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Anion-conducting fluoride and oxyfluoride glasses

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Abstract. Main mechanisms of the anion (fluoride ion) transport in fluoride and oxyfluoride glasses are analysed. The variation in the transport number of F^- ions depending on the glass composition is followed. Methods for optimisation of the conductivity characteristics of the glasses in question are considered. The prospects of using fluoride-conducting glasses in electrochemical devices are discussed. The bibliography includes 90 references.

I. Introduction

The discovery [1] of the anionic (fluoride) conductivity of fluoroberyllate glasses of the $BeF_2 + MF$ (M = Na or Cs) type and fluorophosphate glasses of the $Ba(PO_3)_2 + MF_2$ (M = Ca, Sr, Ba or Mg) type and, particularly, the preparation of fluorozirconate glasses in systems involving ZrF_4 and BaF_2 and investigations [2] of their transport properties gave impetus to extensive studies of fluoride transport in glassy materials. Glasses possessing high F^- ionic conductivity constitute a special class of anion-conducting solid electrolytes. Since the glassy state is characterised by a distinctive structural solid-state disordering, one would expect that high anionic conductivity can be achieved in amorphous materials. In addition, fluoride glasses are of practical interest in a search for new solid electrolytes because of their technological effectiveness and cheapness as compared to crystalline materials. A search for glassy solid electrolytes follows two main directions: first, new glass-forming systems are investigated and, second, the electrophysical properties of the known fluoride glasses are modified by doping (by increasing the number of components).

Difficulties encountered in preparing fluoride glasses are associated with their high tendency to crystallisation. With the aim of suppressing this effect, various metal fluorides are introduced as stabilisers, which complicates the glass composition. By varying the composition, one can enhance the chemical stability of glasses, prepare specimens up to ~ 1 cm in thickness,[3] extend the temperature range of their application, reveal the contributions of various components to the dynamics of the ionic conductivities and obtain information on the mobility and concentration of charge carriers.

Problems of the formation and atomic structures of glasses in fluoride systems were surveyed in reviews.[4–9] Structural models are generally constructed based on comparison of the structural data for glassy and crystalline phases with the same chemical composition. Presently, a disordered network is used as the basic model for the glass structure.[10] According to this model, the glass structure represents a disordered (the long-range order is absent) three-dimensional glass-forming network consisting of coordination polyhedra of glass-forming cations, which are linked to each other through shared vertices occupied by bridging F_b^- anions. The cavities of the network are occupied by modifying cations bound to non-bridging F_{nb}^- anions. To gain insight into the glass structure, the reasons for the formation of disordered networks need to be revealed.

The model for a disordered network (the short-range order in the glass structure) is refined taking into account up-to-date experimental data. Among various structural models for fluoride glasses, the cluster (the short-range order and 'medium-range' order in the glass structure) model (see, for example, Ref. 11), which is closely related to the model for the disordered network, is most universally employed.[8] Structures of fluoride crystalline phases, which are chemically close to glasses, contain infinite chains of coordination polyhedra of glass-forming cations linked through F_b^- anions. The chains of the polyhedra, in turn, are linked in a three-dimensional disordered glass-forming network. Large low-charge modifying cations are not involved in this network and give rise to ionic cation–fluoride bonds. The introduction of modifying fluoride ions exhibiting high bond ionicity leads to strengthening of covalent bonds in the glass-forming network through the charge transfer.

The keys to an understanding of the anion transport in fluoride glasses are, apparently, the formation of the F_{nb}^- anions and the variation in the coordination number of glass-forming cations. It is the ability of glass-forming cations to adapt themselves to the change in the coordination number that promotes jumps of mobile anions between the adjacent polyhedra. The results of ^{19}F NMR studies [12–14] and computer simulation [15] demonstrated that it is precisely the F_{nb}^- anions located in the vicinity of the modifying cations that serve as mobile charge carriers. Local motions of F_{nb}^- anions initiate the diffusive motion of fluoride anions (anionic conductivity) through the glass-forming network.

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Glasses possessing ionic conductivity are characterised by dielectric relaxation associated with the jump migration of charge carriers resulting in the frequency dependence of the ionic conductivity.[16] Ion-conducting glasses follow the universal relationship: the direct-current conductivity σ is directly proportional to the dielectric relaxation frequency ω_m. This universal regularity was explained [17] within the framework of a model for the potential barrier distribution according to which the frequency of the dielectric loss peak is the minimum jump frequency of conducting ions. Hence, the directly proportional dependence of σ on ω_m is physically justified. Within the framework of this approach, the characteristic features of the jump mechanism for electric current carriers in ZrF_4-based fluoride glasses were examined.[18–20] The anionic conductivity in fluoride glasses depends primarily on the activation energy of the ion transport.

Particular mechanisms of the anion transport in glasses remain poorly studied because the available structural data are scarce. A necessary condition for the manifestation of essential anionic conductivity is the existence of glass-forming cations, which adopt high coordination numbers and differ in the form and size of their coordination polyhedra. Low coordination numbers of glass-forming cations (in fluoroberyllate and fluoroaluminate glasses) are responsible for low anionic conductivities.

For cation-conducting glasses, the polycationic (polyalkali) effect is well known. This effect lies in the fact that the replacement of one alkali metal cation by another gives rise to a minimum in the composition dependence of the ionic conductivity. The polycationic effect in fluoride and oxyfluoride glasses is manifested if the cationic conductivity exceeds the fluoride-ionic conductivity.[21–24] In the $Ba(PO_3)_2 + NaX$ (X = F, Cl or I) and $Ba(PO_3)_2 + BaF_2 + BaX_2$ (X = Cl or Br) glasses, the polyanionic effect (which was called by analogy with the polycationic effect) was experimentally observed upon the replacement of one halogen by another.[25,26] The polyanionic effect was confirmed for the $ZrF_4 + BaX_2$ (X = F or Cl) [27] and $30\,SiO_2 \cdot 55\,PbO \cdot 15\,Pb(F_{1-x}Cl_x)_2$ ($0 \leqslant x \leqslant 1$) glasses.[28] The $ZrF_4 + BaF_2 + MX$ (M = Li or Na; X = F or Cl) [29] and $ZrF_4 + BaF_2 + MF_n + LiF$ glasses ($M^{n+} = La^{3+}$ or Th^{4+}, the Li^+ and F^- mobile ions) exhibit the combined effect associated with lowering of the conductivity due to the simultaneous presence of mobile cations and anions.[30]

