The Phase Diagram of the System Cs$_3$AlF$_6$-Li$_3$AlF$_6$

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This work is a part of the phase investigations in binary systems of the type $M_3^IAlF_6 - M_3^{II}AlF_6$ (M = alkali metal), which were started by Holm [1] (1963) and later carried on by Holm and Jenssen Holm [2] (1970).

In the series $M_3AlF_6 - Li_3AlF_6$ we have earlier examined the systems $Na_3AlF_6 - Li_3AlF_6$,[2] $K_3AlF_6 - Li_3AlF_6$, and $Rb_3AlF_6 - Li_3AlF_6$.[3] This series is now concluded with an examination of the system $Cs_3AlF_6 - Li_3AlF_6$.

Experimental. Materials. AlF$_3$; aluminium fluoride, anhydrous (Mac Kay, USA) was sublimated twice in a vacuum furnace at 910°C. The method used has been described by Henry and Dreisbach.[4] Pure crystals were picked out from the product and used for these experiments. CsF; anhydrous CsF, 99.9 %, (Schuchardt, München, Germany), and LiF; anhydrous LiF (Baker Analyzed reagent, Deventer, Holland) were purified by melting

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in a platinum crucible under nitrogen atmosphere, and pure crystals were selected for the preparation of cesium and lithium cryolites. All handling of CsF was done in a dry box. For the preparation of Li$_3$AlF$_6$ and Cs$_3$AlF$_6$, stoichiometric amounts of the alkali fluoride and aluminium fluoride were mixed in the dry box and melted in a platinum crucible under nitrogen atmosphere at a temperature of 790°C for Li$_3$AlF$_6$ and 820°C for Cs$_3$AlF$_6$.
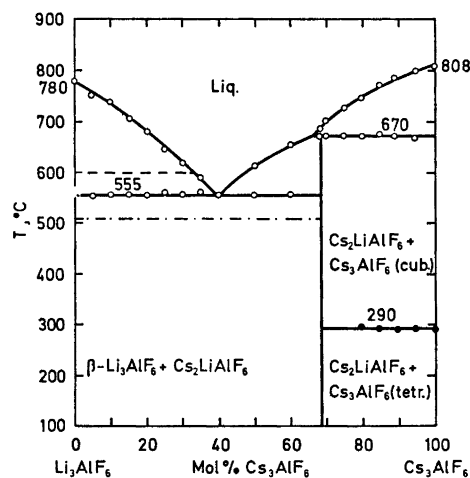

Fig. 1. The phase diagram of the system, Cs$_3$AlF$_6$ — Li$_3$AlF$_6$. $\bigcirc$, liquid-solid transitions; $\bullet$, Cs$_3$AlF$_6$(tetr) $\rightleftarrows$ Cs$_3$AlF$_6$(cubic); dotted line, Li$_3$AlF$_6$(tetr) $\rightarrow$ Li$_3$AlF$_6$(cubic);[6] dash-dotted line, Li$_3$AlF$_6$(orthorhombic) $\rightarrow$ Li$_3$AlF$_6$(tetr).[6]

Table 1. X-Ray data for the compound Cs$_2$LiAlF$_6$ at 25°C.

h k l	Int.	$\sin^2\theta_{obs} \times 10^4$	$\sin^2\theta_{calc} \times 10^4$	$d(hkl)_{obs}$
1 1 0	w	203	206	5.40
1 1 1	vs	439	444	3.67
2 0 0	s	614	616	3.11
2 2 0	m	819	823	2.691
0 0 2	s	949	954	2.501
2 2 1	s	1057	1061	2.370
1 1 2	w	1155	1160	2.256
3 1 0	w	1434	1438	2.034
2 0 2	w	1565	1571	1.947
3 1 1	m	1672	1677	1.883
2 2 2	vw	1773	1777	1.829
3 3 0	s	1853	1854	1.789

vs = very strong, s = strong, m = medium, w = weak, and vw = very weak

The composition was checked by DTA, and adjusted by addition of AlF_3 if necessary.

