



NaAlF₄: Preparation, crystal structure and thermal stability

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ABSTRACT

The compound NaAlF₄ has been obtained in the form of thin fibrous crystals or fine colorless powder by condensation at 18 °C of vapors arising over chiolite Na₅Al₃F₁₄ or NaCaAlF₆, heated up to 800 °C. Thermal stability has been investigated by the methods of thermal analysis and high temperature X-ray diffraction. When heated in air, NaAlF₄ is stable up to 390–400 °C, then there is an exothermal solid state decay into Na₅Al₃F₁₄(s) and AlF₃(s). At higher temperature Na₅Al₃F₁₄(s) decays into Na₃AlF₆(s) and NaAlF₄(g). The crystal structure (space group *Cmcm*, *a*=3.6124(1) Å, *b*=14.9469(7) Å, *c*=5.2617(3) Å, *V*=284.10 Å³) has been determined by X-ray powder diffraction method. In the crystal structure of NaAlF₄ the octahedrons [AlF₆] are joined through vertices and form corrugated layers, sodium ion layers being located between them. The distances between the atoms of Al–F are in the range 1.791–1.814 Å, and those for Na...F are in the range 2.297–2.439 Å. In spite of limited thermal stability of the crystal form, the compound NaAlF₄ is the main component of the gas mixture over solid and molten salts in the ternary system NaF–AlF₃–CaF₂ and participates in chemical transformations between the phases at high temperature.

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0. Introduction

The binary system NaF–AlF₃ is of great importance for aluminum production. Well-established conceptions on the NaF–AlF₃ phase diagram, formulated in Ref. [1], imply at atmospheric pressure the presence of two compounds: cryolite (Na₃AlF₆), melting congruently at 1010 °C and chiolite (Na₅Al₃F₁₄), melting incongruently at 737–739 °C. The same type of the system is also discussed in the last review devoted to this problem [2]. Moreover, many researches report the presence of another compound NaAlF₄ [3–8]. Howard [3] was the first to obtain NaAlF₄ in solid state by condensing the vapor of NaF–AlF₃ mixture. Ginsberg and Wefers [5] established that the compound NaAlF₄ forms when cooled according to the peritectic reaction at 710 °C and decays at 680 °C according to the equation: NaAlF₄(s) → 1/5 Na₅Al₃F₁₄(s) + 2/5 AlF₃(s). Holm et al. repeatedly studied the thermodynamic stability of the solid NaAlF₄ [6,8–10]. Based on the results of the investigation it was concluded that NaAlF₄ is metastable at all temperatures and, therefore, should not be presented as an equilibrium phase in the NaF–AlF₃ phase diagram. Thermodynamic modeling of the binary system was performed in Ref. [11]. The authors came to an unexpected

conclusion that sodium tetrafluoroaluminate (NaAlF₄) is thermodynamically stable above 507 °C, but below this temperature it can exist in the metastable state.

The compound NaAlF₄ manifests itself not only in the binary, but also in ternary systems. When studying high-temperature transformations of the ternary fluorides in the system NaF–AlF₃–CaF₂ we found that mutual transitions between the phases NaCaAlF₆ and Na₂Ca₃Al₂F₁₄ do not go, as one expected, through the addition of CaF₂, but via the reaction with NaAlF₄ [12,13].

The available in literature results which deal with the mass-spectrometric composition determination of vapor over the salt compositions of the NaF–AlF₃ system [14,15] show that the vapor is mainly composed of neutral particles consisting of NaAlF₄ and, to the lower extent, of their dimers (NaAlF₄)₂. Normally, the concentration of ions is 5–8 orders of magnitude lower than the concentration of neutral species. The absence of noticeable quantity of (AlF₃)_n species in the vapor was quite an unexpected result. It is also appropriate to note that there is some evidence concerning the presence of [AlF₄][−]-anions in the molten salts of [MF–AlF₃]-systems [16,17].

