STUDIES ON THE MATERIALS DESIGN AND STRUCTURE OF GLASSES BY MOLECULAR DYNAMICS

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In order to apply the computer calculation and simulation to the materials design of glasses and structure of glasses we studied an expert system for materials design of glass which uses AI softwares ESHELL or KBMS. By using the expert system we can obtain various kinds of properties of glass by a dialogue method with a personal computer. Glass composition which has desired properties can be selected from table of 60 oxides. Molecular dynamics simulation has been made on the glass to clarify the structure of glass. Fluorophosphate glass was simulated and vibrational frequencies are compared with experimental results. This kind of simulation is useful for the prediction of properties of glasses and materials design.

1. INTRODUCTION

New glasses provided with new functions different from those of the conventional glass materials are now attracting the general attention, and materials of various kinds falling under this category of new glass have been developed. As typically represented by glass for optical fiber, these materials are now playing an important role supporting the present informational society. As in other ceramic materials, glass materials having new functions quite different from those of the conventional ones are being watched as optoelectronic, electrical and electronic, and biological and biochemical materials.

However, since these new glass materials are composite compositions comprising many compounds, particularly many oxides, it is not easy to achieve desired physical properties by precisely controlling their composition and physical properties. It is therefore essential to accumulate experimental findings through innumerable trials and utilize them in the development of new glass materials. Design of raw material composition and component ratios into prescribed ones thus requires much time and labor. It has therefore been practically very difficult to achieve a glass composition having desired physical properties.

The one of the purposes of the present paper is therefore to show system for support of glass design, which uses AI softwares, ESHELL or KBMS, and overcomes the conventional problems of consumption of much time and labor required for the achievement of a glass material having desired composition or functions, and permits easy and efficient selection of a

composition of vitrifying multielement composite oxides and selection of physical properties of glass. The present system which uses AI softwares allows considerable saving of time and labor which have largely been consumed in the conventional practices of design of glass materials and permits a simulation of design of glass material which has been nearly impossible up to now.

The another purpose is to show the computer simulation of structure of glass. Fluorophosphate glass can be use for high power lasers as a host glass.[1] The nonlinear index of this glass is lower than those of silicates or phosphates glasses because the hyperpolarizability of the fluorine anion is smaller than that of oxygen.[2] Schott(LG-812), Owens Illinois(E-309) and Hoya(LHG-10) are known as typical fluorophosphate laser glasses. These glasses contain AlF_3, CaF_2 and a little P_2O_5 component. The optical and physical properties of the fluorophosphate glass have been investigated and the spectroscopic properties of Nd^{3+} in this glass have been reported.[1,3] The effective linewidth of Nd^{3+} for this glass is larger than for phosphate or BeF_2-based glasses. This broadened spectrum is attributed to a distribution of oxygen and fluorine coordination around Nd^{3+}. An understanding of local fields and interactions at an activator ion site in this glass is important for the laser applications.

We have investigated the structure of AlF_3-based glasses by means of x-ray and neutron diffraction analyses, molecular dynamics (MD) simulation and Raman spectra.[4,5] Good agreement has been obtained between observed radial distribution functions and those calculated from the structural models simulated using MD method. In this study, we have estimated the vibrational frequencies of Al-F, P-O and P-F bonds in AlF_3-based glass and fluorophosphate glasses using MD simulation to verify the atomic potentials. Furthermore, the structure around a P atom in the mixed anion (oxygen and fluorine) glasses will be discussed.

2. EXPERT SYSTEM FOR MATERIALS DESIGN OF GLASS

We accumulated data base and knowledge base for materials design of glasses. The data base composed of many numerical values, for example, atomic radius, dissociation energy, molecular weight and so forth. The knowledge base was constructed by accumulating the glass formation ranges, general common sense on the glass composition and so on. By combining the data base and knowledge base by means of AI soft wares ESHELL or KBMS we made an expert system for materials deign of glasses.

An example we developed is shown as follows; a desired composition if selected from the list of component compounds displayed on the display unit, and the selected composition is entered on the input unit. For example, in the case of oxides as component compounds, those of a desired composition as selected from the list are entered through operation of a mouse, for example, as shown in Fig. 1.

After the completion of this input, values of physical properties corresponding to the selected ratios of composition are calculated: in this case, the value of only a representative or particularly watched physical property may first be calculated, and after determining the

appropriateness of this value, values of the other physical properties may be calculated[6].