In the present review, the results of studies of the fluoride-ion transport in glassy solid electrolytes are analysed. Mechanisms of the cation transport in fluoride and oxyfluoride glasses call for a special discussion and are beyond the scope of the present review. The abundant experimental data on fluoride glasses are classified, wherever possible, into groups according to the type of the basis glass-forming fluoride. It should be noted that this classification becomes more difficult as the composition of multicomponent glasses is complicated (the most stable fluoride glasses contain three or more components). Various families of glasses based on MF_2, MF_3 or MF_4 are considered. Recently, glasses based on MF_5, where M = Nb, Ta, V or Mo, have been discovered (the glass transition temperature T_g varies from -45 to -60 °C; the crystallisation temperature T_{cr} ranges from 0 to -10 °C),[31] but their electrophysical properties remain to be explored. The characteristics of the anionic conductivities of some two- and three-component fluoride and oxyfluoride glasses are given in Table 1.

Fluoride glasses attract considerable interest because they are transparent in the IR region and possess low glass transition temperatures as well as because they are promising materials for fibre optics. According to the results of calculations, theoretical losses in the optical transmission of information in these glasses are an order of magnitude smaller than those in traditional oxide (silicate) glasses.

Table 1. Characteristics of the fluoride-ionic conductivity in two- and three-component fluoride and oxyfluoride glasses.

Glass	σ /S m^{-1}	T /°C	E_a /eV	Ref.
Fluoride glasses based on MF_2				
$80\,BeF_2 \cdot 20\,CsF$	6×10^{-11}	150	1.12	32 [a]
$67\,MnF_2 \cdot 33\,BaF_2$	1×10^{-4}	180	0.55	32
$67\,ZnF_2 \cdot 33\,BaF_2$	2×10^{-4}	180	0.59	32
$55\,ZnF_2 \cdot 45\,PbF_2$	4×10^{-4}	180	0.55	32
$30\,ZnF_2 \cdot 25\,AlF_3 \cdot 45\,LiF$	1×10^{-4}	200	0.86	33
$35\,ZnF_2 \cdot 20\,BaF_2 \cdot 45\,LiF$	3×10^{-3}	200	0.85	34
$45\,ZnF_2 \cdot 30\,BaF_2 \cdot 25\,YF_3$	1×10^{-3}	200	0.73	34
Fluoride glasses based on MF_3				
$30\,AlF_3 \cdot 40\,PbF_2 \cdot 30\,ZnF_2$	2×10^{-7}	150	0.79	32
$40\,AlF_3 \cdot 22\,CaF_2 \cdot 38\,YF_3$	5×10^{-9}	150	0.83	32
$40\,AlF_3 \cdot 40\,BaF_2 \cdot 20\,YbF_3$	4×10^{-7}	200	1.13	35
$30\,GaF_3 \cdot 50\,PbF_2 \cdot 20\,MnF_2$	2×10^{-4}	200	0.61	32
$40\,GaF_3 \cdot 40\,BaF_2 \cdot 20\,YbF_3$	1×10^{-5}	200	0.96	35
$40\,ScF_3 \cdot 40\,BaF_2 \cdot 20\,YbF_3$	1×10^{-3}	200	0.75	35
$40\,ScF_3 \cdot 40\,BaF_2 \cdot 20\,YF_3$	1×10^{-3}	200	0.70	12
$54\,InF_3 \cdot 36\,BaF_2 \cdot 10\,LiF$	6×10^{-3}	200	0.64	36
$25\,InF_3 \cdot 45\,PbF_2 \cdot 30\,ZnF_2$	4×10^{-3}	200	0.57	32
$35\,InF_3 \cdot 35\,PbF_2 \cdot 30\,MnF_2$	4×10^{-3}	200	0.56	32
$35\,InF_3 \cdot 35\,PbF_2 \cdot 30\,SnF_2$	2×10^{-3}	150	0.49	32
$40\,InF_3 \cdot 45\,PbF_2 \cdot 15\,BaF_2$	5×10^{-2}	200	0.535	37
$40\,InF_3 \cdot 40\,BaF_2 \cdot 20\,YbF_3$	1×10^{-3}	200	0.78	35
$30\,InF_3 \cdot 35\,BaF_2 \cdot 35\,BiF_3$	3×10^{-2}	200	0.52	38
Fluoride glasses based on MF_4				
$60\,ZrF_4 \cdot 15\,BaF_2 \cdot 25\,CsF$	1×10^{-5}	200	0.74	32
$62\,ZrF_4 \cdot 30\,BaF_2 \cdot 8\,LaF_3$	3×10^{-5}	200	0.79	32
$60\,ZrF_4 \cdot 30\,BaF_2 \cdot 10\,AlF_3$	1×10^{-4}	200	0.77	39
$59\,ZrF_4 \cdot 26\,BaF_2 \cdot 15\,BiF_3$	1×10^{-5}	200	0.73	32
$62.5\,ZrF_4 \cdot 28\,BaF_2 \cdot 9.5\,ThF_4$	3×10^{-5}	200	0.79	32
$59\,ZrF_4 \cdot 26\,BaF_2 \cdot 15\,HfF_4$	2×10^{-5}	200	0.76	32
$60\,ZrF_4 \cdot 33\,ThF_4 \cdot 7\,LaF_3$	3×10^{-6}	200	0.83	32
$70\,HfF_4 \cdot 30\,BaF_2$	8×10^{-5}	200	0.925	35
$55\,HfF_4 \cdot 30\,BaF_2 \cdot 15\,CsF$	2×10^{-5}	200	0.71	32
$62\,HfF_4 \cdot 30\,BaF_2 \cdot 8\,NdF_3$	9×10^{-5}	200	0.88	35
$62\,HfF_4 \cdot 30\,BaF_2 \cdot 8\,YbF_3$	9×10^{-5}	200	0.88	35
Oxyfluoride glasses				
$20\,Al(PO_3)_3 \cdot 80\,PbF_2$	8×10^{-7}	200	1.00	32
$10\,Al(PO_3)_3 \cdot 85\,PbF_2 \cdot 5\,MnF_2$	1×10^{-2}	200	0.63	32
$10\,Pb(PO_3)_2 \cdot 35\,PbF_2 \cdot 55\,MnF_2$	8×10^{-3}	200	0.56	32
$20\,NaPO_3 \cdot 40\,BaF_2 \cdot 40\,MnF_2$	4×10^{-6}	200	1.09	12
$10\,B_2O_3 \cdot 90\,PbF_2$	1×10^{-3}	200	0.91	34
$30\,B_2O_3 \cdot 50\,PbO \cdot 20\,PbF_2$	2×10^{-5}	127	0.55	40
$5\,Bi_2O_3 \cdot 95\,PbF_2$	1×10^{-4}	200	0.85	34
$10\,V_2O_3 \cdot 90\,PbF_2$	5×10^{-7}	200	0.85	34
$10\,SnO_2 \cdot 90\,PbF_2$	2×10^{-4}	200	0.79	34
$10\,GeO_2 \cdot 90\,PbF_2$	3×10^{-5}	200	1.05	34
$15\,GeO_2 \cdot 15\,PbO \cdot 15\,PbF_2$	3×10^{-5}	300	1	41
$10\,GeO_2 \cdot 80\,PbF_2 \cdot 10\,BiF_3$	9×10^{-4}	200	0.80	34
$10\,GeO_2 \cdot 80\,PbF_2 \cdot 10\,PbCl_2$	1×10^{-3}	200	0.84	34
$35\,SiO_2 \cdot 50\,PbO \cdot 15\,PbF_2$	5×10^{-5}	200	0.74	32
$30\,SiO_2 \cdot 30\,PbO \cdot 40\,PbF_2$	6×10^{-4}	200	0.75	42

