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# Phase transitions in K<sub>3</sub>AlF<sub>6</sub>

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#### Abstract

Phase transitions in the elpasolite-type K<sub>3</sub>AlF<sub>6</sub> complex fluoride were investigated using differential scanning calorimetry, electron diffraction and X-ray powder diffraction. Three phase transitions were identified with critical temperatures  $T_1 = 132$  °C,  $T_2 = 153$  °C and  $T_3 = 306$  °C. The  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> phase is stable below  $T_1$  and crystallizes in a monoclinic unit cell with a = 18.8588(2)Å, b = 34.0278(2)Å, c = 18.9231(1)Å,  $\beta = 90.453(1)$ ° ( $\mathbf{a} = 2\mathbf{a}_c - \mathbf{c}_c$ ,  $\mathbf{b} = 4\mathbf{b}_c$ ,  $\mathbf{c} = \mathbf{a}_c + 2\mathbf{c}_c$ ;  $\mathbf{a}_c$ ,  $\mathbf{b}_c$ ,  $\mathbf{c}_c$ —the basic lattice vectors of the face-centered cubic elpasolite structure) and space group I2/a or Ia. The intermediate  $\beta$  phase exists only in very narrow temperature interval between  $T_1$  and  $T_2$ . The  $\gamma$  polymorph is stable in the  $T_2 < T < T_3$  temperature range and has an orthorhombic unit cell with a = 36.1229(6)Å, b = 17.1114(3)Å, c = 12.0502(3)Å ( $\mathbf{a} = 3\mathbf{a}_c - 3\mathbf{c}_c$ ,  $\mathbf{b} = 2\mathbf{b}_c$ ,  $\mathbf{c} = \mathbf{a}_c + \mathbf{c}_c$ ) at 250 °C and space group *Fddd*. Above  $T_3$  the cubic  $\delta$  polymorph forms with  $a_c = 8.5786(4)$ Å at 400 °C and space group  $Fm\bar{3}m$ . The similarity between the K<sub>3</sub>AlF<sub>6</sub> and K<sub>3</sub>MoO<sub>3</sub>F<sub>3</sub> compounds is discussed.

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### 1. Introduction

Many fluorides, oxyfluorides and oxides with the general A<sub>2</sub>BB'X<sub>6</sub> composition are known to crystallize in the elpasolite (K<sub>2</sub>NaAlF<sub>6</sub>) (or ordered double perovskite) structure. The parent structure of these compounds can be easily derived from the perovskite structure type by ordering the octahedrally coordinated B and B' cations over the B-sublattice in a chess-board manner reminiscent of the atomic arrangement in the rock salt structure (Fig. 1). According to Anderson et al. [1], such ordering is driven by charge and size differences between the B and B' cations. The pecularities of the preparation techniques, crystal chemistry and phase transitions in these compounds are described in several comprehensive reviews [1-3]. However, only limited information is available on K<sub>3</sub>AlF<sub>6</sub> being compared with its closest analogues cryolite Na<sub>3</sub>AlF<sub>6</sub> and elpasolite K<sub>2</sub>NaAlF<sub>6</sub>. It has been reported that the room temperature form of K<sub>3</sub>AlF<sub>6</sub> has a tetragonally distorted elpasolite-type structure, which transforms into the high symmetry cubic phase above 300–310 °C [4,5]. Jenssen reported two phase transitions at 131 °C from the tetragonal to an orthorhombic phase and at 318 °C from the orthorhombic to the cubic phase [6]. No structural characterization is available, however. Nevertheless, this compound deserves particular attention, not only as an important representative of a wide structural family, but also as a compound of high technological importance. Due to increasing ecological demands to the aluminum production using high-temperature electrolysis of cryolite-alumina melt, alternative technologies based on modified melts with lower melting point are widely discussed. K<sub>3</sub>AlF<sub>6</sub> is considered as one of the basic components of the melts for low-temperature electrolysis in aluminum smelting [7]. A precise knowledge of the cell dimensions of all melt constituents is necessary to analyze the frozen melt using X-ray powder diffraction. We discovered that the room temperature X-ray powder diffraction pattern of K<sub>3</sub>AlF<sub>6</sub> cannot be fully interpreted

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Fig. 1. The crystal structure of the  $A_2BB'X_6$  elpasolite. Larger B cations are situated at the centers of the grey octahedra, the smaller  $B'X_6$  octahedra are darker shaded. The A cations are shown as spheres.

with the tetragonal unit cell proposed by Steward et al. [5]. This inspired us to undertake a more detailed investigation of this compound at different temperatures. In this contribution we report a sequence of phase transitions in  $K_3AlF_6$  along with the data on unit cell dimensions and space symmetry of three major polymorphs.