In the example shown in Fig. 2, Young's modulus[7] is adopted as the representative or particularly watched physical property value. Young's modulus is adopted here because attention is given to the property of glass as modulus of elasticity. The relationship between the composition ratio and Young's modulus in this case is represented in Fig. 2.

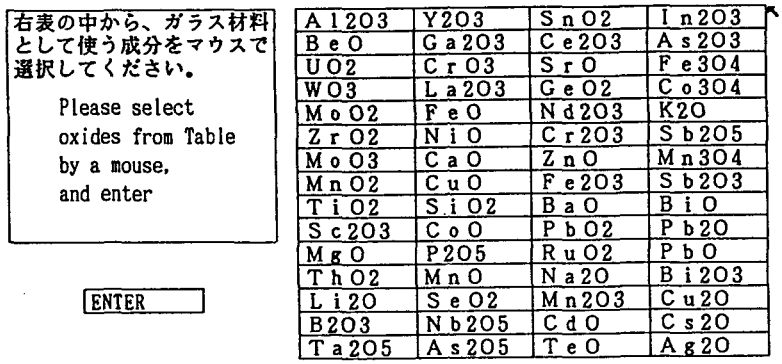

Fig.1 A view illustrating examples of display (glass composition to properties).

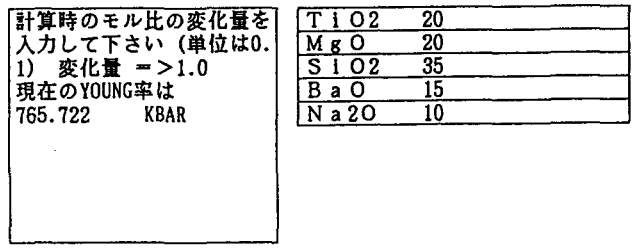

Fig.2 A view illustrating examples of display (glass composition to properties).

Young's modulus in this case is calculated as 765.7 kbar, which is judged to be rather low as a property of glass. When the value of Young's modulus is too low, a corrected value is entered again on the input unit. When appropriated, calculation is further performed for the other physical properties[6,8].

A physical property (p) of glass such as Young's modulus can be expressed generally by the following formula:

$$P = \Sigma P_i X_i$$

where, P_i : coefficient for the property of component compound i,

X_i : molar fraction for component compound i.

As Pi is an empirical value, the value of physical property (P) of glass is of course an approximate value.In actual calculation more theoretical or semiempirical formula were used[6,7,8].

Fig. 3 shows a typical display of calculated values of physical properties including the other properties. When these calculated values of physical properties are different from the

desired ones of the target glass material, another glass composition aiming at obtaining necessary physical properties entered again while comparing it with the component compounds. Fig.4 illustrates another example of the system for support of glass design.

In this example, an appropriate composition is derived from the values of physical properties of glass. More specifically, as shown in Fig. 4, desired values of physical properties are entered. In this case, a Young's modulus > 1000, a density < 5, and a thermal expansion coefficient < 30 are entered.

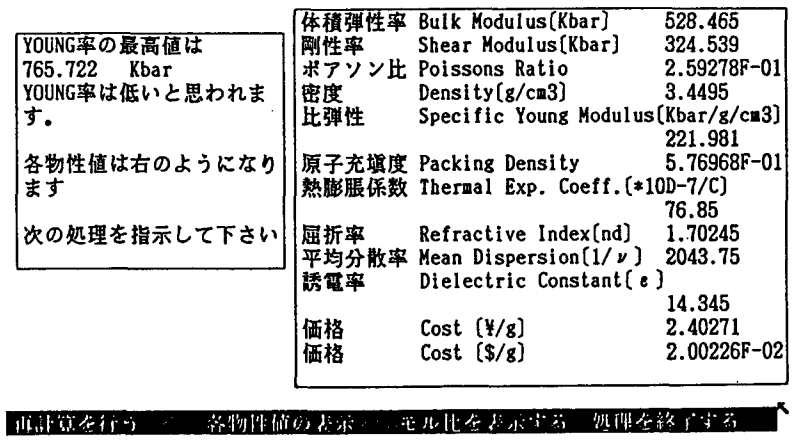

Fig.3 A view illustrating examples of display (glass composition to properties).