The X-ray powder pattern of NaAlF₄, as the evidence of the real presence of the solid state phase was for the first time reported by Howard [3] in 1954 and later by Mashovets et al. [4] in 1957. The most recent data were presented by Holm et al. [6], who obtained almost pure compound and gave an accurate description of the X-ray diffraction pattern (JCPDS-ICCD-PDF file #00-051-1675). Attempts were made to identify the structure in Ref. [4], and in Refs. [6,18] indexing of X-ray patterns was performed and lattice

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parameters suggested. Unfortunately, there is not any agreement in the structural data in literature. The X-ray pattern calculated using the crystal structure data published in Ref. [4], disagrees with the experimental data. It is worth noting that NaAlF_4 synthesis is, as a rule, accompanied by impurities which not only make it difficult to solve the structure, but also give rise to a certain distrust in the little evidence on the chemical composition [3,10].

In the present work attempts have been made to obtain reliable data on the existence, composition and crystal structure of NaAlF_4 . The need for these data is due to the tasks to decrease fluoride salts consumption at electrolysis on one hand, and on the other hand, it is necessary to specify the ternary system ($\text{NaF}-\text{AlF}_3-\text{CaF}_2$), which really describes the electrolyte state in an electrolysis bath when obtaining aluminum. The compound NaAlF_4 was obtained by the decomposition of two different reagents. The thermal stability was studied by thermal analysis, high-temperature X-ray diffraction and quenching method. The crystal structure is determined using X-ray powder diffraction approach.

1. Experimental

The technique of the synthesis of the NaAlF_4 compound was borrowed with small changes from [9]. The chiolite $\text{Na}_5\text{Al}_3\text{F}_{14}$ or

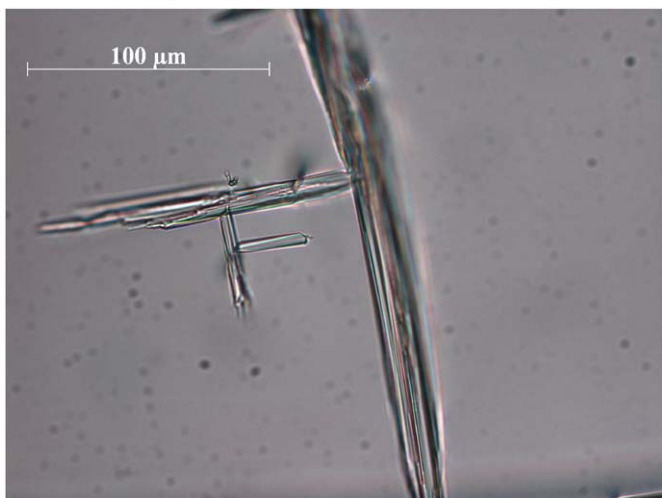


Fig. 1. NaAlF_4 crystals obtained by condensation from the gaseous phase at 18 °C.

sodium calcium aluminum fluoride NaCaAlF_6 was used as the initial material for the synthesis. Both initial materials were previously synthesized from the corresponding fluoride mixtures: NaF , AlF_3 and CaF_2 according to the techniques described in Refs. [12,13]. The chiolite or NaCaAlF_6 was set into a platinum boat-like container located in a horizontal reactor, heated by a tube furnace and blown out by a dry nitrogen flow. The furnace was heated to 800 °C. The gas phase appearing above the sample was transferred by the nitrogen flow to the part of the water-cooled surface 4 cm² in area, where the condensation took place. The temperature of the surface being cooled was maintained at about 18 °C by the water flow. In the condensed substance it is possible to distinguish parts with different morphology: as thin colorless fibers or fine white powder. A separate crystal fiber is presented in Fig. 1.

NaAlF_4 in a mixture with chiolite and AlF_3 was also obtained by the quenching method [19] from the equimolar mixture of NaF and AlF_3 . The sample was loaded in platinum crucible with a lid and heated to 740 °C for half an hour. Then, the temperature in the furnace was adjusted to a certain point in the interval from 670 to 740 °C. The sample was held for another half hour and then the crucible was quickly taken from the furnace and its bottom part was loaded into water at 18 °C. The loss of weight in the course of heating was < 2 mass%.