# 2. Experimental

Samples of  $K_3AlF_6$  were prepared from anhydrous  $AlF_3$  ("Reakhim", "pure" purity grade) and KF. The raw  $AlF_3$  was additionally annealed at 300 °C for 12h to remove possible traces of absorbed water. According to Xu et al. [8] such thermal treatment allows to avoid pyrohydrolisis. Anhydrous KF was prepared by a dehydration of KF · 2H<sub>2</sub>O ("Reakhim", "pure for analysis" purity grade) at 500 °C. The purity of the initial materials was confirmed using X-ray powder diffraction. A sample with an overall mass of 60 g and a KF:AlF<sub>3</sub> = 3.1:1 ratio was prepared in a glove box, placed in a closed graphite crucible, melted at 1000 °C for 1.5 h and cooled down to room temperature with 100 °C/h cooling rate. The crystallized melt was crushed and the excess of KF was removed by washing with distilled water.

Phase analysis and cell parameter determination at room temperature were performed using X-ray powder diffraction (XRPD) with a Huber G670 Guinier diffractometer (Cu $K\alpha_1$ -radiation, image plate detector) and a STADI-P diffractometer (Cu $K\alpha_1$ -radiation, curved Ge monochromator, transmission mode, linear PSD). High-temperature XRD patterns were obtained with a SIEMENS D500 powder diffractometer (Cu $K\alpha$  radiation, reflection mode) equipped with a BRAUN position-sensitive detector. The JANA2000 program package was used for the refinement of the lattice parameters by Le Bail fitting [9]. Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were performed on a NETZSCH STA 409 thermoanalyzer in the temperature range from 20 to 800 °C with heating/cooling rates of 10 °C/min.

Electron diffraction (ED) investigation was made on a crushed  $K_3AlF_6$  sample deposited on holey carbon grids. ED patterns in the temperature range from room temperature to 350 °C were obtained in a Philips CM20 electron microscope equipped with a double-tilt heating holder.

## 3. Results

The TG curve in the temperature range from 20 to 800 °C (Fig. 2, top) does not show any feature, confirming the constant chemical composition of the sample over the entire temperature range. The heating DSC curve exhibits three well pronounced peaks (Fig. 2, top) at  $T_1 = 132 \,^{\circ}\text{C}$ ,  $T_2 = 153 \,^{\circ}\text{C}$  and  $T_3 = 306 \,^{\circ}\text{C}$ . The sharpness of the peaks allows to attribute them to first-order phase transitions. The transition temperature  $T_3 = 306$  °C coincides well with the temperature of the polymorphic transformation  $(310 \degree C)$  in K<sub>3</sub>AlF<sub>6</sub> measured by K. Grojtheim et al. [4]. Steward et al. [5] reported that the cubic  $K_3AlF_6$  phase exists above 300 °C and transforms into a tetragonal phase on cooling, but Jenssen [6] observed a transition between an orthorhombic and the cubic polymorph at 318 °C. According to Jenssen [6], the critical temperature  $T_1$ corresponds to the tetragonal  $\leftrightarrow$  orthorhombic phase transition. The critical temperature  $T_3$  coincides on heating and cooling curves (Fig. 2, bottom), whereas the two transitions at 132 and 153 °C produce a single peak at 129 °C on the cooling DCS curve due to a noticeable hysteresis. This thermal behavior was reproduced in several heating and cooling cycles, indicating the reversibility of the phase transitions. One can therefore expect the existence of four K<sub>3</sub>AlF<sub>6</sub> polymorphs in the studied temperature interval: the  $\alpha$  polymorph is stable at room temperature, the intermediate  $\beta$  polymorph only exists in a very narrow temperature interval between 132 and 153 °C, the  $\gamma$  polymorph between 153 °C and 306 °C and the hightemperature  $\delta$  polymorph, that is stable above 306 °C.