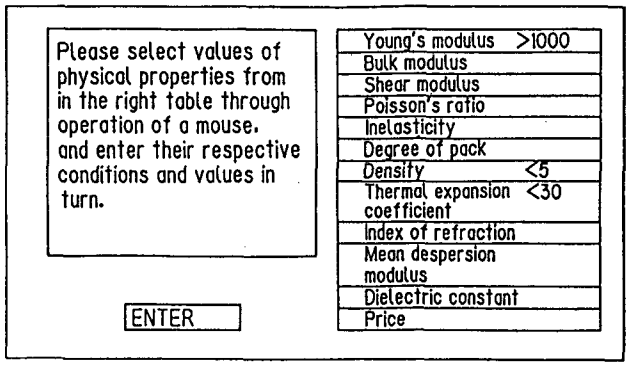

Fig.4 A view illustrating examples of display (properties to composition).

Arrangement is made so that compositions are calculated for the case satisfying all the conditions of physical property values and for cases satisfying only part of these conditions as well. Then, a composition comprising the following values of molar fraction is displayed as shown in Fig. 5 :

Values of the other physical properties are then also displayed.

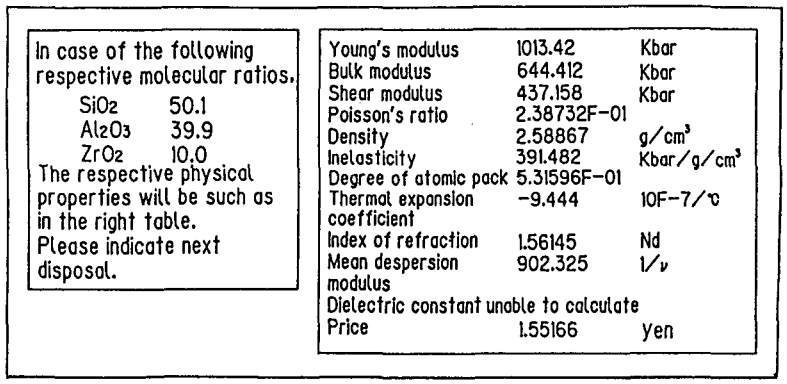

Fig.5 A view illustrating examples of display (properties to composition).

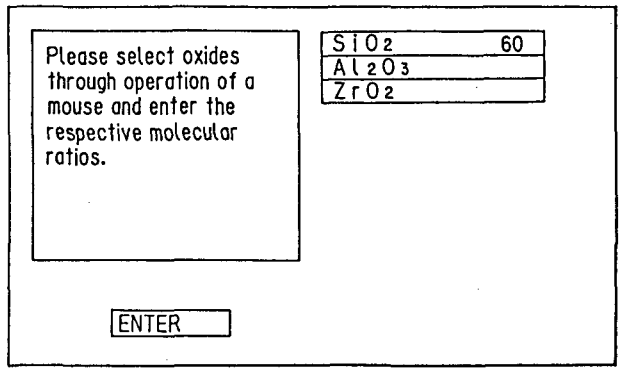

Fig.6 A view illustrating examples of display (changing the composition).

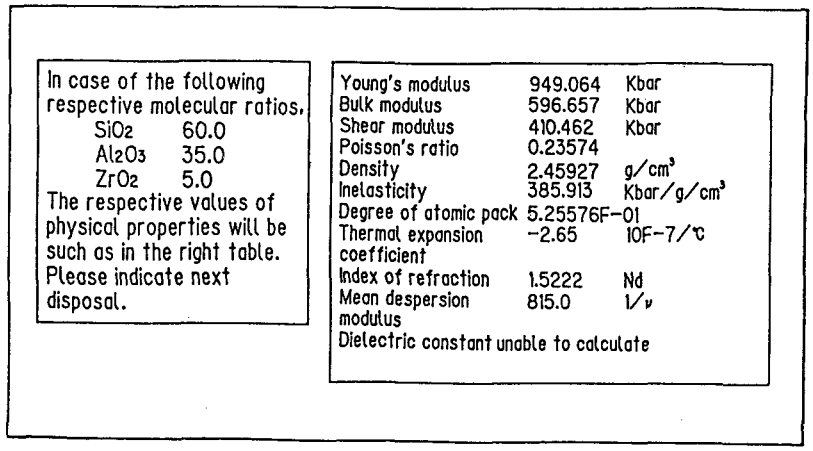

Fig.7 A view illustrating examples of display (properties to composition).