The experimental methods and equipment used during the investigation (DTA, X-ray and density measurements) were the same as described previously.[2,3,5]

Results and discussion. The phase diagram is presented in Fig. 1. The experimental points were obtained from DTA cooling curves. The phase diagram of this system is similar to the two systems $Li_3AlF_6 - K_3AlF_6$ and $Li_3AlF_6 - Rb_3AlF_6$.[3] The system contains one incongruently melting compound, $2Cs_3AlF_6.Li_3AlF_6$, corresponding to Cs_2LiAlF_6. A peritectic point was found at 670°C and 85.5 mol % Cs_3AlF_6 while a eutectic point was established at 555°C and 40 mol % Cs_3AlF_6.

A preliminary investigation of the structure of the compound Cs_2LiAlF_6 was carried out. The X-ray data for the compound Cs_2LiAlF_6 are given in Table 1. Single crystal X-ray diffraction analysis indicated that the compound has an orthorhombic structure with a C-centered lattice and the cell constants $a = 6.21 \pm 0.04$ Å; $b = 10.72 \pm 0.03$ Å; $c = 4.99 \pm 0.01$ Å. This gives a calculated density of 4.14 g cm^{-3} (2 formula units in the cell) compared to a measured value at 25°C of 4.04 g cm^{-3}.

1. Holm, J. L. *Undersøkelser av struktur og faseforhold for en del systemer med tilknytning til aluminiumelektrolysen*, Lic. Thesis, Institute of Inorganic Chemistry, NTH, Trondheim 1963.
2. Holm, J. L. and Jenssen Holm, B. *Acta Chem. Scand.* **24** (1970) 2535.
3. Grjotheim, K., Holm, J. L., Malinovský, M. and Mikhaiel, S. A. *Acta Chem. Scand.* **25** (1971) 1695.
4. Henry, J. L. and Dreisbach, S. H. *J. Am. Chem. Soc.* **81** (1959) 5274.
5. Holm, J. L. and Jenssen Holm, B. *Thermochim. Acta* **5** (1973) 273.
6. Holm, J. L. and Jenssen Holm, B. *Acta Chem. Scand.* **23** (1969) 1065.

Perchlorate and Fluoride Complexes of Thallium(I) in Aqueous Solution

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When weak complex systems are investigated in perchlorate media, different experimental methods may give different apparent stability constants, if the perchlorate ion is not completely inert but forms a complex with the central ion.[1] Central ion measurements, in a wide sense, give lower values of the stability constants than do ligand measurements. In the extreme case, when the perchlorate complex is stronger than that of the ligand studied, central ion measurements may give negative apparent constants. The $Tl^+ - F^-$ system appears to behave in this manner. The system has been previously studied with potentiometric and polarographic methods.[2-4] As the effects observed are small, it might be argued that they are caused mainly or in part by changes, at constant ionic strength, in liquid junction potentials and activity coefficients. Such changes are, however, not likely to be the same for different methods. Therefore, in the present work, the system has been studied with other methods than those used earlier, *viz.* two solubility methods, the first being, in effect, a central ion measurement, the second a ligand measurement. The measurements have been carried out at 25°C in a $NaClO_4$ medium of $I = 0.5$, where

$$I = [L] + [A] \tag{1}$$

L and A denote fluoride and perchlorate ion, respectively.

Solubility of $TlIO_3(s)$. Solutions in the range $0 \le [L] \le 0.5$ M were saturated in a column with $TlIO_3(s)$, and analyzed for IO_3^- by the thiosulphate method.[5] The solubilities could be reproduced within 1%.

In a separate experiment, IO_3^- but no F^- was added. The solubility, S, then was inversely proportional to $[IO_3^-]$. Thus, no

Table 1. Solubility of $TlIO_3(s)$: $[L]/M$, $S \times 10^3/M$; 0.000, 3.289; 0.100, 3.245; 0.200, 3.219; 0.300, 3.159; 0.400, 3.107; 0.500, 3.057.