The chemical composition in the samples was characterized by the atomic ratio of Na/Al/F. In the case of the synthesis from NaCaAlF_6 , calcium was not observed in the sample composition. The measurements were taken by an X-ray fluorescent spectrometer Axios Advanced (PANalytical, Netherland).

The thermal analysis was performed with a thermal analyzer "STA449-QMS403c" ("Netzsch"). The sample weighing 5 mg was loaded into a platinum crucible, heated in the argon flow (30 ml/min) in the temperature range 25–700 °C, at heating rate – 10 °C/min. The DSC and TG curves are given in Fig. 2.

The X-ray powder patterns were scanned using a diffractometer X'pert Pro (PANalytical, Netherland), with Bragg-Brentano geometry, equipped with PIXel and a graphite monochromator. $\text{CuK}\alpha$ radiation was used. The sample was ground in air in an agate mortar and pressed into a silicon cuvette 10 mm in diameter with "nonreflecting" edges. The scan interval was from 10° to 110° and the step 0.026°. High temperature X-ray studies were carried out in air using a high temperature chamber NTK1200N Anton Paar. The sample was prepared in a flat platinum cuvette 10 mm in diameter. The heating rate between the scans was 50 °/min. The X-ray diffraction patterns are given in Figs. 3–5.

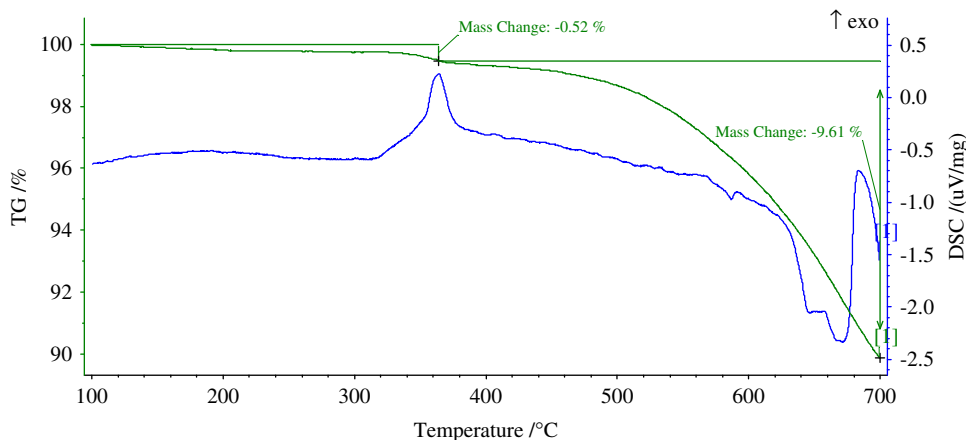


Fig. 2. DSC and TG curves of NaAlF_4 .