Note. E_a is the activation energy of the conductivity. Different researchers calculated the E_a values according to the formula: $\sigma T = A\exp(-E_a/kT)$ or $\sigma = A\exp(-E_a/kT)$. The results differ by less than 0.05 eV.

[a] The original studies were cited in Ref. 32.

II. Fluoride glasses based on MF_2

Of simple fluorides MF_n ($n = 1-4$), BeF_2 is the only fluoride compound capable of undergoing a glass transition. The coordination polyhedron of the glass-forming Be^{2+} cation is the $[BeF_4]^{2-}$ tetrahedron (the coordination number is 4). The structural motif of crystalline BeF_2 (isostructural to SiO_2) is based on an ordered three-dimensional framework formed by the $[BeF_4]^{2-}$ tetrahedra, which are linked to each other *via* shared vertices. The transformation of BeF_2 into the glassy state occurs through rotations of the tetrahedra about the bridging $Be-F_b-Be$ bonds accompanied by distortions of the angles in the tetrahedra. As a result, a disordered three-dimensional framework consisting of the distorted $[BeF_4]^{2-}$ tetrahedra is formed. This framework is characterised by the absence of the long-range order. Tetrahedral fluoroberyllate glasses are structural analogues of silicate glasses. The introduction of alkali metal fluorides acting as modifiers leads to the cleavage of the bridging $Be-F_{nb}-M$ bonds and the occurrence of non-bridging fluorine atoms. It was found that the ratio between the cationic and anionic components of the conductivities in alkaline fluoroberyllate glasses is a function of the alkali metal–fluorine bond. Measurements of the transport numbers demonstrated that the $BeF_2 + MF$ and $BeF_2 + MF + M'F$ glasses (M and M′ = Na or Cs) exhibit virtually unipolar anionic conductivities.[1] The mechanism of the anionic conductivity in these glasses is associated with the increase in the amount of mobile non-bridging F^-_{nb} ions as the content of the MF modifying component increases. However, the fluoride-ionic conductivities are low and reach $\sim 10^{-6}$ S m^{-1} at 300 °C.

The electrical properties of multicomponent glasses based on manganese and zinc fluorides in the MnF_2-BaF_2, ZnF_2-MF_2 (M = Ba or Pb), ZnF_2-BaF_2-LiF, $ZnF_2-BaF_2-YF_3$, $ZnF_2-PbF_2-AlF_3-LiF$ and $ZnF_2-BaF_2-InF_3-SrF_2-NdF_3-MF$ systems (M = Li, Na, K or Rb) were studied.[33,34,43,44]. Apparently, crystalline phases formed in the ZnF_2-BaF_2 system, for example $BaZnF_4$, are most similar in structural units to fluorozincate glasses.[45,46] The crystal structure of $BaZnF_4$ consists of the $[ZnF_6]^{4-}$ octahedra linked in chains through shared vertices, whereas the barium atoms are located in the cavities. An analogous motif composed of the $[ZnF_6]^{4-}$ octahedra is observed in the structure of Ba_2ZnF_6. It can be assumed that fluorozincate glasses retain the short-range order of the arrangement of the $[ZnF_6]^{4-}$ octahedra, whereas the Ba^{2+} positions are partially occupied by the modifying Sr^{2+}, Nd^{3+}, Y^{3+}, Li^+, Na^+, K^+ or Rb^+ cations, their arrangement meeting the condition for charge compensation. The indium atoms, which adopt the coordination numbers of 6 and 7 in fluoride structures,[9] are, apparently, incorporated into the glass-forming network. In the octahedral $50\,ZnF_2 \cdot 19.5\,BaF_2 \cdot 10\,InF_3 \cdot 10\,SrF_2 \cdot 0.5\,NdF_3 \cdot 10\,MF$ glasses, the conductivity at 127 °C changes from 5×10^{-6} to 3×10^{-4} S m^{-1} and the activation energy E_a changes from 0.82 to 0.68 eV as the ionic radius of M^+ increases from 0.9 (Li^+) to 1.66 Å (Rb^+)†. In the $30\,ZnF_2 \cdot 25\,AlF_3 \cdot (45-x)\,PbF_2 \cdot x\,LiF$ ($0 \leqslant x \leqslant 20$, T_g = 230–275 °C) glasses, the ZnF_2-AlF_3 group acts as a glass-forming agent, whereas PbF_2 and LiF serve as modifiers. The anionic conductivity (at 200 °C) decreases from 1×10^{-4} to 1×10^{-5} S m^{-1}, whereas the activation energy E_a increases from 0.86 to 1.24 eV as the LiF content increases due to capture of mobile F^- ions by Li^+ cations.