In order to determine the crystallographic characteristics of  $K_3AlF_6$  at different temperatures an electron diffraction investigation was undertaken. The most prominent ED patterns of the room temperature  $\alpha$  phase are shown in Fig. 3. The brighter spots can be attributed to the elpasolite sublattice; they can be indexed on a face centered cubic lattice with  $a \approx 8.5$  Å. Weaker spots are the superlattice reflections. Breaking the crystal symmetry at a phase transition introduces numerous orientational variants due to the loss of rotation axes and mirror planes [10], and many investigated crystals were found to be highly twinned. Nevertheless, single domain areas were also observed, and the ED patterns on Fig. 3 were taken from crystallites free from twinning. The superlattice reflections



Fig. 2. TG and DSC curves for K<sub>3</sub>AlF<sub>6</sub>.

can be indexed on a body-centered tetragonal lattice with unit cell parameters  $a \approx 18.9$  Å,  $c \approx 34.0$  Å. However, the precision of the electron diffraction technique allowed to detect deviations from the tetragonal symmetry: the a/bratio was found to be ~0.996 and  $\beta^* \approx 89.55^\circ$ . Further interpretation of the XRPD pattern of the room temperature phase (see Fig. 8, bottom) supports decreasing symmetry down to monoclinic. According to that, the indexation on Fig. 3 is consistently done with a monoclinic unit cell with  $a \approx 18.9$  Å,  $b \approx 34.0$  Å,  $c \approx 18.9$  Å,  $\beta \approx 89.6^{\circ}$ . The reflection conditions for a body-centered lattice (hkl, h + k + l = 2n) and a glide plane perpendicular to the b axis (h0l, h, l = 2n) were clearly obeyed, resulting in the possible space groups I2/a and Ia (non-standard settings of the space groups C2/c (No. 15) and Cc (No. 9), respectively). The transformation matrix from the cubic elpasolite subcell with  $a \approx 8.5$  Å to the monoclinic supercell is given as

$$\begin{pmatrix} 2 & 0 & -1 \\ 0 & 4 & 0 \\ 1 & 0 & 2 \end{pmatrix}.$$

Various slow heating rates (5 and  $10 \,^{\circ}\text{C/min}$ ) were applied in order to observe the  $\beta$  polymorph, which exists only in a very narrow temperature range. However, a precise temperature control while heating in the electron microscope is difficult due to the additional heating by the electron beam, and only the direct  $\alpha \rightarrow \gamma$  transformation was observed. The ED patterns of  $\gamma$ -K<sub>3</sub>AlF<sub>6</sub> taken in the temperature range 200-250 °C are shown in Fig. 4. As for  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub>, the elpasolite sublattice can easily be identified by the brighter basic spots. A complete indexation of the ED patterns was performed on the base of a face-centered orthorhombic lattice with unit cell parameters  $a \approx 36.1$  Å,  $b \approx 17.1 \text{ Å}, c \approx 12.04 \text{ Å}.$  The reflection conditions 0kl, k + l = 4n, h0l, h + l = 4n, hk0, h + k = 4n allow to chose the space group *Fddd*. Very weak reflections which do not obey the reflection conditions imposed by d glide planes can be observed on the [203]\* and [101]\* ED patterns. They appear due to multiple diffraction since these forbidden reflections do not show up in the [010]\* and [001]\* ED patterns. The transformation matrix from the cubic elpasolite subcell with  $a \approx 8.5 \text{ \AA}$  to the orthorhombic supercell is given as

$$\begin{pmatrix} 3 & 0 & 3 \\ 0 & 2 & 0 \\ 1 & 0 & -1 \end{pmatrix}.$$

Heating the sample above  $T_3$  makes the compound extremely unstable under the incident electron beam. Nevertheless, the observation of the behavior of the superlattice reflections on going across the third phase



Fig. 3. Electron diffraction patterns of  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub>. The *hkl*<sub>c</sub> indexes belong to the parent cubic face-centered elpasolite structure.