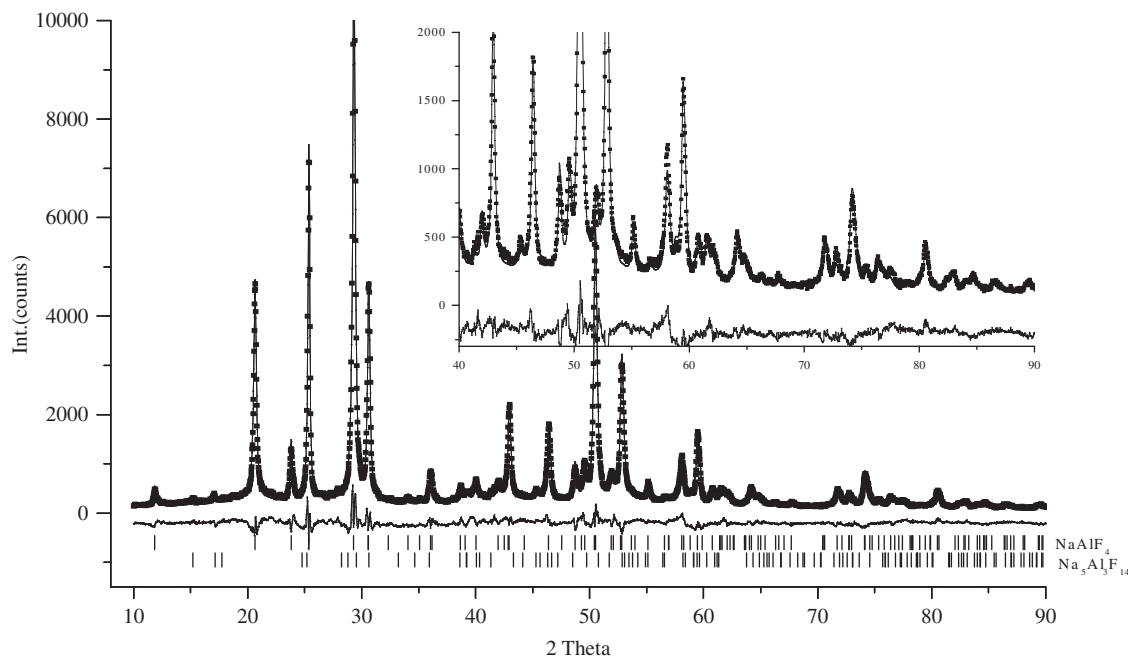


Fig. 3. The comparison of the experimental and calculated X-ray diffraction patterns of NaAlF_4 . $R_{\text{wp}}=10.7\%$, $R_p=8.2\%$, $R_i=6.8\%$. Shown in the insertion is a scaled-up distant area of the XRD pattern. Given below is a line-diagram of NaAlF_4 and $\text{Na}_5\text{Al}_3\text{F}_{14}$ powder patterns.

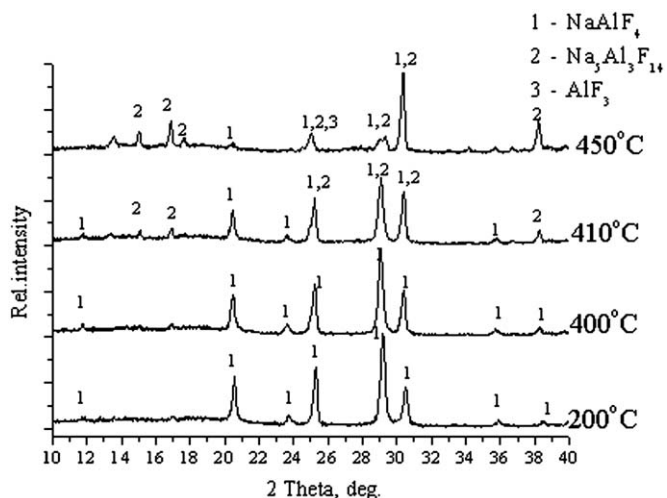


Fig. 4. X-ray powder diffraction patterns of NaAlF_4 heated in X-ray high temperature chamber. The chiolite peaks can be observed distinctly at 410°C in the region from 15° to 18° . Other peaks are not visible due to overlapping with the peaks of NaAlF_4 . On the pattern at 450°C the peak at 13.60° corresponds to beta- AlF_3 .

The lattice parameters were determined using the software Ito, Powder [20,21]. The space group $Cmcm$ (63) was defined according to the regular reflection absence and the result of the final structure refinement. The crystal structure was solved by direct methods from the X-ray powder diffraction data using the software EXPO [22], and the structure was refined by Rietveld method [23] using DBWS program [24]. When refining the structure a small amount of chiolite presented in the condensed substance was taken into account. Given in Fig. 3 are the experimental and calculated X-ray diffraction patterns corresponding to the final crystal structure data. The crystal structure is presented in Fig. 6.