By comparing the composition and the values of physical properties, only the mol ratio of :

SiO_2 : 60

is entered again as a value similar to that displayed as above as shown in Fig. 6. As a result, a correspondence between the composition and the physical properties as shown in Fig. 7 is available.

Of course, when calculation or comparison of composition and physical property values is impossible in the case presented above, a display to that effect appears on the display unit to urge reentry.

3. MOLECULAR DYNAMICS SIMULATION

Our simulations consisted of about 200 atoms in a cubic basic cell. The volume of a basic cell at 5000 K was 2 times larger than that calculated from the observed density at room temperature and was reduced with temperature. Initial coordinates of atoms were given at random and the temperature was lowered by reducing the average kinetic energy of the atoms finally to 300K in 1.8×10^{-11} s (18000 steps). The inter atomic potential energy included a Coulomb term and a Born-Mayer repulsion for atoms i and j of the form $B_{ij}\exp(-r/\rho)$. The Coulomb potential was evaluated as the Ewald method. Time interval, Δt, in Verlet's algorithm took a value of 1×10^{-15} s. Potential parameters were taken as the same values as those used in the simulations of AlF_3-based[4,5] and Na_2O-Al_2O_3-P_2O_5 glasses. The parameters for atomic pairs excluded in these studies were estimated from the ionic radii. The values of potential parameters, compositions and sizes of cells at 300K were listed in Tables I and II.

The vibrational spectra were estimated by the Fourier transformation of the time-dependent autocorrelation functions of the atomic distances in the structural units, such as AlF_n and PX_4 (X=O,F). The autocorrelation function were obtained by the simulation for 10000 steps at 300K. To avoid distorting the spectra as the result of the Fourier transformation of the finite time histories, the four-term 74 dB Blackman-Harris window[9] was used.

Computations were made with HITAC S-820 computer in the Computer Center, Institute for Molecular Science, Okazaki National Research Institute.

Table I Number of atoms in the basic cells and size of cells at 300K.

system	Mg	Ca	Sr	Ba	Al	P	F	O	total	size(A)
$40AlF_3 \cdot 40CaF_2 \cdot 20BaF_2$	-	24	-	12	24	-	144	-	204	14.13
fluorides + PO_4	5	18	5	5	25	1	138	4	201	13.67
fluorides + $AlPO_4$	5	18	5	5	25	9	114	36	217	13.94
fluorides + $Al(PO_3)_3$	5	18	5	5	25	9	132	27	226	14.12

3.1 $40AlF_3 \cdot 40CaF_2 \cdot 20BaF_2$ GLASS

Table II Repulsive constant B_{ij} ($\times 10^{-16}$J)

	Ca	Ba	Al	P	F	O
Ca	3.86	7.95	2.25	2.34	2.42	13.87[a]
Ba		18.43	4.34	4.84	5.59	41.03[a]
Al			1.95	1.63	1.20	5.27[a]
P				1.33	1.86[a]	18.02[b]
F					0.84	1.06[c]
O						1.18[d]

$\rho = 0.3$(A), a) 0.25, b) 0.18, c) 0.32 and d) 0.35

Firstly, the vibrational spectra of AlF_n polyhedra in $40AlF_3 \cdot 40CaF_2 \cdot 20BaF_2$ were calculated from MD simulation for 10000 steps at 300K. The structure feature of this glass have been described previously.[4] The parameters of the pair potential, which used in MD simulations for the diffraction and vibrational analysis, are listed in Table II. In Fig.8, the vibrational spectrum caluclated from only symmetric stretching vibrational mode of AlF_n polyhedra. We can see the strong band located in the range of 550 to 680cm^{-1} which is assigned to the stretching vibration of AlF_n polyhedra. Kawamoto et al.[10] have been reported that the stretching vibrational band with high depolarization locate at 550 cm^{-1} in Raman spectra of $40AlF_3 \cdot 39CaF_2 \cdot 21BaF_2$ glass. Frequency of stretching mode shifted to a little higher than the observed one.