III. Fluoride glasses based on MF_3

Trifluoride-based glasses are formed in systems containing MF_3 (M = Al, Fe, Ga or In) or AF_2 (A = Ba or Pb).[48,49] As for the glass-forming $MF_3 + M'F_2 + M''F_2$ (M = Fe, Ga or In; M′ = Pb or Ba; M″ = Mn, Zn, Cd, Sn or Ba) systems, the most stable glasses appear in the $InF_3-BaF_2-PbF_2$ system (T_g = 250–280 °C, $\Delta T = T_g - T_{cr} \approx 70$ °C). The structures of MF_3-based glasses consist of the $[MF_6]^{3-}$ octahedra linked in zigzag chains through fluorine atoms. The $[AlF_4]^-$ and $[GaF_4]^-$ tetrahedra can be present, but they are not involved in formation of glass networks. The data on the $46.7\,InF_3 \cdot 19\,PbF_2 \cdot 23.8\,BaF_2 \cdot 1.9\,AlF_3 \cdot 4.9\,SrF_2 \cdot 2.8\,YF_3$ glass obtained by Raman spectroscopy, the optical transmission method and magneto-chemistry[50,51] are indicative of octahedral coordination about the small indium ($r_{In^{3+}}$ = 1.06 Å) and aluminium ($r_{Al^{3+}}$ = 0.675 Å) atoms; whereas the large lead ($r_{Pb^{2+}}$ = 1.43 Å) and barium ($r_{Ba^{2+}}$ = 1.56 Å) atoms act as modifiers and occupy cavities in the three-dimensional octahedral glass-forming network. Consideration of the structure of this glass from the standpoint of the close packing of fluorine atoms leads to the same conclusion, *viz*., small In^{3+} and Al^{3+} cations occupy octahedral positions in the anionic packing, whereas large Pb^{2+} and Ba^{2+} cations introduce strong disturbance in the packing of fluoride anions.[52] It was assumed that the $[InF_7]^{4-}$ polyhedra are present in the glass-forming networks of indium-containing glasses.[9]

The properties of the $40\,MF_3 \cdot 40\,BaF_2 \cdot 20\,YbF_3$ glasses (M = Al, Ga, Sc or In) whose compositions are determined by the position of a low-melting eutectic in the phase diagrams of the $MF_3-BaF_2-YbF_3$ systems were examined.[35] In the course of formation of these glasses, the MF_3 trifluorides serve as glass-forming agents. The structures of the $40\,ScF_3 \cdot 40\,BaF_2 \cdot 20\,YbF_3$ and $40\,InF_3 \cdot 40\,BaF_2 \cdot 20\,YbF_3$ glasses contain fragments both of two-dimensional networks formed by the seven- and eight-vertex $[MF_n]^{-n+3}$ polyhedra (n = 7 or 8) and chains formed by the $[MF_6]^{3-}$ octahedra. Since the Al^{3+} and Ga^{3+} ions cannot be incorporated in seven-vertex polyhedra, the structure of the glass-forming network changes.[53] These glasses are characterised by a sharp increase (by three orders of magnitude) in the isothermal conductivity as the ionic radius of M^{3+} increases (as the $M^{3+}-F^-$ chemical bond is weakened) due to a linear decrease in the activation energy of the conductivity (see Table 1). The introduction of GaF_3 into the fluoroindate glasses $(40-x)\,InF_3 \cdot x\,GaF_3 \cdot 20\,ZnF_2 \cdot 16\,BaF_2 \cdot 20\,SrF_2 \cdot 2\,GdF_3 \cdot 2\,NaF$ ($0 \leqslant x \leqslant 30$) also leads to a sharp decrease in their conductivities.[54]

The mobility of the fluoride ions and the conductivities of glasses in the $InF_3-BaF_2-PbF_2$, $InF_3-BaF_2-BiF_3$ and $InF_3-BaF_2-PbF_2-AlF_3-LiF$ systems were examined.[36–38,55] The addition of AlF_3 and LiF to the former system promotes the preparation of $InF_3 + BaF_2 + PbF_2$ glasses and allows one to vary their composition over a wider range. Two phases were identified among the crystallisation products obtained in the $InF_3-BaF_2-PbF_2-AlF_3$ system,[56] *viz*., a fluorite-like solid solution based on PbF_2 and BaF_2 and a solid solution based on the high-temperature tetragonal modification of $Ba_3In_2F_{12}$. The conductivities of glasses of the $InF_3-BaF_2-PbF_2-AlF_3-LiF$ system are improved as the PbF_2 content increases, whereas the conductivities are impaired as the AlF_3 content increases. At room temperature, the anionic conductivity of the $20\,InF_3 \cdot 50\,PbF_2 \cdot 10\,BaF_2 \cdot 10\,AlF_3 \cdot 10\,LiF$ glass is 30 times as large as that of the superionic conductor β-PbF_2, which is widely used in scientific and applied studies. This fact underlines the important role of indium and lead fluorides in the preparation of new amorphous superionic conductors.

IV. Fluoride glasses based on MF_4

In the middle 1970s, ZrF_4 and BaF_2-based fluoride glasses were prepared. This result was unexpected because the glass-forming Zr^{4+} cation is characterised by high ($\geqslant$6) coordination numbers, which is contradictory to the conventional criteria for glass formation. The data of analysis of the shielding tensors and the chemical shifts of the signals in the ^{19}F NMR spectra[14,57] and the results of calculations by the Monte-Carlo method and molecular dynamics[58] demonstrated that the short-range structures in the barium fluorozirconate glasses $50\,ZrF_4 \cdot 50\,BaF_2(BaZrF_6)$ and $60\,ZrF_4 \cdot 40\,BaF_2$ are similar to the structure of crystalline

† The crystal-chemical ionic radii were taken from Ref. 47.

α-$BaZrF_6$ and that the medium-range ordering of the cluster type occurs along with the short-range order. Fluorozirconate glasses can contain Zr polyhedra with the coordination numbers of 6, 7 or 8. The structural networks of the glasses consist predominantly of the $[ZrF_7]^{3-}$ and $[ZrF_8]^{4-}$ polyhedra linked through bridging bonds; BaF_2 acts as a modifier.[59] The glass-forming ability of the ZrF_4-BaF_2 system is insufficient for the preparation of glasses several millimetres in thickness. These glasses can be prepared by introducing additional MF_n components ($n = 1-4$); the number of the components can be 10 or even larger.

