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Flux growth of crystals of some transition metal fluorides

Part 3 *Pyrochlores and others*

B. M. WANKLYN, F. R. WONDRE, B. J. GARRARD, J. CERMAK*
Clarendon Laboratory, University of Oxford, Oxford, UK

W. DAVISON
School of Physics, University of Newcastle upon Tyne, Newcastle upon Tyne, UK

The flux growth of the following complex fluorides is reported: $KNiCrF_6$; $RbCoCrF_6$, $RbMnCrF_6$; $CsCoAlF_6$, $CsCoCrF_6$, $CsCoFeF_6$; $CsCrAlF_6$; $CsMgAlF_6$, $CsMgCrF_6$, $CsMgFeF_6$; $CsMnAlF_6$, $CsMnCrF_6$, $CsMnFeF_6$; $CsNiAlF_6$, $CsNiCrF_6$, $CsNiFeF_6$; $CsZnFeF_6$. Octahedral crystals of some of these materials with edges up to 1 cm have been grown. Most of them are cubic, but several are twinned, indicating a structural phase transition below the growth temperature. The growth of $KCr_2F_{6.5}$ and $BaNiF_{3.6}Cl_{0.4}$ crystals is also described. Larger faceted crystals of K_2FeF_5 are reported. The growth of crystals of KFe_2F_6, previously only prepared under HF and N_2, has been achieved in air.

1. Introduction

The flux growth method has been successfully used to prepare crystals of many fluoride materials [1]. Among its advantages are the following: (1) NH_4HF_2 can be included to hydrofluorinate oxide impurities in the starting materials; (2) incongruently melting materials can be crystallized; (3) large crystals can often be prepared in the absence of information on melting properties and solubility curves.

There is considerable interest in the spin-glass behaviour of some of the compounds $AM^{2+}M^{3+}F_6$ (A = alkali ion), which have pyrochlore structures. Previous reports on the structures dealt largely with sintered and rapidly cooled samples; preparation by that method may have quenched-in the high-temperature cubic structures observed [2–10]. Of the crystals described in the present work, only $CsAlNiF_6$ and $RbMnCrF_6$ [4] were previously reported to have distorted structures.

Crystals of some of the compounds with A = Rb and Cs have previously been prepared under dry N_2 according to the reaction:

$$8RbCl + CoCl_2 + 3CoF_2 + 2CrF_3 \rightarrow 2RbCoCrF_6 + 6RbCl + 2CoCl_2 \qquad (1)$$

with a maximum temperature of 950° C [11]. This yielded 8 mm crystals of $RbCoCrF_6$, and crystals of other products much smaller in size. Anhydrous MCl_2, however, has to be specially prepared for these experiments, because of its hygroscopic nature. The present paper reports the growth of crystals of the pyrochlore fluorides with dimensions up to 1 cm on edge in some cases. Details of the growth of faceted crystals of K_2FeF_5, much larger than previously reported [12], are also given. The growth of KFe_2F_6, previously only prepared under HF + N_2 [13], has been achieved in air, using platinum crucibles. Single crystals of $BaNiF_4$ containing 6% Cl have been grown from $BaCl_2$ as flux. The compound $KCr_2F_{6.5}$ which contains divalent as well as trivalent chromium has not been reported before.

2. Chemicals

The chemicals used were: BDH Optran Grade

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* Present address: Faculty of Engineering, The Technical University, Prague.

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TABLE I Starting compositions, furnace programmes and results for $AM^{2+}M^{3+}F_6$ compounds