2. Results and discussion

The substance sublimed from the gaseous phase is a mixture of colorless fibrous and prismatic crystals (Fig. 1), which, when ground, give white soft cloddy crystalline powder, stable in normal conditions in air. Small prismatic crystals form the first layer on the coldest part of the surface being cooled. The fibrous crystals start the formation over the powder layer, likely, due to the creation of more favorable conditions. The presence of crystals of considerable sizes indicates the possibility of external conditions in which the equilibrium between the solid and the gaseous phases is established. The hydrolysis of the substance due the contact with the humid air was not observed. In spite of different morphology the crystals are the same crystalline phase. The X-ray powder pattern of the substance (Fig. 3) obtained has almost perfect correspondence to the data obtained by Holm et al. [6]. It is worth noting that, as in Ref. [6], the presence of a small amount of chiolite was observed. The synthesis result was almost not influenced by the type of the initial substance: $\text{Na}_5\text{Al}_3\text{F}_{14}$ or NaCaAlF_6 . The composition of NaAlF_4 , estimated at the final stage of the structure refinement using the Rietveld method indicates that the main phase NaAlF_4 is present in the amount of 95.4 mass%, and the admixture $\text{Na}_5\text{Al}_3\text{F}_{14}$ is in the amount of 4.6 mass%. The X-ray analysis of the condensed phase composition gives the following ratio of chemical elements in mass%: $\text{Na}:\text{Al}:\text{F}=19.4:25.9:54.2$, which is rather close to the atom ratio 1:1:4. The X-ray analysis of the substance remained in the initial container revealed the presence of the mixture Na_3AlF_6 and $\text{Na}_5\text{Al}_3\text{F}_{14}$ or the mixture of NaCaAlF_6 and CaF_2 in it. It allows one to assume that the formation of NaAlF_4 goes due to the decay according to one of the reactions: $\text{Na}_5\text{Al}_3\text{F}_{14}(\text{s}) \rightarrow \text{Na}_3\text{AlF}_6(\text{s}) + 2\text{NaAlF}_4(\text{g})$ or $\text{NaCaAlF}_6(\text{s}) \rightarrow \text{CaF}_2(\text{s}) + \text{NaAlF}_4(\text{g})$, and the subsequent condensation: $\text{NaAlF}_4(\text{g}) \rightarrow \text{NaAlF}_4(\text{s})$.

The thermal stability of $\text{NaAlF}_4(\text{s})$ was studied using two methods. On the DSC curve (Fig. 2) at $T=390^\circ\text{C}$ there is an exo-effect without the weight change after which there occurs a considerable weight loss in the sample. By the method of high temperature X-ray diffraction at 400°C the solid state decay of NaAlF_4 into $\text{Na}_5\text{Al}_3\text{F}_{14}(\text{s})$ and $\text{AlF}_3(\text{s})$ was confirmed. In Fig. 4 there

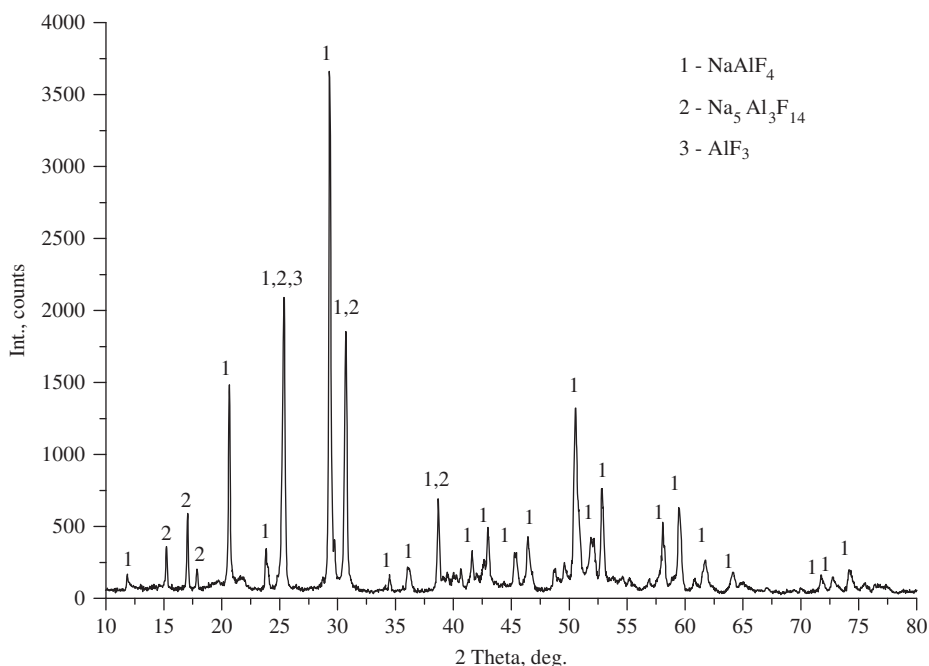


Fig. 5. The X-ray diffraction patterns of the sample quenched from 780 °C. The phases NaAlF₄, Na₅Al₃F₁₄ and AlF₃ are presented.