The pioneering study on the anionic conductivities of fluorozirconate glasses[2] was concerned with the glasses $ZrF_4 + BaF_2 + ThF_4$ (55 mol.% – 62.5 mol.% ZrF_4, 28 mol.% – 36.3 mol.% BaF_2 and 7.5 mol.% – 13.8 mol.% ThF_4, $T_g \approx 320$ °C), $62\,ZrF_4 \cdot 30\,BaF_2 \cdot 8\,MF_3$ (M = La, Pr or Nd; $T_g = 310$ °C), $60\,ZrF_4 \cdot 33\,ThF_4 \cdot 7\,LaF_3$ ($T_g = 455$ °C) and $60\,ZrF_4 \cdot 25\,BaF_2 \cdot 8\,ThF_4 \cdot 7\,LaF_3$ ($T_g = 320$ °C). Measurements of the transport numbers demonstrated that the glasses possess unipolar fluoride-ionic conductivities (the transport numbers of the electron transport are $< 10^{-3}$). In the $ZrF_4 + BaF_2 + ThF_4$ glasses, the conductivity increases moderately as the content of the BaF_2 modifier increases. On the average, the fluoride-ionic conductivity in these glasses is $\sim 10^{-4}$ S m^{-1} at 200 °C and $E_a \approx 0.8$ eV.

Later on, the electrophysical properties of the multicomponent glasses $ZrF_4 + BaF_2 + AlF_3$,[39] $ZrF_4 + BaF_2 + MF_n$ (M = Li, Na, Rb, Cs, Ca, Sr, Ba, Sb^{3+}, Bi, La, Nd or Hf),[60] $60\,ZrF_4 \cdot 30\,BaF_2 \cdot 10\,LnF_3$ (Ln = La – Lu or Y),[61] $ZrF_4 + M'F_2 + M''F_3$ (M' = Ba or Sn^{2+}; M'' = Ga, La or Nd),[62,63] $ZrF_4 + BaF_2 + AlF_3 + LnF_3$ (Ln = La or Y),[64] $ZrF_4 + BaF_2 + LaF_3 + M'F$ (M' = Na or Li),[19,20] $ZrF_4 + BaF_2 + ThF_4 + LiF$,[20] $ZrF_4 + MF_n + AlF_3 + YF_3 + NaF$ (M = Ba or La),[18,19,65] $ZrF_4 + BaF_2 + LaF_3 + LiF + NaF$[66] and $ZrF_4 + BaF_2 + AlF_3 + YF_3 + ZnF_2 + CdF_2 + LiF$[67] were examined with the aim of improving the anion-transport characteristics. It was found that the anionic conductivity of fluorozirconate glasses depends primarily on the activation energy of the conductivity. The polarisability and the ionic radius of M^{n+} are the major factors influencing the E_a value. The activation energy of the fluoride-ion transport decreases as the ionic radius and the polarisability of the M^{n+} cations increases, which is, apparently, due to weakening of the $M^{n+} - F^-$ bond. The ZrF_4-BaF_2-CsF system exhibits the most promise for preparing glasses possessing high fluoride-ionic conductivity.

According to the ^{19}F NMR data,[12–14,64] the mechanism of the anionic conductivity in fluorozirconate glasses is associated with the non-bridging F^-_{nb} anions localised at the modifying cations. These anions execute local motions ($E_a \approx 0.2$ eV) in the vicinity of the modifying cations and diffusion motions ($E_a \approx 0.6$ eV) between the modifying cations. The fluorine diffusion is limited by the potential barriers between the modifying cations. In the $55\,ZrF_4 \cdot (38.5-x)\,BaF_2 \cdot 4AlF_3 \cdot (2.5+x)\,LaF_3$ ($0 \leqslant x \leqslant 7$) and $55\,ZrF_4 \cdot (37-x)\,BaF_2 \cdot 4\,AlF_3 \cdot (4+x)\,YF_3$ ($0 \leqslant x \leqslant 5$) glasses, the conductivity is enhanced as the BaF_2 content increases.[64]

In lithium fluorozirconate glasses containing less than 20 mol.% of LiF, the conductivities are determined by the Li^+ and F^- ions, whereas the conductivities in the glasses containing more than 20 mol.% of LiF are conditioned only by the Li^+ cations. In the sodium fluorozirconate glasses, the conductivities are governed exclusively by the F^- ions. For the $50\,ZrF_4 \cdot (45-x)\,BaF_2 \cdot 3\,AlF_3 \cdot 2\,YF_3 \cdot x\,NaF$ ($10 \leqslant x \leqslant 40$) and $45\,ZrF_4 \cdot 3\,LaF_3 \cdot 3\,AlF_3 \cdot 4\,YF_3 \cdot 45\,NaF$ glasses, the concentrations of the charge carriers were estimated within the framework of the jump mechanism of the conductivity.[18,19] A small portion of fluoride ions (3% – 5% of their total amount) is responsible for the transport properties of these glasses. The conductivity decreases as the NaF content increases due to a decrease in the mobility of the charge carriers and partial capture of mobile F^- anions by Na^+ cations.

Since zirconium and hafnium tetrafluorides (the ionic radii $r_{Zr^{4+}} = 0.98$ and $r_{Hf^{4+}} = 0.97$ Å) have similar physicochemical and structural characteristics, fluorohafnate glasses are isovalent analogues of fluorozirconate glasses. The electrolytic properties of glasses in the HfF_4-BaF_2 and $HfF_4-BaF_2-MF_3$ systems (M = Nd, Yb or Y) were investigated.[35,68] The parameters of the anion transport in HfF_4-containing glasses are virtually independent of the type and concentration of trifluorides of rare-earth elements, *viz.*, $\sigma \approx 3 \times 10^{-4}$ S m^{-1} at 223 °C and $E_a \approx 0.9$ eV. Trivalent rare-earth cations replace zirconium (hafnium) in glass-forming networks. Apparently, the addition of trifluorides of rare-earth elements with substantially different ionic radii (for example, $r_{Nd^{3+}} = 1.249$ and $r_{Yb^{3+}} = 1.125$ Å) to the glass-forming HfF_4-BaF_2 system has no effect on the surface contour of the potential energy (~ 0.9 eV), where the fluoride ions move. These results of conductometric studies are, apparently, indicative of microheterogeneity of glasses including large (from the viewpoint of the atomic scale) spatial regions free of trifluorides of rare-earth elements.