Formula	Starting composition molar ratios ACl:MF:MF	Crucible volume (cm³)	Maximum temperature (°C)	Reset temperature (°C)	Rate of cooling (K h⁻¹)	Final temperature (°C)	Weight loss (g)	Size of crystals (mm)	Notes on the crystals
$KNiCrF_6$	8:3:2	20	1290	930	3.0	450	0.0	1 × 1 × 1	Not isotropic, green
$RbCoCrF_6$	8:3:2	10	1045	940	1.6	500	1.8	5 × 5 × 4	Isotropic, black
$RbMnCrF_6$	6:3:2	15	1100	970	3.0	570	0.0	3 × 3 × 3	Opaque, twinned, green
$CsCoAlF_6$	9:3:2	20	1200	1080	2.0	450	10.0	5 × 3 × 3	Opaque, twinned, scarlet
$CsCoCrF_6$	8:3:2	20	1200	1080	2.0	450	0.0	11 × 7 × 7	Isotropic, dark grey-green
$CsCoFeF_6$	8:3:2	20	1075	940	3.0	600	0.6	5 × 5 × 4	Isotropic, red
$CsCrAlF_6$*	8:3:2	30	1170	1105	2.0	550	22.2	2 × 1 × 1	Opaque, twinned, dark green
$CsMgAlF_6$	8:3:2	15	1200	1080	2.0	500	2.7	3 × 3 × 3	Not isotropic, colourless
$CsMgCrF_6$	8:3:2	20	1200	1115	1.9	570	0.2	6 × 4 × 4	Isotropic, dark green. MgF_2 also crystallized
$CsMgFeF_6$	9:3:2	20	1200	1115	1.9	570	2.5	5 × 4 × 0.5	Isotropic, yellow. MgF_2 also crystallized
$CsMnAlF_6$	8:3:2	20	1200	1080	1.9	570	0.4	2 × 2 × 1	Opaque, twinned, colourless
$CsMnCrF_6$	8:3:2	20	1200	1115	1.9	570	0.1	4 × 3 × 3	Isotropic, dark green
$CsMnFeF_6$	8:3:2	50	1200	1080	2.0	500	0.7	10 × 10 × 10	Isotropic, green
$CsNiAlF_6$	9:3:2	20	1200	1115	1.9	570	0.5	2 × 2 × 1	Opaque, yellow
$CsNiCrF_6$	8:3:2	20	1200	1080	2.0	500	0.2	12 × 10 × 10	Isotropic, green (Fig. 1)
$CsNiFeF_6$	8:3:2	20	1075	940	3.0	600	4.2	10 × 10 × 10	Isotropic, green
$CsZnFeF_6$	9:3:2	20	1200	1120	3.0	430	6.1	1 × 1 × 1	Isotropic

*Grown under H_2 and N_2 in Mo crucible.

TABLE II Starting compositions, furnace programmes and results for the other fluoride crystals

Formula	Starting composition (g)	Crucible volume (cm³)	Maximum temperature (°C)	Rate of cooling (K h⁻¹)	Final temperature (°C)	Crystal products
$KCr_2F_{6.5}$	7.5 CrF_2, 9.7 KF, 69.5 $PbCl_2$ (Mo crucible under N_2 + H_2)	30	840	2.5	480	Dark green, hexagonally faceted rods up to 6 mm × 2.5 mm × 2.5 mm as shown in Fig. 2. Second phase, plates of K_2CrF_5
KFe_2F_6	24 FeF_2, 15 KCl, 5 NH_4HF_2	50	1045 reset to 940	1.2	600	Black crystals, faceted, up to 10 mm × 4 mm × 4 mm
K_2FeF_5	24.8 FeF_3, 34.4 KHF_2, 60.0 $PbCl_2$, 6.0 NH_4HF_2	50	760 reset to 690	0.8	560	Crystals up to 25 mm × 5 mm × 2 mm as shown in Fig. 3
$BaNiF_{3.6}Cl_{0.4}$	14.5 $BaCl_2$, 6.8 NiF_2, 1.4 NH_4HF_2	20	1100 reset to 970	3.0	570	Sheets of untwinned yellow crystal plates through melt

CoF_2, AlF_3, NiF_2, ZnF_2; BDH Analar grade $BaCl_2$, MgF_2; BDH Laboratory Reagent grade NH_4HF_2, CsCl, KF, $PbCl_2$; BDH Extra Pure grade PbF_2; and FeF_2, FeF_3, CrF_3, MnF_2, CrF_2, RbCl from Koch Light.

3. Experimental details

The crystals described in this paper were grown either in air or under $N_2 + H_2$. For those grown in air, platinum crucibles of 0.5 mm wall thickness, having closely fitting platinum lids, were used. Furnaces and control equipment have been described previously [14]. The starting compositions and furnace programmes which produced the best crystals are given in Tables I and II.