transition was performed. Fig. 5 shows the ED pattern taken from a crystallite of the  $\gamma$ -K<sub>3</sub>AlF<sub>6</sub> at 220 °C along the [203]\* zone axis. Upon heating up to 340 °C the superlattice spots disappear completely resulting in the [001]\* ED pattern of the  $\delta$  polymorph, which has a face-centered cubic elpasolite-type structure with  $a \approx 8.55$  Å. Being cooled down to 275 °C the  $\gamma$  polymorph is completely restored, but now in the [010]\* orientation. Also the reversibility of the  $\alpha \leftrightarrow \gamma$  phase transition was observed by heating and cooling the sample inside the electron microscope, but the  $\gamma \rightarrow \alpha$  transformation on cooling

unavoidably results in strongly twinned crystallites. This is depicted in Fig. 6. An ED pattern from a crystallite of the  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> polymorph at room temperature along the [010]\* zone axis is shown at the top of the figure. Upon heating up to 175 °C the  $\alpha \rightarrow \gamma$  transformation takes place resulting in the [010]\* ED pattern of the  $\gamma$  polymorph. On cooling down again to 25 °C the single domain is not recovered and a twinned structure with two [010]\* orientational variants of the  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> phase is formed. Twinned structures are also observed for the  $\gamma$ -K<sub>3</sub>AlF<sub>6</sub> phase. In



Fig. 4. Electron diffraction patterns of  $\gamma$ -K<sub>3</sub>AlF<sub>6</sub>. The *hkl*<sub>c</sub> indexes belong to the parent cubic face-centered elpasolite structure.

Fig. 7 an ED pattern is shown with four orientational variants of the  $\gamma$ -K<sub>3</sub>AlF<sub>6</sub> polymorph.

Due to the instability of the sample under the focused electron beam, required for recording high resolution electron microscopy images, no investigation of the atomic and defect structure in real space has been successful.

The unit cells derived from the ED data were further used for indexation of the XRPD patterns. The XRPD patterns of the  $\alpha$ ,  $\gamma$  and  $\delta$  phases are shown in Fig. 8. The superlattice reflections and splitting of the basic reflections due to the pseudotetragonal unit cell are clearly visible on the pattern of the  $\alpha$  phase (the indices of the sublattice reflections can be revealed when comparing with the XRPD pattern of the  $\delta$  phase (top in Fig. 8)). On the XRPD pattern of the  $\gamma$  phase the superlattice reflections change their position and intensity. Both the superlattice reflections and splitting of the peaks of the basic structure disappear on the XRPD pattern of the  $\delta$  polymorph. The sublattice reflections on the XRPD pattern of the  $\alpha$  phase were indexed on a tetragonal *F*-centered lattice with a = 8.427(1)Å, c = 8.497(1)Å, in agreement with the unit cell reported by Steward et al. [5]. Due to the very large unit



Fig. 5. Transformation of the [203]\* ED pattern of the  $\gamma$  phase into the [010]\* ED pattern of the  $\delta$  phase upon heating above T<sub>3</sub> and back to the [010]\* pattern of the  $\gamma$  phase on cooling.

cell volume (>12,000 Å<sup>3</sup>) of the superlattice for  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> and the large amount of overlapping reflections, the final refinement of the unit cell parameters was performed using Le Bail fitting procedure. The Le Bail fit was performed using a monoclinic unit cell with *I*2/*a* space symmetry, according to the results of the electron diffraction observations and obvious analogy with the superlattice observed recently in K<sub>3</sub>MoO<sub>3</sub>F<sub>3</sub> [11] (see also Section 4 below). The refinement resulted in the unit cell parameters a = 18.8588(2)Å, b = 34.0278(2)Å, c = 18.9231(1)Å,  $\beta = 90.453(1)^{\circ}$ . For the  $\gamma$  polymorph the Le Bail fitting



Fig. 6.  $\alpha \leftrightarrow \gamma$  transformations by heating and cooling a K<sub>3</sub>AlF<sub>6</sub> crystallite inside the electron microscope. From the top to the bottom: [010]\* ED pattern of  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> at room temperature, [010]\* ED pattern of the  $\gamma$ polymorph at 175 °C, twinned [010]\* type zone axis ED pattern of the  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> at 25 °C and schematic representation of the twinning structure. Black circles indicate the elpasoite sublattice reflections and black and open squares mark the two different [010]\* orientations of the superlattice reflections, respectively.