According to the NMR data,[69] high mobility of the F^- ions is observed in glasses based on tin tetrafluoride, *viz.*, in $SnF_4-BaF_2-MF_3$ (M = Al, Sc or Ga); however, the data on their ionic conductivities are lacking.

V. Oxyfluoride glasses

To prepare glasses, fluorides are added to mixtures of oxides. Thus, no glass was obtained from a mixture of pure oxides SiO_2, Al_2O_3 and BeO, whereas a transparent glass was prepared in the presence of even a small amount (several mass percent) of CaF_2. This is associated with a decrease in viscosity and an increase in mobility of structural units in melts in the presence of fluoride. The properties of these glasses are determined by the influence of fluorides on the structure of the oxide matrix. Glasses possessing unipolar fluoride-ionic conductivities were prepared by introducing fluorides MF_n ($n = 1-3$) into glass-forming oxyphosphate compounds of the $NaPO_3$, $M(PO_3)_2$ (M = Ba, Pb, Sr or Zn) and $Al(PO_3)_3$ types.[1,32,70] In the $Ba(PO_3)_2-MgF_2$ system whose glass-forming region extends to 70 mol.% of MgF_2, as an example, the fluoride-ion transport number reaches 0.98. For the most extensively studied fluorophosphate glasses, the following regularities were revealed:

(1) the fraction of fluoride anions involved in the conductivity increases sharply as the fluoride content in the glass increases;

(2) the F^- transport number is determined by the strength of the metal – fluorine bond;

(3) glasses with a fluoride content higher than 30 mol.% – 50 mol.% (depending on the system) are characterised predominantly by anionic conductivity.

The electrophysical properties of fluorine-containing oxyfluoride glasses were studied in the $Ba(PO_3)_2-AlF_3-MF_2$ (M = Mg, Ca, Sr or Ba; $T_g = 450-550$ °C), $ZnB_2O_4-CdB_2O_4-AlF_3-PbF_2$ ($T_g = 250-500$ °C) and $BaGeO_3-BaAl_2GeO_8(Ca_2Al_2GeO_7, Pb_2GeO_4)-CaF_2-MgF_2$ ($T_g = 550-700$ °C) systems.[71] Fluorine plays a binding role in the construction of the structural networks of glasses. The meta-, pyro- and monofluorophosphate groups and the fluoride fragments coexist in networks of fluorophosphate glasses. In borofluoride glasses, the function of fluorine consists primarily in changing the coordination of the boron atoms. The germanate and fluoride structural fragments coexist in fluorogermanate glasses. At 20 °C, the conductivity of fluorophosphate glasses varies from 10^{-11} to 10^{-6} S m^{-1} and the conductivity of borofluoride glasses ranges from 10^{-11} to 10^{-4} S m^{-1}.

In glassy oxyfluoride systems, fluorine can serve different functions depending on the type of the modifying cation. The structural positions and the dynamics of fluoride ions in glasses of the $Al(PO_3)_3-BaF_2$, $Ba(PO_3)_2-CdF_2$ and $Al(PO_3)_3-BaF_2-AlF_3-MF_n$ systems (M = Li, Na, K, Rb, Cs, Mg, Zn or Cd) were studied by ^{19}F NMR spectroscopy.[72,73] Several structurally

nonequivalent positions of the fluorine atoms involved in the coordination polyhedra about Ba, Al and Cd were found. In glasses of the $Al(PO_3)_3-BaF_2$ system, the F^- anions exhibit high mobility, the most mobile anions being bound to the barium atoms. In glasses of the $Ba(PO_3)_2-CdF_2$ system, no mobility of fluoride ions was observed.

Particular attention was given to PbF_2-containing glasses formed in the $M_nO_m-PbF_2$ ($M_nO_m = B_2O_3$, Bi_2O_3, V_2O_3, SnO_2, GeO_2),[34] $Al(PO_3)_3-PbF_2-MnF_2$,[74] $Pb(PO_3)_2-PbF_2-MnF_2$,[75] $SiO_2-PbO-PbF_2$,[32,42,76,77] $B_2O_3-PbO-PbF_2$ and $B_2O_3-PbO-PbF_2-AlF_3$ systems.[40] For glasses of the $M_nO_m-PbF_2$ systems, the activation energy of the conductivity varies from 0.8 to 1.0 eV and the conductivity at 127 °C ranges from 1×10^{-8} to 1×10^{-5} S m^{-1}. In the $SiO_2-PbO-PbF_2$ system, the F^- transport number increases as the concentration of PbF_2 rises from 0.4 for the $95(2\,PbO:SiO_2)\cdot5\,PbF_2$ glass to 1 for the $80(2\,PbO:SiO_2)\cdot20\,PbF_2$ glass. The change of the proton conductivity exhibited by the above-mentioned oxide glasses to the fluoride-ionic conductivity is attributed to a decrease in the content of structurally bound water as PbF_2 is added. The fluoride-ionic conductivity of the $80(2\,PbO:SiO_2)\cdot20\,PbF_2$ glass is $\sim10^{-4}$ S m^{-1} at 200 °C. The electron transport occurs primarily with the participation of the F^- ions bound to the Pb^{2+} ions. The structures of the $30\,B_2O_3\cdot(70-x)\,PbO\cdot x\,PbF_2$ ($0\leqslant x\leqslant25$) and $10\,B_2O_3\cdot20\,AlF_3\cdot(70-x)\,PbO\cdot x\,PbF_2$ ($0\leqslant x\leqslant60$) glasses are formed by borate groups and aluminium atoms each coordinated by six fluorine atoms. The charge transport involves F^- anions. The conductivity of glasses increases (or decreases) by several orders of magnitude as the concentration of PbF_2 increases (or upon addition of AlF_3).