For the experiments in air, the materials were weighed and mixed and part of the mixture, usually about 80%, was placed in the crucible. To reduce evaporation and oxidation, a smaller platinum crucible was inverted inside the crucible containing the mixed powders, and the remains of the mixture were packed over the top of the inverted crucible. The material above the inner crucible was expected to evaporate, leaving a salt seal around the junction with the outer crucible [15]. The lid was finally fitted as closely as possible and the crucible was placed inside a Sillimanite D-muffle inside the crystal-growing furnace. The muffle was necessary to protect the Crusilite elements from the reactive flux vapours [16]. The crucibles stood on the base of the D-muffle on a bed of alumina powder and the D-muffle was located inside the furnace in such a position as to ensure that the base was the coolest part of each crucible. The entrance of the D-muffle was then blocked with refractory brick.

The furnace was initially heated at $100\,K\,h^{-1}$ to a temperature well above the liquidus, then cooled rapidly by setting the furnace temperature to a lower value before slow cooling was begun. Slow cooling continued until the final temperature, about 50° C above the expected eutectic, was reached, when the crucibles were inverted to drain the flux from the crystals. These were then easily removed from the crucibles.

The procedure for growing the materials under $N_2 + H_2$ has been described [17]. The crucibles were cooled at $100\,K\,h^{-1}$ from the final temperature to room temperature, after which they were inverted and reheated under N_2 to drain the flux.

4. Results

The crystals produced are described in Tables I and II, and some are shown in Figs 1 to 3. Lattice parameters of the cubic crystals, calculated from X-ray powder pattern data, are compared with published data in Table III. Some of the crystals had powder patterns similar to those of the cubic materials but with slightly broadened lines and Laue photographs showed that these crystals were twinned and therefore not cubic. In Table IV, the powder pattern data for the compounds with distorted structures are given. The powder pattern data for $KCr_2F_{6.5}$ is given in Table V; it is quite probable that it has a distorted pyrochlore structure but this has not been established.

The growth of crystals of $BaNiF_4$ containing lead and chlorine impurities has been reported previously [18]. By using $BaCl_2$ as a flux, $BaNiF_4$

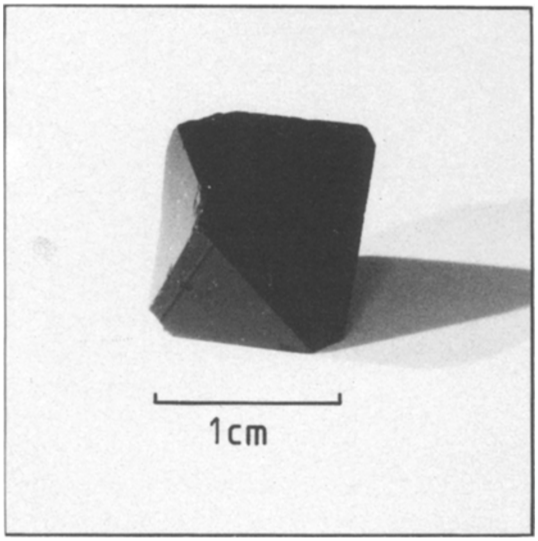

Figure 1 A typical octahedral crystal of $CsNiCrF_6$.

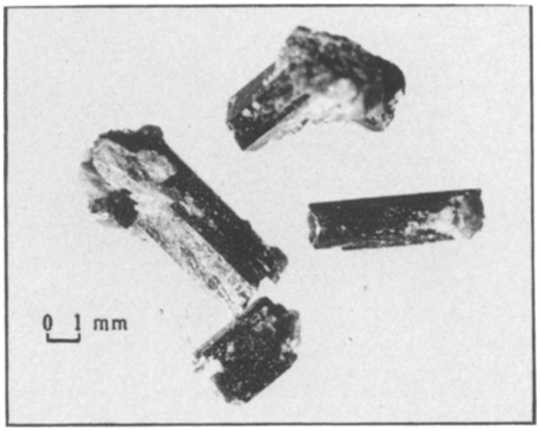

Figure 2 Rods of $KCr_2F_{6.5}$.

