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Abstract

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ON A NEW COMPOUND IN THE SYSTEM NaF–AlF_3

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The phase diagram of the system sodium fluoride–aluminum fluoride has been studied many times, since the cryolite (Na_3AlF_6) formed in it is the principal component of the electrolyte used in the electrolytic production of aluminum from its oxide.

Earlier investigations ([1–6]) established that, in the indicated system, in addition to cryolite there is formed chiolite, which according to various authors has the composition $Na_5Al_3F_{14}$ or $Na_3Al_2F_9$.

The conclusion that only cryolite and chiolite are present in the system mentioned has been confirmed by numerous studies, despite the fact that, according to theoretical calculations ([7]) based on taking into account the magnitudes of ionic charges and radii, in a system consisting of alkali-metal fluorides and aluminum fluoride the most stable aluminum configuration should occur in an equimolecular compound of composition $MeAlF_4$.

The existence of a compound of this type with potassium and the monovalent thallium and rubidium has long been established ([8,9]). As for the compound with sodium, apart from $NaAlF_4 \cdot H_2O$ ([10]), nothing was known, unless one counts the assumptions concerning the possibility of its formation in the NaF –AlF_3 system ([11]), during the fusion of cryolite with aluminum fluoride ([12]), which, however, were not confirmed by special investigations ([5]).

The first X-ray data relating to sodium tetrafluoroaluminate ($NaAlF_4$) were published by Howard ([13]); they were obtained as the result of studying sublimates formed while passing one of the gases–nitrogen, hydrogen, carbon monoxide, or argon–at 1000° through melts consisting of sodium fluoride and aluminum fluoride.

It should be pointed out, however, that not all of the interplanar spacings given in this article correspond to the crystal lattice of $NaAlF_4$. Some of them belong to chiolite and aluminum fluoride. At the same time, certain values of interplanar spacings characteristic of this compound are not indicated. In view of this, the principal X-ray data published by Howard for $NaAlF_4$ cannot be regarded as sufficiently complete.

Independently of Howard' s work, in 1954 we detected the compound $NaAlF_4$ in the condensate of sublimates obtained by melting cryolite–alumina melts in an argon atmosphere at 1020°. The amount of this compound, which differs from the starting substances, from chiolite, and from aluminum fluoride, increased as the AlF_3 content in the melt increased. The greatest amount of it (of the new compound) was found in the sublimates of melts whose molecular ratio of NaF to AlF_3 was 1.67 and 1.00, i.e., in the region corresponding to the so-called "acid electrolytes."

Since the condensation products of sublimates from the indicated melts always consist of very fine powders representing a mixture of $NaAlF_4$ and products of its decomposition (chiolite and aluminum fluoride), it is possible

considered that this compound is very unstable under ordinary conditions and that it is preserved partially in the presence of argon or other gases.

X-ray investigation of the samples obtained by us was carried out in copper filtered radiation in a high-resolution camera with a drum diameter of 143.25 mm. This made it possible to separate on the radiographs the interference maxima of chiolite and aluminum fluoride. After excluding them from consideration, the remaining unidentified maxima, characteristic of the crystal lattice of the new phase, were used for the corresponding calculations.

The calculated values of the interplanar spacings, the relative intensities of the interference maxima, and the indices of the reflecting planes, found by a graphical method for a tetragonal lattice, are given in Table 1.

Table 1

hkl	I_{exp}	d_{exp}, Å	I_{theor}	d_{theor}, Å	*hkl*	I_{exp}	d_{exp}, Å	I_{theor}	d_{theor}, Å
100	7	3.49	7	3.48	204	0.5	1.164	2	1.167
002	4	3.11	5	3.145	300	2	1.160	0.5	1.160
101	10	3.03	10	3.045	301	0.5	1.140	0.5	1.141
110	1	2.475	4	2.462	115	0.5	1.122	0.5	1.120
102	3	2.320	3	2.332	214	0.5	1.105	0.5	1.106
111	0.5	2.275	6	2.292	302	0.5	1.090	0.1	1.088
003	3	2.100	2	2.096	223	2	1.058	1	1.061
112	3	1.950	0.5	1.938	006	0.5	1.051	0.5	1.048
103	10	1.800	7	1.795	106	0.5	1.005	0.01	1.004
200	5	1.727	7	1.740	215	0.5	0.984	0.5	0.978