Therefore, the best characteristics of the fluoride-ionic conductivity were achieved for oxyfluoride glasses with a high PbF_2 content in the $Al(PO_3)_3-PbF_2-MnF_2$ and $Pb(PO_3)_2-PbF_2-MnF_2$ systems. The conductivity of the $Al(PO_3)_3+PbF_2+MnF_2$ glasses containing 70 mol.%–80 mol.% of PbF_2 reaches $\sim10^{-2}$ S m^{-1} at 200 °C, which is comparable with that of the oxide glass $67\,B_2O_3\cdot33\,Na_2O$. A model was proposed for the superionic glass $10\,Al(PO_3)_3\cdot80\,PbF_2\cdot10\,MnF_2$ In the latter case, the glass structure is described by alternating layers of a conductor and an insulator.[78]

VI. Optimisation of characteristics of fluoride-conducting glasses and prospects of their practical applications

In the study,[8] the crystal-chemical concept of isomorphism was extended to the glassy state. Isovalent (in some cases, heterovalent) substitutions can be realised in series of glass-forming cations and/or in series of modifying cations. Cations, which can isomorphically replace each other, must have close sizes, similar bond ionicities and coordination polyhedra of the same type and occupy approximately equal volumes. For fluoride glasses, the following isomorphous series are most important: Li–Na–K–Rb–Cs, Ca–Cd–Sr–Pb–Ba, $Mg-Ni^{2+}-Co^{2+}-Fe^{2+}-Zn-Mn^{2+}$, Ln–Bi–Y–In–Sc, $Al-Ga-V^{3+}-Fe^{3+}-Cr^{3+}-In-Sc$ and Zr–Hf–U–Th.

The possibility of the application of the crystal-chemical concept of isomorphism to the glassy state was experimentally exemplified by the execution of the control over the electrophysical properties of glasses by changing their chemical compositions in the isoconcentration series $55\,ZrF_4\cdot20\,BaF_2\cdot25\,MF$ (the conductivity increases in the series Li < Na < Cs), $59\,ZrF_4\cdot26\,BaF_2\cdot15\,MF$ (Na < Rb < Cs),[60] $50\,ZnF_2\cdot19.5\,BaF_2\cdot10\,InF_3\cdot10\,SrF_2\cdot10\,MF\cdot0.5\,NdF_3$ (Li < Na < K < Rb),[34] $65\,ZrF_4\cdot25\,BaF_2\cdot10\,MF_2$ (Ca < Sr < Ba),[60] $59\,ZrF_4\cdot26\,BaF_2\cdot15\,MF_3$ (Sb < Nb < Bi),[60] $60\,ZrF_4\cdot30\,BaF_2\cdot10\,LnF_3$ (Lu < Gd < La)[61] and $40\,MF_3\cdot40\,BaF_2\cdot20\,YbF_3$ (Al < Ga < Sc < In).[35]

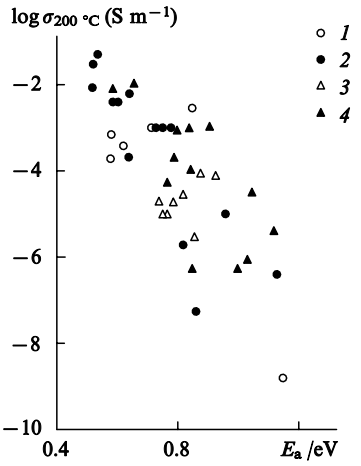


Figure 1. Dependence of $\log\sigma_{200\,^\circ C}$ on the activation energy of the conductivity for various families of fluoride glasses.
(*1*) MF_2-based glasses; (*2*) MF_3-based glasses; (*3*) MF_4-based glasses; (*4*) oxyfluoride glasses. The conductivity was calculated for 200 °C, the activation energy was calculated by the equation $\sigma T = A\exp(-E_a/kT)$.

The dependence of the conductivity on its activation energy for various families of anion-conducting glasses is shown in Fig. 1. It can be seen that the fluoride-ionic conductivity is determined primarily by the activation energy. To perform the directed search for glassy fluoride-conducting solid electrolytes and optimisation of their transport characteristics, it is necessary to reveal the factors responsible for the mechanism of the conductivity. The following facts are evidence for the high fluoride-ionic conductivity in glasses:

(1) the presence of highly coordinated glass-forming cations located in polyhedra of different types and sizes;[12]

(2) high polarisability of the cations;[60]

(3) weak energy of the cation–fluorine bond;[12]

(4) an increase in the molar volume of the glass.[34,35]

From the aforesaid it follows that the Ba^{2+} and Pb^{2+} ions acting as modifiers have the most substantial and yet different effect on the fluoride-ion transport. Taking into account the essential role of the electron shells of the ions in interionic interactions, it can be assumed that this distinction is due to the difference in the configuration of the outer electron shells of the Pb^{2+} ion (Group IV element) and the M^{2+} ions (M = Ca, Sr, Ba and Cd, which are Group II elements). Studies of the mixed $Pb_{1-x}Cd_xF_2$ crystals demonstrated[79,80] that the anionic conductivity in these isovalent solid solutions occurs predominantly with the participation of the fluoride ions whose nearest environment is formed by lead cations. This is confirmed by the fact that the energies of formation of Frenkel defects in the β-PbF_2 and BaF_2 crystals are substantially different (1 and 1.8 eV, respectively[81]). The temperature dependences of the anionic conductivity for fluoride glasses and crystalline conductors based on PbF_2 are shown in Fig. 2. It can be seen that the conductivities of glasses are higher than that of the superionic conductor PbF_2 but lower than those of the fluorite solid solutions $Pb_{0.85}Yb_{0.15}F_{2.15}$ and $Pb_{0.9}In_{0.1}F_{2.1}$.

Presently, problems associated with the environmental protection from various fluorine-containing pollutants gain momentum. The use of fluoride solid electrolytes as functional elements in detectors and chemical current sources is a topical line of investigations in this field.[70,85,86] Let us consider the prospects of the practical use of fluoride-conducting glassy solid electrolytes in electrochemical devices. Since glasses are isotropic and have no grain boundaries (as opposed to ceramics), their conductivities do not decrease as the temperature is lowered due to the blocking effect of grain boundaries. The chemical composition and the structure of glasses can be varied over wide ranges (the composi-

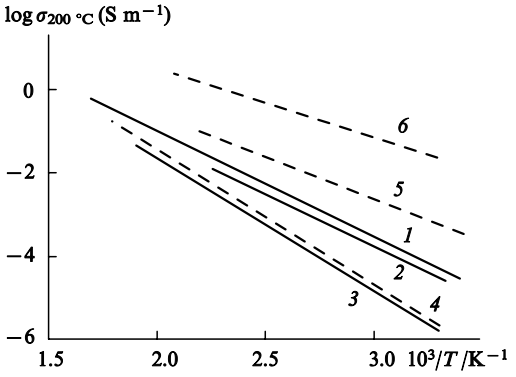


Figure 2. Temperature dependences of the anionic conductivities for glassy and crystalline fluoride solid electrolytes; (*1*) the $40\,InF_3 \cdot 45\,PbF_2 \cdot 15\,BaF_3$ glass,[37] (*2*) the $30\,InF_3 \cdot 35\,BaF_2 \cdot 35\,BiF_3$ glass,[38] (*3*) the $10\,Al(PO_3)_3 \cdot 85\,PbF_2 \cdot 5\,MnF_2$ glass,[32] (*4*) β-PbF_2 single crystal,[82] (*5*) $Pb_{0.85}Yb_{0.15}F_{2.15}$ single crystal,[83] (*6*) $Pb_{0.9}In_{0.1}F_{2.1}$ polycrystal.[84]

tional and structural flexibility), which allows one to optimise the requirements imposed on materials used in devices and ensure a good interface contact between solid electrolytes and electrodes taken in the glassy state, thus eliminating the problems inherent in crystalline systems.

