Phase Equilibria in the System CaF_2—AlF_3

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Parts of the phase diagram of the system CaF_2-AlF_3 have been examined by differential thermal analysis (DTA) combined with microscopic and X-ray diffraction studies of samples in the system. The results from the DTA examinations are plotted in a phase diagram in Fig. 1, together with the results from a work by Fedotiev and Iljinsky [1] on the same system. According to their work, the system forms a simple binary eutectic with an eutectic point at 37.5 mole% AlF_3 and 820°C.

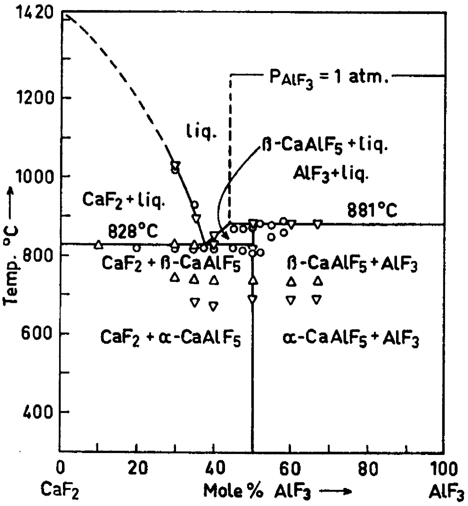

Fig. 1. The phase diagram of the system CaF_2-AlF_3. O: Observed points by Fedotiev and Iljinsky.[1] ▽: Cooling curves. △: Heating curves.

From the obtained DTA-diagrams taken during heating as well as cooling, it is clear that a reaction occurs at 828°C (Fig. 2a, c and d). This temperature is only slightly higher than the temperature observed by Fedotiev and Iljinsky [1] and corresponds to the eutectic temperature in the system. However, it appears from the DTA-diagrams that the eutectic reaction does not seem to take place for mixtures containing more than 50 mole% AlF_3. Instead the diagrams for these AlF_3-rich mixtures contain a peak at approximately 881°C (Fig. 2d and e).

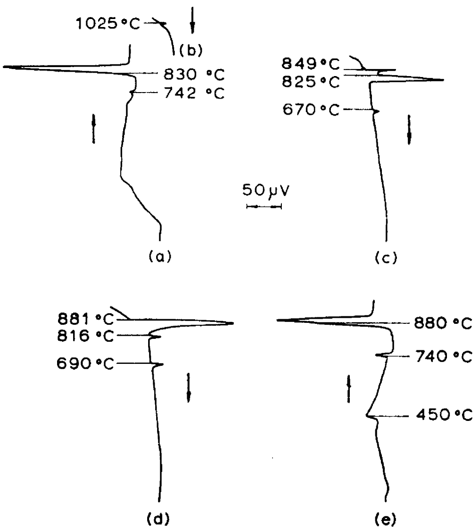

Fig. 2. DTA heating and cooling curves for CaF_2-AlF_3 mixtures: a) 70 mole% CaF_2 (heating curve) b) 70 mole% CaF_2 (cooling curve) c) 60 mole% CaF_2 (cooling curve) d) 50 mole% CaF_2 (cooling curve) e) 40 mole% CaF_2 (heating curve).

Thus, the DTA experiments indicate that an incongruently melting compound is formed at the 50:50 composition. This is further verified by microscopic and X-ray diffraction examinations of samples in the system. In the microscope, crystals of the primary phase could easily be distinguished from the very fine crystals in the eutectic and peritectic mixture (see Fig. 3). The observed primary phases for each of the examined mixtures are given in Table 1.

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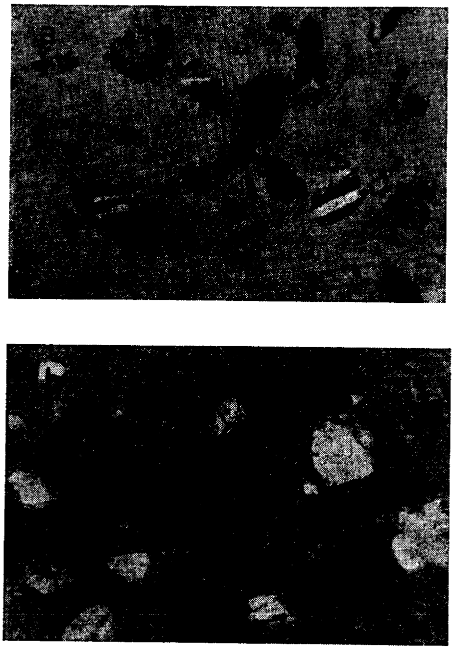

Fig. 3. Photomicrographs of: a) 60 mole% CaF_2 + 40 mole% AlF_3 mixture, showing primary crystals of $CaAlF_5$ in the eutectic mixture. b) 50 mole% CaF_2 + 50 mole% AlF_3 mixture, showing crystals of $CaAlF_5$.

The compound $CaAlF_5$ seems to form highly twinned crystals with a mean refractive index of about 1.375. X-Ray powder diffraction data for $CaAlF_5$ are given in Table 2. The structure of the compound is not known at the present. The density of the compound has been determined and found to be 2.947 g/cm^3. According to the DTA-diagrams, $CaAlF_5$ exhibits a polymorphic transition at about 740°C. At ordinary cooling rates, 5°C/min, the transition point is observed at 690°C.

