Phase Transitions and Structure of the High-Temperature Phases of some Compounds of the Cryolite Family

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Complex compounds of composition M_3AlF_6 can be made by fusing alkali fluorides and aluminium fluoride in the proportion 3:1. For these compounds, only the crystal structure of the well known mineral cryolite, Na_3AlF_6, has been completely determined (Naray-Szabo and Sasvari [1]). Cryolite is monoclinic, belonging to the space group $P2_1/m$. It is also known that Na_3AlF_6 has a phase transition from the low-symmetry to a high-symmetry structure at 560°C. Different works (Steward and Rooksby,[2] Holm [3]) show that the structure becomes strictly isomorphous with the $(NH_4)_3AlF_6$ structure (space group $Fm3m-O_h^5$) at this temperature.

Brosset [4] has determined the unit cell dimensions of K_3AlF_6 from powder photograph data. The unit cell is assumed to be tetragonal body-centered with $a = 5.94$ Å and $c = 8.47$ Å. High temperature study of K_3AlF_6 by Steward and Rooksby [2] shows that the tetragonal deformation is reduced at higher temperatures. At 300°C the structure becomes cubic with a cell constant $a_0 = 8.56$ Å.

In the present work the three compounds K_3AlF_6, Rb_3AlF_6, and Cs_3AlF_6 have been examined by differential thermal analysis (DTA) and X-ray diffraction analysis. The three DTA diagrams obtained by cooling are given in Fig. 1. The diagram for K_3AlF_6 contains two exothermic peaks, one at 143°C and one at 327°C, while the two other diagrams contain one

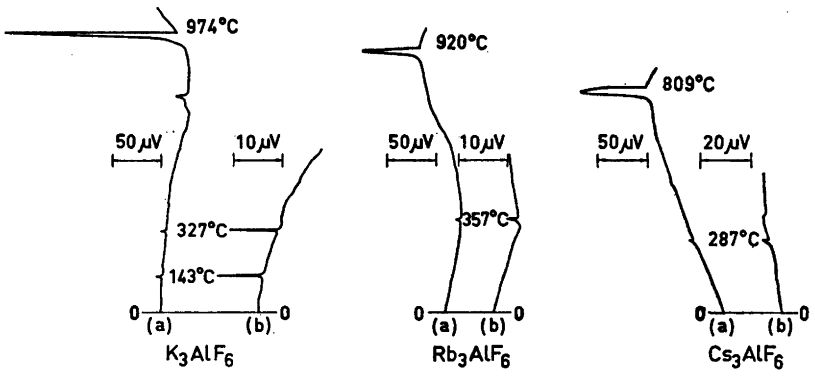

Fig. 1. DTA cooling curves for K_3AlF_6, Rb_3AlF_6, and Cs_3AlF_6.

Table 1. Phase transitions of M_3AlF_6 compounds.

Compound	Structure of low temperature modification	Phase transition temperature	Structure of high temperature modification
Na_3AlF_6	monoclinic	560°C	cubic
K_3AlF_6	tetragonal	(I) 143°C (II) 327°C	»
Rb_3AlF_6	»	357°C	»
Cs_3AlF_6	»	287°C	»

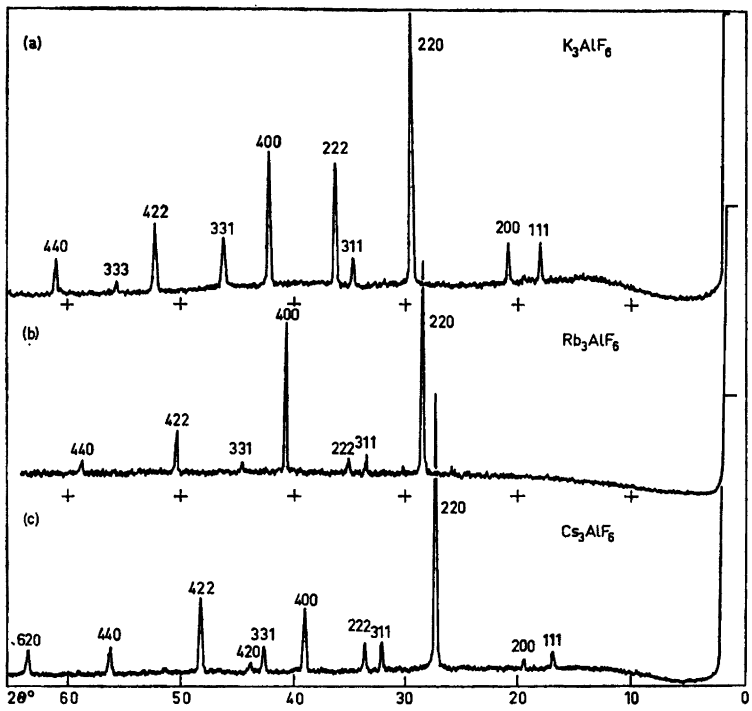

Fig. 2. X-Ray diffraction diagrams for the cubic high-temperature modification of a) K_3AlF_6; b) Rb_3AlF_6; c) Cs_3AlF_6.