The use of solid electrolytes as active elements of detectors is based on the Nernst equation:

$$E = \frac{RT}{nF} \ln\left(\frac{a'_F}{a''_F}\right),$$

where E is the electromotive force of the electrochemical cell , n is the number of electrons involved in the electrode reaction, F is the Faraday constant, a'_F and a''_F are the activities (in particular cases, the concentrations) of fluorine at two solid electrolyte–electrode interfaces.

The ionic conductivity is responsible for the rate of the establishment of thermodynamic equilibrium between the electrode and the solid electrolyte with respect to the F^- ions (the response speed of the detector). It is generally essential that the anionic conductivity of a solid electrolyte should be higher than 10^{-4} S m^{-1} for it to be used in detectors. This anionic conductivity of a fluoride glass can be achieved by various means.

The construction of chemical current sources based on fluoride solid electrolytes is appealing due to high free energies of the formation of fluorides. Taking into account these values, high calculated electromotive forces (several Volts) were obtained. The fluoride-ionic conductivities of fluoride glasses used presently in chemical current sources are in the range of 10^{-5}–10^{-4} S m^{-1} at room temperature. The internal resistances of these sources are higher than those of traditional cells based on liquid electrolytes. To reduce the internal resistance of a current source, it is necessary to use either high temperature (heating to 150 °C) or a thin-film technology. It should be noted that amorphous solid electrolytes readily form thin films, which do not require high annealing temperatures and are compatible with the silicon technology.

VII. Conclusion

By applying the principles of the isomorphism of atoms to the glassy state, multicomponent glasses possessing the required electrophysical properties can be prepared in the basic glass-transition region of the fluoride system. Isovalent substitutions in the series $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, $Ba^{2+} < Pb^{2+}$, $Al^{3+} < Ga^{3+} < Sc^{3+} < In^{3+}$ and $Hf^{4+} < Zr^{4+}$ lead to the enhancement of the ion transport in fluoride glasses. However, it should be noted that the introduction of hygroscopic KF, RbF and CsF or readily hydrolysable PbF_2, InF_3 and BiF_3 leads to a decrease of the chemical stability of glasses.[8]

Compositions of fluoride glasses, which possess high anionic conductivities and can serve as a basis for ion-selective membranes and detectors, have been formulated. An increase in the fluoride-ionic conductivity is associated primarily with a decrease in the activation energy of migration of charge carriers. High conductivities are characteristic of fluoroindate glasses of the $40\,InF_3 \cdot 45\,PbF_2 \cdot 15\,BaF_3$ ($\sigma_{200\,°C} = 5 \times 10^{-2}$ S m^{-1}) and $30\,InF_3 \cdot 35\,BaF_2 \cdot 35\,BiF_3$ ($\sigma_{200\,°C} = 3 \times 10^{-2}$ S m^{-1}) types and also of fluorophosphate glasses of the $10\,Al(PO_3)_3 \cdot 85\,PbF_2 \cdot 5\,MnF_2$ type ($\sigma_{200\,°C} = 1 \times 10^{-2}$ S m^{-1}).

Investigations of the cation (particularly, lithium) transport in fluoride glasses call for special consideration. For example, high lithium-ionic conductivities are manifested by the fluoride and oxyfluoride glasses $50\,LiF \cdot 30\,Li_2O \cdot 20\,Al(PO_3)_3$ ($\sigma_{300\,°C} = 1$ S m^{-1}),[87,88] $80\,LiF \cdot 20\,UF_4$ ($\sigma_{150\,°C} = 1 \times 10^{-1}$ S·m^{-1}), $60\,LiF \cdot 30\,ThF_4 \cdot 10\,BaF_2$ ($\sigma_{170\,°C} = 2 \times 10^{-2}$ S m^{-1}, $E_a = 0.58$ eV), $80\,LiF \cdot 20\,Al(PO_3)_3$ ($\sigma_{200\,°C} = 3 \times 10^{-3}$ S m^{-1}, $E_a = 0.61$ eV),[32] $60\,LiF \cdot 20\,ZrF_4 \cdot 10\,ThF_4 \cdot 10\,BaF_2$ ($\sigma_{175\,°C} = 2 \times 10^{-2}$ S m^{-1});[89] high sodium-ionic conductivities are exhibited by the glasses $80\,NaF \cdot 20\,Al(PO_3)_3$ ($\sigma_{200\,°C} = 2 \times 10^{-3}$ S m^{-1}, $E_a = 0.80$ eV)[23] and $50\,NaF \cdot 50\,B_2O_3$ ($\sigma_{200\,°C} = 2 \times 10^{-5}$ S m^{-1}, $E_a = 0.93$ eV);[90] potassium-ionic conductivity is manifested by the $80\,KF \cdot 20\,Al(PO_3)_3$ glass ($\sigma_{200\,°C} = 4 \times 10^{-6}$ S m^{-1}, $E_a = 0.76$ eV).[23]

Studies of crystallisation of glasses are of interest in connection with the possibility of the construction of nanocrystalline superionic conductors. One of the problems is the design of a microcrystalline structure in an amorphous glass by crystallisation (the preparation of superionic composites); in fluoride systems, the conductivities of partially disordered crystalline phases (solid solutions) are higher than those of glassy phases (see Fig. 2). To produce a microcrystalline structure in a glass, annealing should be carried out in such a way that a large number of crystallisation centres appear and the rate of crystal growth is low. The first stage of crystallisation may involve isolation of small crystals of intermediate metastable phases. It is assumed that the growth of large crystals is retarded by the amorphous phase.

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