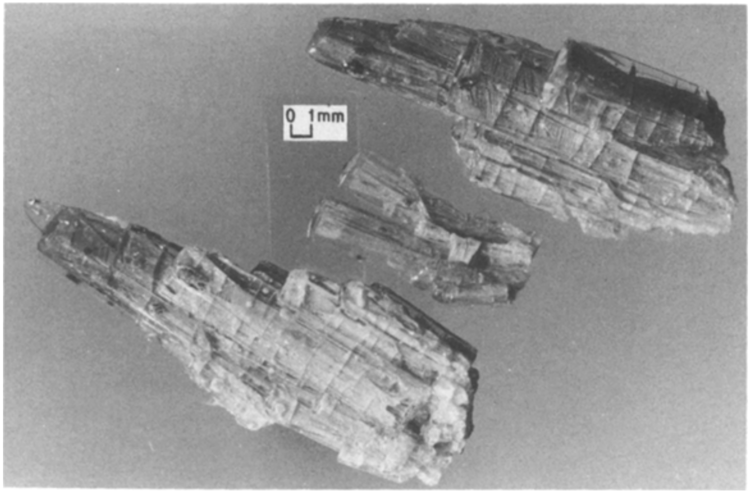

Figure 3 Crystals of K_2FeF_5.

TABLE III Lattice parameters of cubic compounds

Formula	Published lattice parameters		Parameters from present work
	Reference	a(Å)	a(Å)
$CsCoCrF_6$	[3]	10.35	10.36
$CsCoFeF_6$	[3]	10.40	10.42
$CsMgCrF_6$	–		10.26
$CsMgFeF_6$	[2, 4, 10]	10.32–10.35	10.34
$CsMnCrF_6$	[3, 4]	10.47–10.49	10.47
$CsMnFeF_6$	[3–6]	10.522–10.56	10.54
$CsNiCrF_6$	[3]	10.28	10.29
$CsNiFeF_6$	[3–5, 7]	10.35–10.37	10.35
$CsZnFeF_6$	[2, 8, 10]	10.40–10.42	10.40
$RbCsCrF_6$	[9]	10.27	10.30

TABLE IV X-ray pattern data for compounds with distorted pyrochlore structures

$CsMgAlF_6$		$CsCrAlF_6$		$CsCoAlF_6$		$CsMnAlF_6$		$RbCrMnF_6$		$CsNiAlF_6$	
d(Å)	I_{est}	d(Å)	I_{est}	d(Å)	I_{est}	d(Å)	I_{est}	d(Å)	I_{est}	d(Å)	I_{est}
5.81	VW	–	–	–	–	–	–	6.0	VW	–	–
3.55	S	3.74	S	3.60	S	3.61	MS	3.61	S	3.56	S
3.02	VS	3.18	VS	3.06	VS	3.12 3.06	S S	3.11 3.07	VS VS	3.06 3.02	VS VS
2.898	VW	3.06	VW	2.929	VW	2.910	VW	2.971 2.952	VW VW	2.936 2.889	VW W
2.507	M	2.639	VW	2.536	W	2.555	W	–	–	2.513	M
2.302	MS	2.425	W	2.330	W	2.333	M	2.349	W	2.333 2.300	VW W
–	–	–	–	–	–	–	–	2.171	VW	–	–
2.047	W	2.155	VW	2.077	VW	–	–	2.079	VW	2.069 2.044	W VW
1.931	MS	2.028	MS	1.951	M	1.995 1.959	W W	1.980 1.955	M W	1.951 1.926	W M
1.776	MS	1.864	MS	1.794	MS	1.801 1.783	MS VW	1.829 1.805	W MS	1.801 1.779 1.759	VW MS W
1.669	VW	–	–	–	–	–	–	–	–	–	–
1.587	M	1.669	W	1.604	M	–	–	–	–	1.603 1.594	VW W

TABLE V X-ray powder pattern data for $KCr_2F_{6.5}$

d(Å)	I_{est}
8.8	VW
5.4	VW
3.96	VW
3.81	VW
3.71	S
3.62	W
3.10	VS
2.901	M
2.699	MS
2.551	VW
2.476	M
1.901	W
1.789	W

crystals with a greatly reduced impurity content have been produced. The X-ray powder pattern closely resembled published data for $BaNiF_4$ [19].