Fig. 7. ED pattern with four orientational twinned variants of the  $\gamma$ -K<sub>3</sub>AlF<sub>6</sub> polymorph. Black circles indicate the sublattice reflections, while black and open squares and black and open triangles mark the superlattice reflections of the two different [010]\* and [203]\* orientations, respectively.

was performed with the orthorhombic *Fddd* unit cell. The refined values of the lattice parameters are a = 36.1229(6)Å, b = 17.1114(3)Å, c = 12.0502(3)Å at 250 °C. The XRPD pattern of the  $\delta$  phase was indexed on a face-centered cubic lattice with a = 8.5786(4)Å at 400 °C and space group  $Fm\bar{3}m$ .

Unfortunately, the extremely large unit cell volumes for  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> (12144 Å<sup>3</sup>) and  $\gamma$ -K<sub>3</sub>AlF<sub>6</sub> (7448 Å<sup>3</sup>) together with the low symmetry make it impossible to determine and refine these structures from X-ray powder diffraction data. It is hardly possible to expect that single crystals of these phases with a quality suitable for structure determination will be prepared because of the unavoidable twinning due to the phase transitions. Further progress in understanding

the mechanisms of the structural distortions behind these phase transitions could possibly be obtained using a synchrotron X-ray source, providing XRPD patterns with an ultimate resolution, which can play key role in the structure solution.

#### 4. Discussion

The  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> superstructure is identical to that found in the room temperature polymorph of  $K_3MoO_3F_3$  [11]. However, in addition to the sharp superlattice spots, a highly structured three-dimensional continuous diffuse intensity is present on the ED patterns of K<sub>3</sub>MoO<sub>3</sub>F<sub>3</sub>. Withers et al. suggested that the diffuse intensity originates from the O/F ordering in  $K_3MoO_3F_3$ , whereas the sharp superlattice spots have a displacive, rather than a diffusion controlled origin [12]. In our experiments on K<sub>3</sub>AlF<sub>6</sub> we never observed structured diffuse intensity, which is in agreement with the presence of only one type of anion in the structure. The obvious similarity between the superstructures in  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> and K<sub>3</sub>MoO<sub>3</sub>F<sub>3</sub> leads to the assumption about an identical mechanism of structural distortions resulting in breaking down the cubic symmetry of the parent elpasolite-type structure. It is hardly possible to expect that the phase transitions in  $K_3AlF_6$  occur due to diffusion process, for example due to re-distribution of the K and Al atoms over the octahedral sites, because fast atomic long range motion at the temperatures of 132-306 °C seems to be highly unlikely. One must assume that the phase transitions in  $K_3AlF_6$ have a displacive character. The most common origin of displacive phase transitions in the elpasolite-like fluorides and oxyfluorides, as well as in the double perovskites  $A_2BB'(O,F)_6$ , are cooperative tilts and rotations of the  $B(O,F)_6$  and  $B'(O,F)_6$  octahedra in order to optimize the coordination environment for the A-cations, if they are too small to be placed into 12-coordinated cavities of the parent cubic  $Fm\bar{3}m$  structure. Group theory analysis performed for such distortions by Howard et al. [2] and Flerov et al. [3] revealed the unit cell expansions and space symmetries for all possible tilt systems, originally derived by Glazer [13]. The superstructures observed in K<sub>3</sub>AlF<sub>6</sub> and K<sub>3</sub>MoO<sub>3</sub>F<sub>3</sub> are not among these possibilities. However the tilt systems and corresponding symmetries were derived assuming that both the  $B(O,F)_6$ and  $B'(O,F)_6$  octahedra behave as rigid units. As proposed by Withers et al, this is not necessarily true for the  $KF_6$  octahedra [12]. In this case a rotation of the AlF<sub>6</sub> octahedra acquires additional degrees of freedom that can result in much more complicated structural distortions, which can be combined with the off-center displacements of the B-cations creating puzzling superstructures. A structure solution for the low temperature K<sub>3</sub>AlF<sub>6</sub> and K<sub>3</sub>MoO<sub>3</sub>F<sub>3</sub> phases is needed to make an unambiguous conclusion about the mechanism of the phase transitions.



Fig. 8. Parts of the X-ray powder diffraction patterns of  $\alpha$ -K<sub>3</sub>AlF<sub>6</sub> (RT),  $\gamma$ -K<sub>3</sub>AlF<sub>6</sub> (250 °C) and  $\delta$ -K<sub>3</sub>AlF<sub>6</sub> (400 °C).

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