Table 2. Lattice parameters from the present work.

Compound	Low temperature modification		High temperature modification	Densities g/cm³	
	a Å	*c* Å	a_0 in Å at 400°C	obs.	calc.
K_3AlF_6	5.95	8.48	8.55	2.80	2.86
Rb_3AlF_6	6.19	8.84	8.88	3.83	3.90
Cs_3AlF_6	6.52	9.17	9.24	4.52	4.59

peak, one at 357°C for Rb_3AlF_6 and one at 287°C for Cs_3AlF_6.

Preliminary powder X-ray investigations of the three compounds at room temperature indicates that they all have tetragonal symmetry. Unit cell dimensions from the present observations are given in Table 2. If the tetragonal cell is assumed to contain 2 formula units of M_3AlF_6, the calculated densities of the three compounds agree well with the observed values.

The X-ray diffraction diagrams at 400°C given in Fig. 2, show that phase transitions from a low temperature symmetry to a

high temperature symmetry have taken place. The unit cells of the high temperature modifications are all assumed to be face-centered cubic. The lattice parameters are given in Table 2.

A preliminary study of the second modification of K_3AlF_6 (143°C–327°C) indicates that the structure is still tetragonal.

Experimental. The compounds were prepared by fusing aluminium fluoride and the respective alkali fluoride in a mole proportion 1:3. The aluminium fluoride was prepared by vacuum sublimation of anhydrous AlF_3 (A. D. Mackay, Inc., U.S.A.). The method has been described in detail by Rolin.[5] The other chemicals used were commercially available reagent grade potassium fluoride (Baker & Adamson, U.S.A.), rubidium fluoride (Light Laboratories LTD, England) and cesium fluoride (The British Drug Houses LTD, England). The chemicals were carefully dried in a vacuum furnace at 400–500°C before use.

The DTA cooling curves were recorded by a Speedomax G X–Y recorder and by use of a D. C. Microvolt Amplifier (range 50–2000 microvolt, Leeds and Northrup, U.S.A.). The low temperature X-ray investigations were carried out with a Nonius type Guinier camera using Cu$K\alpha$ radiation, $\lambda(K\alpha_1) = 1.5405$ Å. At higher temperatures the samples were investigated by a conventional parafocusing X-ray diffraction technique using the same Cu$K\alpha$ radiation. The intensity was recorded with a Geiger counter connected to a Philips PW 1051 recorder (Philips, Eindhoven, Holland). The temperature in the furnace was held constant within ±5°C by a temperature controller (Siemens, Germany) connected with a Pt/Pt 10 Rh thermocouple. Purified nitrogen (N_2 99.99 %, Norsk Hydro, Norway) was led through the furnace.

The density measurements were carried out at 25°C by a vacuum pycnometric method using Shell Odourless Kerosene as a displacement liquid.

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Tritiated Naphthalene as a Chemical Dosimeter for Low Radiation Doses

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The most commonly used chemical system for the determination of radiation doses is the Fe^{2+}/Fe^{3+}-dosimeter, generally referred to as the Fricke dosimeter, which has been studied by a large number of investigators.[1-3] In spite of its many advantages, this system has a serious drawback, namely its insensitivity, which makes it useful only down to about 1000 R.

Rudstam and Svedberg [4] have tried to improve the Fricke dosimeter by the use of ^{59}Fe, but the internal dose from the isotope seems to limit the usefulness of this system. Another attempt at increasing the sensitivity of this dosimeter involves the addition of organic compounds.[5,6] However, the systems thus produced, are like other systems utilizing chain reactions, *e.g.* those including chlorinated hydrocarbons,[7] sensitive to impurities and strongly dependent on dose rate and temperature.

Other attempts to solve the problem have been the aqueous benzene dosimeter described by Klein [8] and the benzoic dosimeter described by Moroson and Laughlin.[9] Both methods are claimed to be usable for doses down to the region of 10–20 R.

In our search for a more sensitive and reproducible dosimeter, capable of measuring doses over a wide range, we have tested different lipophilic substances yielding more hydrophilic products on irradiation and thereby enabling a separation. In order to extend the dose range to doses