The results of electron probe microanalysis (EPMA) for some of the compounds are given in Table VI.

5. Discussion

The procedure, whereby the mixtures were heated to relatively high temperatures and then rapidly cooled by 80 to 100° C before commencing slow cooling, was based on experimental findings, recently published [20], which showed that the number of crystals that nucleated and grew was less when the temperature was raised considerably above the liquidus temperature. Because of the volatility of the melts, it was judged inadvisable to allow them to remain at the maximum temperature for long periods. This procedure, plus the salt seal which formed around the edges of the inner crucible, was usually very effective and crystals approximately 1 cm^3 in volume were obtained from a number of batches for which the volumes of the melts were as small as 12 cm^3 in 20 cm^3 crucibles, or 25 cm^3 in 50 cm^3 crucibles. This size of crystal is exceptional in flux growth even from much larger melts. As well as reducing evaporation, the salt seal also greatly reduced oxidation, which is often a problem in the flux growth of fluorides. Although substitution of Cl for F in flux-grown fluorides is sometimes substantial [18], analysis of two of the pyrochlore compounds produced in this work showed the chloride content to be less than 0.04%. Attempts to grow the pyrochlore crystals in molybdenum crucibles under N_2 and H_2 were generally not successful, although a few small crystals of $CsCrAlF_6$ were obtained. Evaporation was restricted only by a molybdenum lid which, unlike platinum, could not be formed to give a close fit. Loss of the melt was so great that little remained in the crucibles.

Several compounds were produced, the structures of which, although related to the pyrochlore structure, were clearly distorted, as shown by the line-splitting of the powder patterns (Table IV) and by their optical anisotropy. These crystals were intimately twinned. This indicates that they had undergone a phase transition from a high-symmetry to a low-symmetry form in cooling from the growth temperature.

The pyrochlore structure is characterized by corner-linked, rigid cation–anion groups forming octahedra. In these particular crystals the octahedra consist of randomly distributed divalent or trivalent transition metal ions and fluorine ions. Four corner-sharing octahedra, whose centres form a regular tetrahedron, form the basic building unit of the octahedral framework. The face-centred cubic unit cell, space group *F*d3m, contains four of these tetrahedra. This arrangement

TABLE VI EPMA data for some of the compounds

$CsMnFeF_6$		$CsCoAlF_6$		$KCr_2F_{6.5}$		$BaNiF_{3.6}Cl_{0.4}$	
Formula requires (wt %) •	EPMA indicates (wt %)	Formula requires (wt %)	EMPA indicates (wt %)	Formula requires (wt %)	EPMA indicates (wt %)	Formula requires (wt %)	EPMA indicates (wt %)
Cs 37.2	38.5	Cs 39.9	40.7	K 14.7	14.6	Ba 49.2	49.6
Mn 15.4	16.1	Co 17.7	17.4	Cr 39.0	38.4	Ni 21.0	20.9
Fe 15.6	14.7	Al 8.1	8.1	F 46.3	46.3	F 24.3	27.0
F 31.9	34.8	F 34.3	35.0	Cl –	0.06	Cl 5.5	6.0
Cl –	0.04	Fe –	0.2				
		Cl –	0.006				
Total	104.14		101.4		99.36		103.5

leaves large holes and tunnels running through the structure. The holes are partially occupied by alkali ions which, by their presence, stabilize the framework of octahedra. The caesium ions, because of their large size, are best able to do this and the compounds containing caesium are the most likely to remain cubic.

These considerations suggest that the distortions from the cubic structure are due to polyhedral tilt transitions. According to Hazen and Finger [21] the greater compressibility of the large cation site leads to a lowering of symmetry which can be induced either by a reduction in temperature or by substitution of a smaller cation. In the compounds containing Cs, the reduction of symmetry appears to have been achieved not by a decrease of the cation size, but by the smaller size of the rigid $(AlF_6)^{3-}$ octahedra surrounding the cation site. Structural studies of some of these materials will be undertaken elsewhere.

Acknowledgement

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