hkl	I_{exp}	d_{exp}, Å	I_{theor}	d_{theor}, Å	hkl	I_{exp}	d_{exp}, Å	I_{theor}	d_{theor}, Å
004	3	1.581	2	1.572	224	0.5	0.970	1	0.969
202	0.5	1.520	2	1.523	314	2	0.901	0.5	0.902
211	2	1.497	2	1.511	401	2	0.864	0.1	0.863
114	1	1.312	0.5	1.325	330	0.5	0.817	0.5	0.821
213	1	1.243	3	1.250	403	2	0.807	1	0.804
220	1	1.226	2	1.230	332	0.5	0.791	0.01	0.794
105	2	1.187	0.1	1.183	008	0.5	0.784	0.5	0.785

By calculations using the quadratic formula for the tetragonal system, the lattice constants of the new compound were found: $a = 3.48 \pm 0.01$ Å; $c = 6.29 \pm 0.01$ Å.

The data obtained proved to be close to the constants of the known lattices of compounds of the type $MeAlF_4$. The lattice constants and the radii of the ions of monovalent metals entering into the composition of the corresponding compounds are compared in Table 2.

To establish whether sodium tetrafluoroaluminate ($NaAlF_4$) has the same crystal lattice as the isomorphous compounds with rubidium, thallium, and potassium, schematically shown in Fig. 1, the theoretical values of the intensities of the interference maxima were calculated by the formula:

$$I \sim P \frac{1 + \cos^2 2\vartheta}{\sin^2 \vartheta \cdot \cos \vartheta} \left| \sum_{1}^{n} F_z e^{2\pi i (hx + ky + lz)} \right|^2 ,$$

where P is the multiplicity factor, ϑ is the angle of reflection of the X-rays, F_z are the atomic factors of the elements entering into the crystal lattice, and xyz are the coordinates of the atoms.

Table 2

Compound	Lattice constants, Å	Lattice constants, Å	Radii of univalent ions, according to Goldschmidt, Å
	a	c	
$RbAlF_4$	3.615	6.261	1.49
$TlAlF_4$	3.61	6.37	1.49
NH_4AlF_4	3.587	6.346	–
$KAlF_4$	3.55	6.139	1.33
$NaAlF_4$	3.48	6.29	0.98

Fig. 1

Figure 1: Fig. 1

For the calculations it was assumed that the $NaAlF_4$ lattice belongs to the space group D_{4h}^2–$P4/mmm$.

The parameter z for the two fluorine ions located within the unit cell was taken as equal to 0.21, i.e., the same as in the lattices of isomorphous compounds with potassium, rubidium, and thallium.

The results of the intensity calculations, reduced to a 10-point system, are given in Table 1. Also indicated there for comparison are the theoretically calculated values of the interplanar spacings. The data obtained indicate their satisfactory agreement. On this basis it may be considered that sodium tetrafluoroaluminate ($NaAlF_4$) has the same crystal lattice as the indicated isomorphous compounds.

Na Al F

Fig. 1

It should be noted, however, that there is some difference between individual theoretically calculated intensity values and the experimental ones. This is explained by the superposition, on certain interference maxima of $NaAlF_4$, of individual maxima from chiolite, aluminum fluoride, and, apparently, another unknown compound. It is also possible that the discrepancy in intensity values is caused by distortion of the octahedron formed by six fluorine ions, four of which are located at the centers of the side faces of the tetragonal lattice.

The distortion of the octahedron is evident from the fact that the doubled sum of the radii of the trivalent aluminum ion and the monovalent fluorine ion is 3.80 Å. The crystal-lattice constant a, which represents the distance between the centers of fluorine ions located on opposite faces, is 3.485 Å. The difference between these values (~ 0.3 Å) indicates considerable polarization of the fluorine ion. This increased polarization is due to the smaller radius of the sodium ion (0.98 Å), located at the nodes of the tetragonal lattice, in comparison with the ionic radius of potassium (1.33 Å). It is possible that this is precisely the reason for the instability, under ordinary conditions, of sodium tetrafluoroaluminate in comparison with the other isomorphous compounds.

On the basis of the foregoing, it must be assumed that the compound $LiAlF_4$ should be still less stable, since the radius of the lithium ion is 0.73 Å.

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Note: Figure translations are in progress. See original paper for figures.