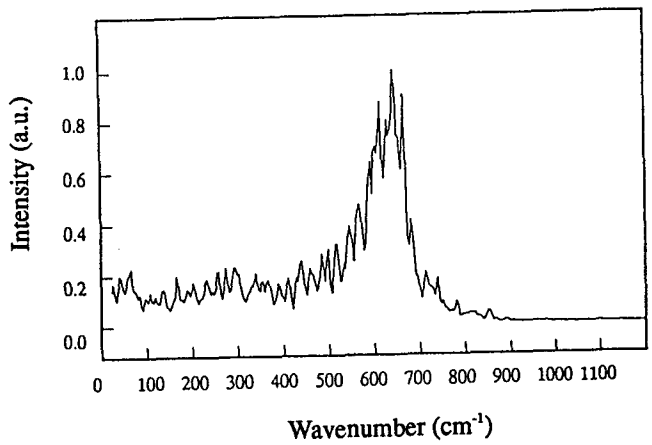

Fig.8 The vibrational spectrum of AlF_n polyhedra in the structure model for $40AlF_3 \cdot 40CaF_2 \cdot 20BaF_2$ glass.

3.2 A PO_4 UNIT IN AlF_3-BASED GLASS

Secondly, the simulations of AlF_3-based glass with a PO_4 unit were carried out. In this case, the initial coordinates of a PO_4 tetrahedron were given at the center of a basic cell and other atoms were given at random. Though a P-O bond was the strongest bond in a basic cell, a PO_4 tetrahedron did not always retain its P-O bonds on quenching. When all 4 O atoms in the tetrahedron were coordinated with Al atoms by chance, the PO4 tetrahedron retained its structure. In other cases, a F atom displaced an O atom which was not coordinated with an Al atom and PO_xF_{4-x} tetrahedron was formed. The dissociated O atom was coordinated by two Al atoms, such as Al-O-Al bond. These results were suggested that P-O-Al and Al-O-Al bonds were stable and Alkaline earth atoms did not coordinated an O atom in low-oxygen-content fluorophosphate glasses.

In Fig.9(a) and (b), the vibrational spectra of PO_4 and PO_3F tetrahedra calculated were shown with the vibrational modes of these tetrahedra reported by Buhler et al.[11] As the

vibrational modes belonging to A1 were active, the band at 1200 cm^{-1} in Fig.9(a) corresponded to the A1 mode at 950 cm^{-1}, which is assigned to the stretching vibration of PO_4^{3-}. And in Fig.9(b), the bands at 1250 and 650 cm^{-1} corresponded to the A1 modes at 1008 and 705 cm^{-1}, respectively. Furthermore, the vibrational spectra of P-F and P-O bonds in this PO_3F tetrahedra were shown in Fig.9(c) and (d), respectively. It was found that the higher band at 1250 cm^{-1} was due to PO_3 and the lower band at 650 cm^{-1} to P-F bond. Our results corresponded to the Buhler's assignments.

