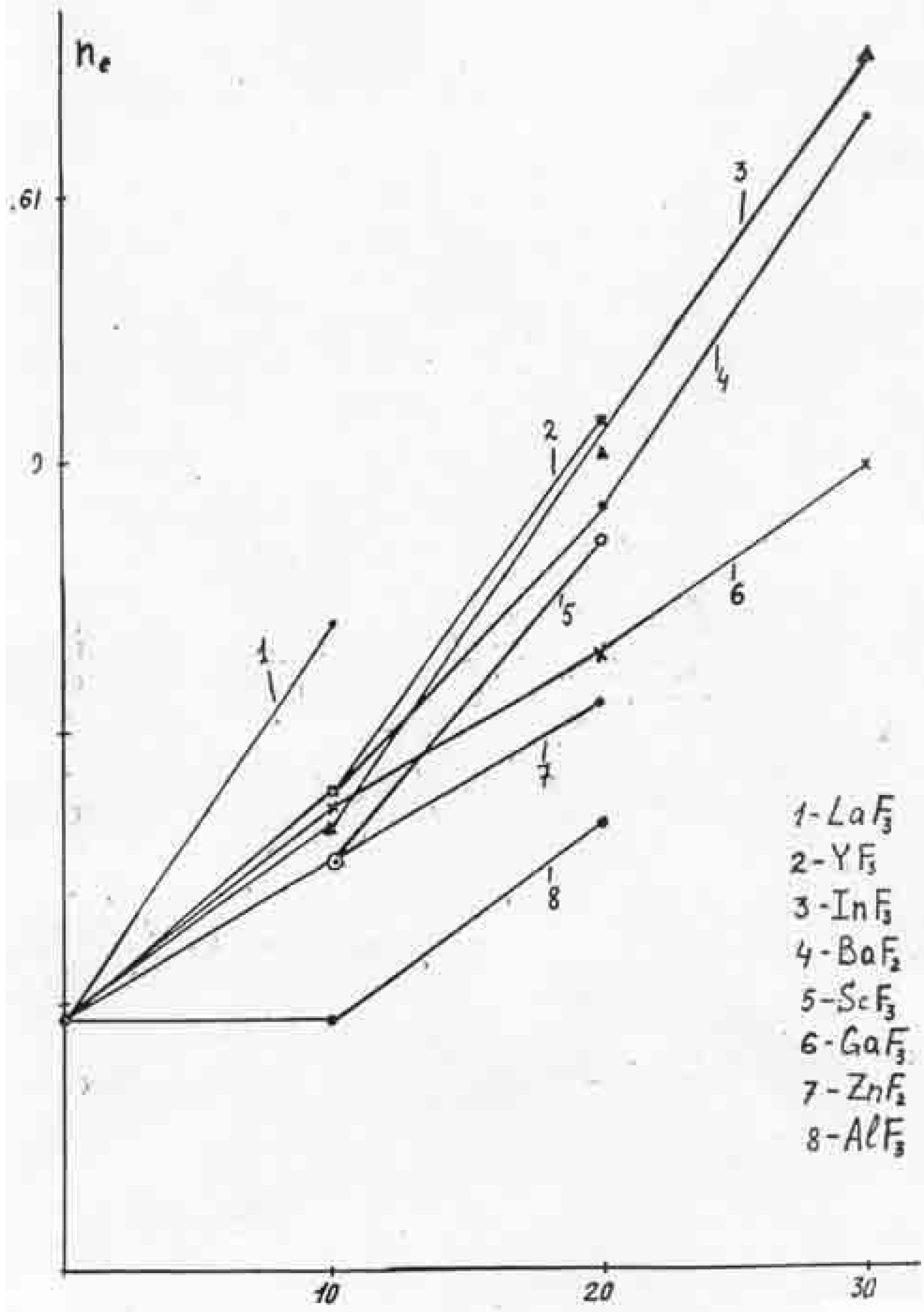

Fig.3 The average dispersion versus the content of fluorides

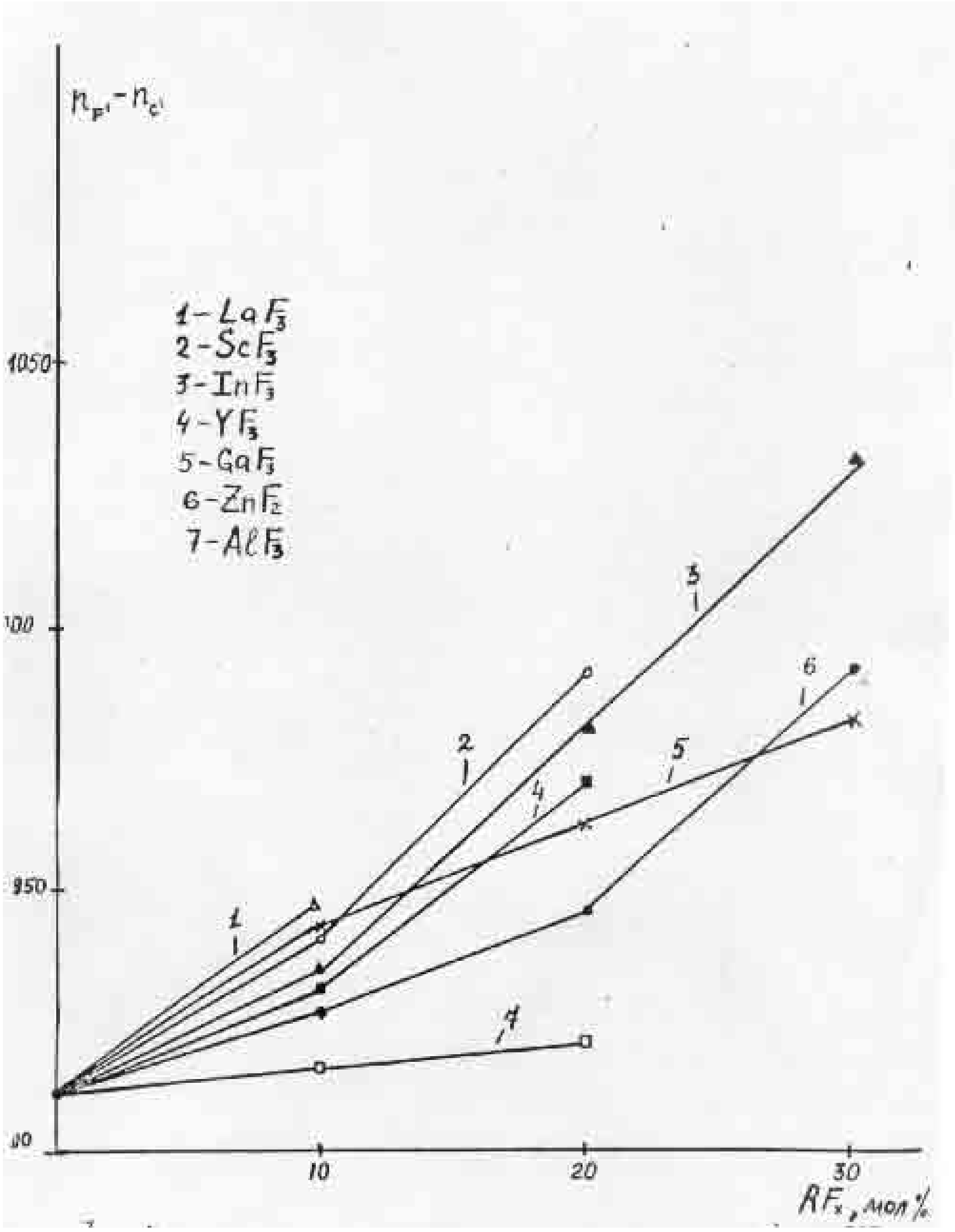