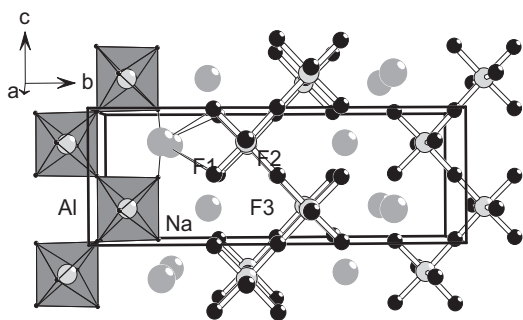


Fig. 6. Crystal structure of NaAlF₄.

are X-ray diffraction patterns corresponding to the NaAlF₄(s) transformation stages. Unfortunately, due to the drastic line overlapping, it was not possible to identify some additional lines appeared at X-ray diffraction pattern of the cooled sample. It is known that AlF₃ has several temperature modifications [25–27], however, none of the forms explains the additional lines at X-ray patterns. It is assumed that the lines were responsible for the products of the material hydrolysis which were already observed in the course of experiments in air [5]. The thermal analysis and X-ray diffraction data obtained in combination allow one to interpret the solid state decay of NaAlF₄(s) as a relaxation process excluding an equilibrium setting. The weight loss observed after the decay of NaAlF₄(s) corresponds to the chiolite decay process. According to the high-temperature X-ray diffraction, the chiolite formed is gradually transformed into cryolite with the formation of the gaseous phase, with its composition corresponding to NaAlF₄(g) [14,15].

The compound NaAlF₄(s) is metastable at a temperature lower 400 °C. In the literature there is apparent evidence that NaAlF₄(s) can exist at temperatures higher than 500 °C [5,7,17], however, doubts still prevail to include it into the equilibrium phase diagram [2,6,17]. To ensure the possibility to obtain NaAlF₄ not only from the gaseous phase but also from liquid or by a solid

state chemical process, some experiments described in literature [5,17] have been repeated using the quenching method with some insignificant alterations. The experiments conducted had similar results obtained in Ref. [17]. The samples which were quenched from the temperature higher than 690 °C presented crystallized melt which consisted of NaAlF₄(s), Na₅Al₃F₁₄(s) and AlF₃(s) (Fig. 5). The pure compound NaAlF₄(s) was never obtained. The incongruent melting of NaAlF₄(s) at about 730 °C is the most probable case because of low content of Na₅Al₃F₁₄(s) and AlF₃(s) in the melt after quenching from temperature higher than 740 °C. On contrary, at a temperature lower than 730 °C Na₅Al₃F₁₄(s) and AlF₃(s) prevailed over NaAlF₄(s). These data also evidence in equilibrium relation between the presented phases. It convinces one of the possibility to synthesize NaAlF₄(s) from condensed components of the system and makes one consider NaAlF₄ as a part of the system. Unfortunately, there are some difficulties to observe the discussed phase relations using high temperature X-ray diffraction because of the intensive gaseous phase formation and deformation of a sample surface at pre-melting conditions.

The crystal structure established is presented in Fig. 6. The structure is in good agreement with the X-ray diffraction data (Fig. 3) and completely corresponds to the composition of NaAlF₄. The specific density is close to the cryolite density (2.952 g/cm³). Atomic coordinates and other structure data of NaAlF₄ are in Table 1. Some additional details on the X-ray data and structure can be found in Ref. [28].

The main structure building unit is an octahedral anion [AlF₂F_{4/2}] with (Al–F) distances in the range of 1.791–1.814 Å. The angles between the (Al–F) bonds are close to 90°. The angle formed by the unshared fluoride atoms is equal to 89.54°. The opposite (F–Al–F) angle in the equatorial plane of the octahedron [AlF₂F_{4/2}] is equal to 92.94° indicating repulsion between the positively charged cations. The octahedrons [AlF₂F_{4/2}] form negatively charged zigzag layers parallel to the plane (ac), joined between each other in a layer by four vertices. Two free vertices are directed into the interlayer space in which sodium cations are located. Each sodium has six nearest neighbors (fluorides) located

Table 1
Crystallographic data of NaAlF₄.