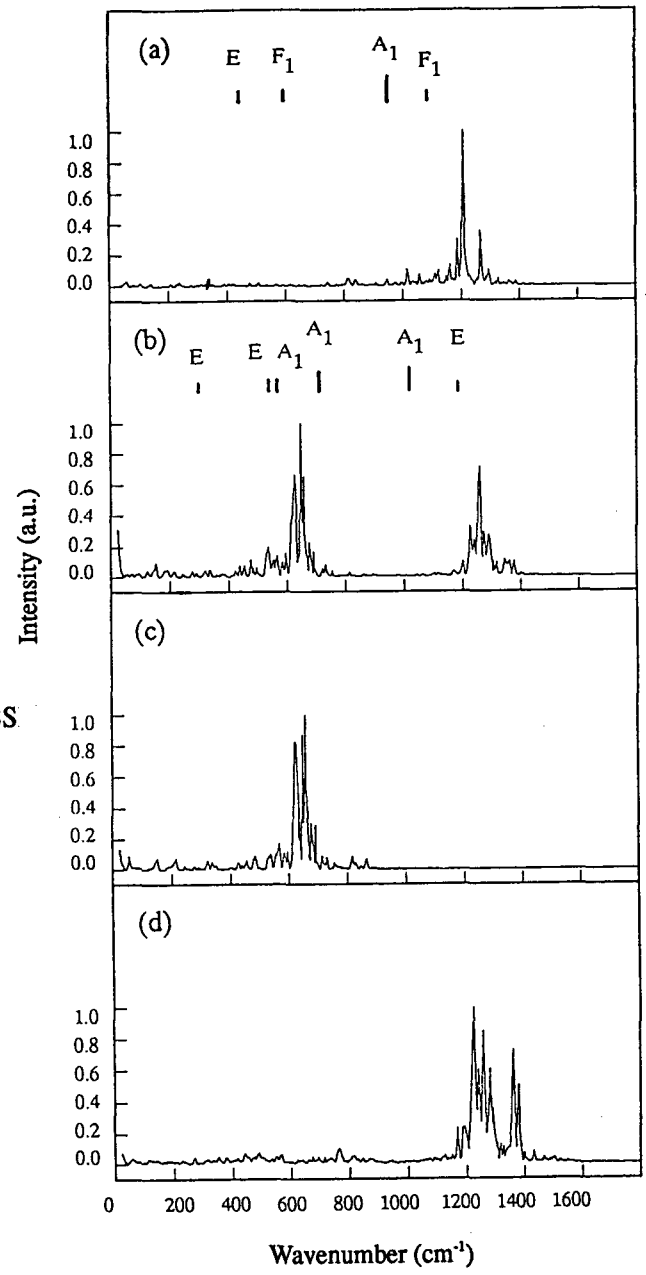

Fig.9 The vibrational spectra of (a) PO_4, (b) PO_3F, (c) P-F and (d) P-O in PO_3F tetrahedron in the structure models for fluorophosphate glasses.

3.3 FLUOROPHOSPHATE GLASS

It was expected in the structure of fluorophosphate glasses that the number of F atoms in the PX_4 tetrahedron depended on the atomic ratio of oxygen to phosphorus (O/P). The MD simulations were made on two systems: fluorides + $AlPO_4$ (O/P=4) and fluorides + $Al(PO_3)_3$ (O/P=3). The compositions were made by replacing AlF_3 and aluminum phosphates and listed in Table I. All O atoms were coordinated with P or Al atoms. 67% and 60% O atoms in basic cells belonged to PX_4 tetrahedra in fluorides + $AlPO_4$ and fluorides + $Al(PO_3)_3$ systems,

respectively. The proportions of PX_4 tetrahedra, which were classified by the number of O atoms, were listed in Table III with those of PX_4 tetrahedra coordinated by O and F atoms randomly. It was concluded that O atoms grouped around P atoms. Average number of O atoms in PX_4 tetrahedra were 2.7 and 1.8 in fluorides + $AlPO_4$ and fluorides + $Al(PO_3)_3$ systems, respectively. These values depended on the O/P ratio. In Table IV, the proportion of P-O-Al and Al-O-Al bonds were higher and there was no R-O-R bond (R=alkaline earth atom). 30% O atoms coordinated with alkaline-earth atoms. It is essential for detailed analysis to examine the influence of quenching rates and cell sizes on these structural units. The structures around O and P atoms in the models with initial coordinates given at random were consistent with those in the model with a PO_4 unit.

Table III The proportions of PX_4 tetrahedra.
(A) MD simulation and (B) random coordination

	+ $AlPO_4$		+ $Al(PO_3)_3$	
	(A)	(B)	(A)	(B)
PO_4	11.2	0.3 (%)	-	0.1 (%)
PO_3F	44.4	4.0	-	1.5
PO_2F_2	44.4	20.0	77.8	11.8
POF_3	-	42.8	22.2	39.5
PF_4	-	32.9	-	47.1

Table IV Coordination around O atoms.

	+ $AlPO_4$	+ $Al(PO_3)_3$
P-O-P	5.6(%)	3.7 (%)
P-O-Al	41.7	40.7
P-O-R	16.7	7.4
Al-O-Al	19.4	25.9
Al-O-R	16.7	22.2
R-O-R	0.0	0.0

R is an alkaline earth atom.

4. CONCLUSIONS

The present system permits calculation of values of physical properties on the basis of numerical information of glass raw materials such as the atomic radius and the dissociation energy, thus making it possible to easily accomplish at a very high efficiency design of a glass material of a desired composition and / or having desired physical properties through comparison of composition and physical properties. Computer simulation on the structure of fluorophosphate glasses showed that O atoms grouped around P atoms and PO_4,PO_3F,PO_2F_2 and POF_3 tetrahedra were formed. Average number of O atoms in PX_4(X=O,F) tetrahedra depended on oxygen content in a basic cell. The vibrational frequencies of AlF_n and PX_4 polyhedra estimated are compared to the experimental ones.

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