Fig.4 The density versus the content of fluorides

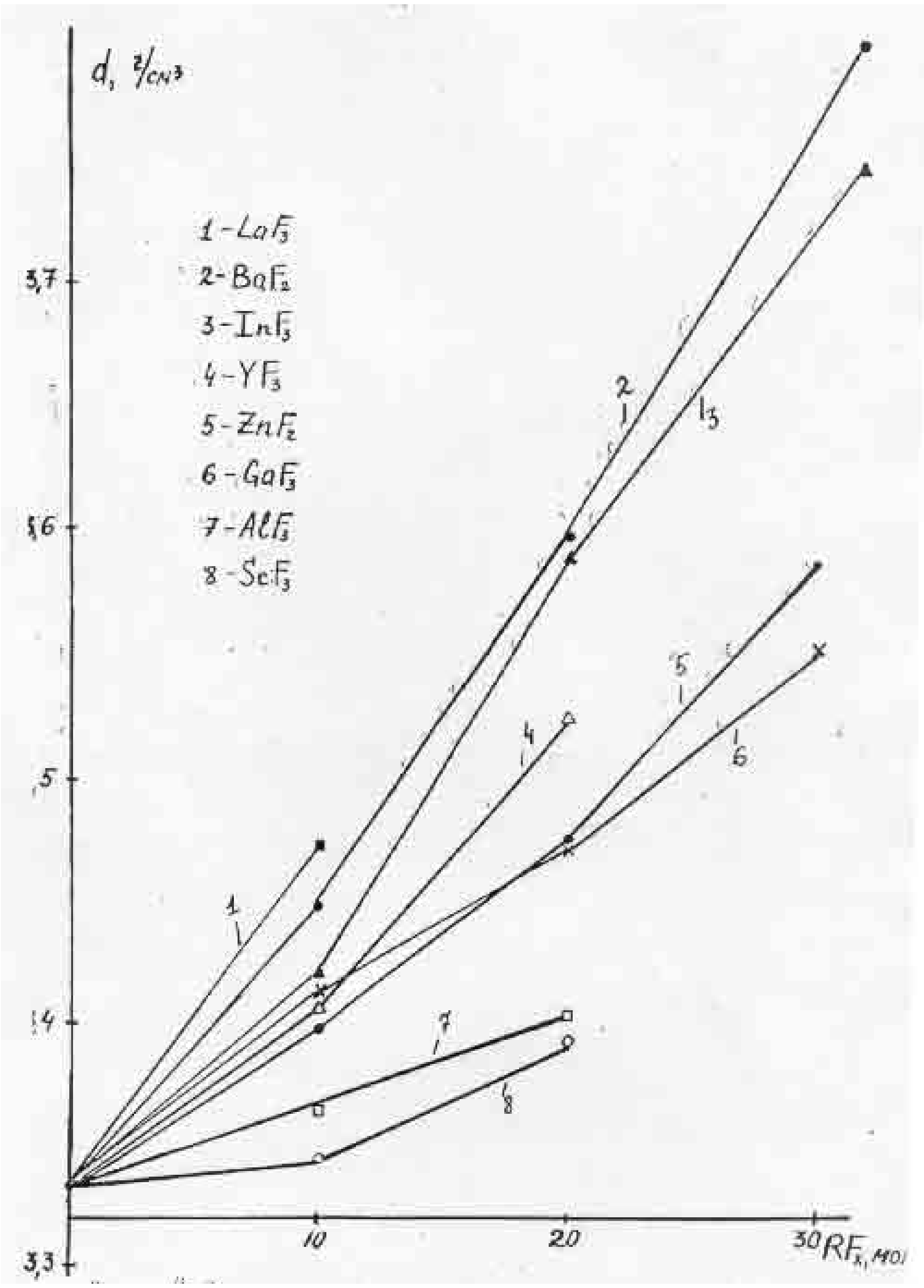

Fig.5 The transmission spectra of the glasses of Ba(PO3)2-Al(PO3)3-La(PO3)3-Y(PO3)3-RFx system in UV and visible spectrum. The thickness of the samples is 10mm.