(a) Crystal data					
Crystal system				Orthorhombic	
Space group				<i>Cmcm</i> (no. 63)	
Unit cell dimensions				<i>a</i> = 3.6124(1) Å <i>b</i> = 14.9469(7) Å <i>c</i> = 5.2617(3) Å	
Cell volume				284.10(2) Å ³	
Z				4	
Density, calculated				2.945 g/cm ³	
(b) Atomic coordinates and isotropic displacement parameters (in Å ²)					
Atom	Wyck. Pos.	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{iso}
Al	4c	1/2	0.0836(2)	1/4	0.020(2)
Na	4c	0	0.1917(2)	3/4	0.021(2)
F1	8f	1/2	0.1691(1)	0.0115(5)	0.028(2)
F2	4c	0	0.0820(4)	1/4	0.025(2)
F3	4b	1/2	0	0	0.030(2)
(c) Selected distances (in Å) and angles (°).					
Al–F1		1.791(3)		Na–F1 ⁱ	2.430(3)
Al–F2		1.806(0)		Na–F1 ⁱⁱ	2.296(2)
Al–F3		1.814(2)		Al–Na ⁱⁱⁱ	3.359(4)
F1–Al–F1 ⁱⁱ		89.54(1)		F1–Al–F3	89.05(8)
F3–Al–F3 ^{iv}		92.94(0)		F3–Al–F2 ^v	89.48(0)
F1–Al–F2 ^v		90.54(0)			

Symmetry codes: (i) $-0.5+x, 0.5-y, 1-z$; (ii) $-x, y, 0.5-z$; (iii) $0.5-x, 0.5-y, -0.5+z$; (iv) $1-x, -y, 0.5+z$; (v) $1+x, y, z$.

according to the prismatic type. The distances (Na–F) are in the range of 2.297–2.439 Å.

The structure of NaAlF₄ is isotypic to BaMgH₄ and BaMgF₄ [29,30] and different from the structures of the known chemical analogs—KAlF₄ [31–33] and NH₄AlF₄ [34,35] by the anion sublattice structure. In different KAlF₄ polymorphs the octahedrons [AlF₆] form a layer with the width of one octahedron, with the opposite octahedron vertices being the unshared ones. In NaAlF₄ a layer is build of octahedrons located in the checkerboard order creating almost double width of the layer. The unshared vertices are the nearest vertices turned into the interlayer space. The cation and anion sublattice structures in the line Na₂AlF₆, Na₅Al₃F₁₄, NaAlF₄ have also some difference due to different numbers of the unshared vertices. However, the most pronounced differences are present in the structural blocks of solid and gaseous phases of NaAlF₄ itself since in the gaseous phase aluminum cannot have octahedron environment due to the lack of atoms in the molecule. Probably, this difference makes these phases different chemical compounds.

The structural results obtained allow one arguing about the real existence of the compound NaAlF₄ with orthorhombic lattice. The formation of stretched crystals indicates equilibrium conditions for its development. The area of the thermodynamic stability lies likely between 690 and 730 °C, where the compound can be synthesized from the condensed components of the system. A rather short temperature interval of stability, borders with the liquid part of the system make the compound difficult to observe, like a phantom, playing, by the way, an important part in melting process. Reviewing the phase diagram of the system NaF–AlF₃ and considering the presence of the additional compound NaAlF₄ allow one to understand equilibriums which are responsible for the most low-melting part of the system. This part also plays a large role in melt and gaseous phase formation. Another basic significance of NaAlF₄ existence is an opportunity of isolating the quasi-binary system CaF₂–NaAlF₄ in the ternary system CaF₂–NaF–AlF₃ and the possibility of explaining the thermal transfor-

mations of ternary fluoride crystal phases present in electrolytes in aluminum industry.

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