It is of interest to compare $CaAlF_5$ with other fluoroaluminates of known structure. According to the well known structural classification of fluoroaluminates by Pabst,[2] the ratio of Al to F becomes 5 when the AlF_6^{3-}-octahedra are linked into chains through the corners. This seems to occur with Tl_2AlF_5. The structure of this compound has been determined by Brosset.[3]

Table 1. Phases present in CaF_2-AlF_3 mixtures.

Comp. Mole% AlF_3	Phases identified by optical examination	Phases identified by X-ray diffraction examination
30	CaF_2 + mix	$CaAlF_5$ + CaF_2
40	$CaAlF_5$ + mix	$CaAlF_5$ + CaF_2
50	$CaAlF_5$ (+ mix)	$CaAlF_5$
60	AlF_3 + mix	$CaAlF_5$ + AlF_3
70	AlF_3 + mix	$CaAlF_5$ + AlF_3

mix = eutectic or peritectic mixture.

Table 2. α-$CaAlF_5$, X-ray diffraction data.

I/I_0	Θ (Cu)	d (meas.), Å.
37	11.30	3.931
100	14.13	3.156
16	19.68	2.288
11	20.00	2.252
7	21.65	2.088
8	22.63	2.003
14	23.05 23.10	1.967
5	23.55	1.833
24	24.85 24.98	1.824
8	25.85	1.767
11	27.45	1.671
10	27.65	1.659
11	29.07 29.17	1.585 1.580
8	35.17	1.337
6	39.98	1.199
5	40.10	1.196

The calcium fluoroaluminate, $CaAlF_5$, decomposes by heating according to:

$$CaAlF_5 \xrightarrow{881°C} AlF_3 + \text{melt} \qquad (1)$$

like the minerals chiolite and weberite (Holm [4]):

$$\underset{\text{chiolite}}{Na_5Al_3F_{14}} \xrightarrow{739°C} \underset{\text{cryolite}}{Na_3AlF_6} + \text{melt} \qquad (2)$$

$$\underset{\text{weberite}}{Na_2MgAlF_7} \xrightarrow{849°C} \underset{\text{neighborite}}{NaMgF_3} + \underset{\text{sellaite}}{MgF_2} \qquad (3)$$

+ melt

Generally one may say that structures where the AlF_6-octahedra are linked together, will not be stable at higher temperatures because of the increased vibrational energy. As can be seen from the three reactions above, the compounds always decompose into more energetically favourable compounds.

In the electrolytic production of aluminium, one often operates with additions of both CaF_2 and AlF_3 to the molten cryolite bath. Since calcium fluoride-aluminium fluoride mixtures seem to have some complex forming properties, it might be possible for the Ca^{2+}-ions in an acid bath to take part in the conductivity process together with the Na^+-ions, as indicated by the conductivity measurements by Yim and Feinleib.[5]

Experimental. The samples were first homogenized by mixing aluminium fluoride and calcium fluoride in the right proposition in 100 % alcohol in a glove box. The aluminium fluoride was prepared by vacuum sublimation of anhydrous AlF_3 (A.D. Mackay, Inc. U.S.A.) in a high-frequency heated furnace. The method has been described in detail by Rolin.[6] Calcium fluoride a.r. from Mallinckrodt Chemical Works, U.S.A., was dried at 400°C in a vacuum furnace before use.

The DTA heating and 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.).

At the eutectic temperature, 828°C, and peritectic temperature, 881°C, equilibrium crystallization occurred only for compositions with more than 40 mole% AlF_3 at cooling rates of about 3$-$5°C/min. On the CaF_2-side of the system the temperature therefore had to be taken from the heating curves.

The X-ray investigations were carried out with a Philips Wide Range Goniometer PW 1050/25, connected to a Philips PW 1051 recorder (Philips, Eindhoven, Holland), and with a Nonius type Gunier camera using Cu$K\alpha$ radiation, $\lambda(K\alpha_1) = 1.5405$ Å.

The density of the 50:50 sample was determined by use of a vacuum pycnometric method using Shell Odourless Kerosone as a displacement liquid.

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Shear Structure of the Wolfram Oxide $WO_{2.95}$

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The preparation of a wolfram oxide, intermediate in composition between WO_3 and $W_{20}O_{58}$, and from its chemical analysis found to have the formula $WO_{2.95}$, was recently reported by Imre and one of the present authors.[1] Structural studies using X-ray single-crystal and powder data have given the following results.

The single-crystal photographs of the new oxide were found to show very close similarities with those of $W_{20}O_{58}$,[2] indicating that $WO_{2.95}$ is actually another representative of a wolfram oxide with crystallographic shear occurring in a ReO_3-type arrangement of atoms. Detailed inspection disclosed that the structural parameters within the planes of shear, *i.e.* the *a* and *b* axes of the monoclinic unit cells, are practically identical in the two oxides. $WO_{2.95}$, however, showed in comparison with $W_{20}O_{58}$ approximately a

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