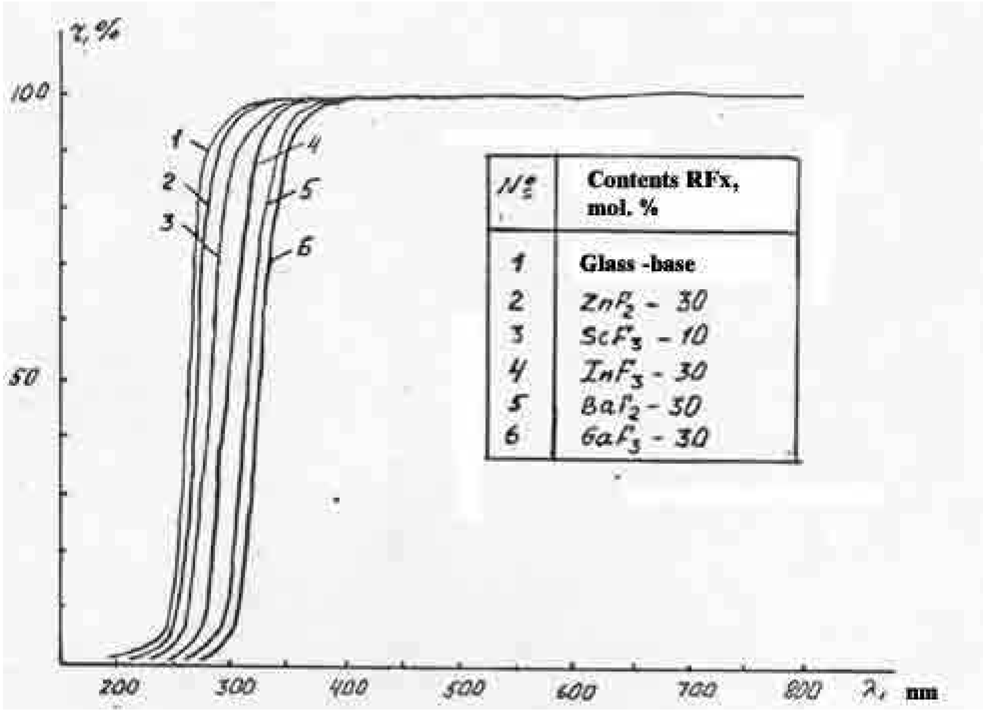

Fig.6 Crystallization of the synthesized fluorophosphate glasses (aging time, hours)

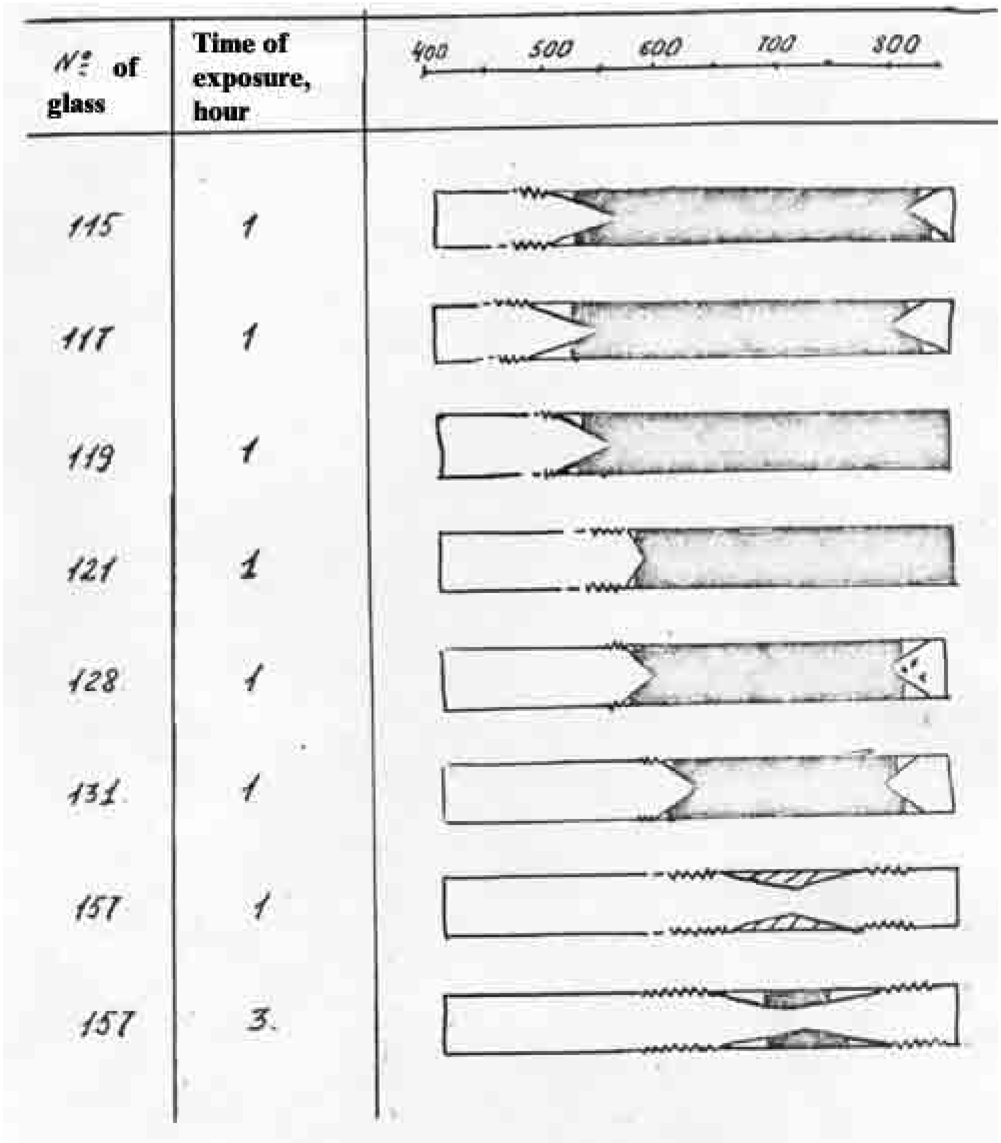

Fig.7 The transmission spectra of fluorophosphate glasses in UV and visible spectrum. The thickness of the samples is 10mm.