Flux growth of crystals of some transition metal fluorides

Part 2

B. M. WANKLYN, F. R. WONDRE, A. MAQSOOD*, K. YANAGISAWA[†] Clarendon Laboratory, Oxford, UK W. DAVISON School of Physics, University of Newcastle upon Tyne, UK

The flux growth of crystals of the following complex fluorides is reported: KAIF₄, KMnF₃, RbFeF₄, Rb₂FeF₅, Rb₃FeF₆, Rb_xFeF₃ (0.18 < x < 0.29), CsFeF₄, CsFe₂F₇, Cs₃Fe₂F₉, Cs_xFeF₃ (0.18 < x < 0.29), Na₂CoFeF₇, Na₂NiFeF₇, Na₂NiAlF₇, Na₂ZnCrF₇, NaCrF₄ and Rb₂Cr₅F₁₇. Flux impurity levels, determined by electron probe microanalysis (EPMA), were low. However, attempts to produce BaNiF₄, BaCoF₄, CsCrF₄ and Cs₂Cr₅F₁₇ resulted in crystals with higher levels of substitutional impurities. X-ray powder patterns and EPMA were used to characterize the crystals.

1. Introduction

Many complex fluorides of the transition metals have been prepared as powder specimens because of interest in their magnetic properties. The flux growth method has previously been successfully used to prepare crystals of some of these materials [1-4] and its further application is reported in this paper. In Table I, the reported magnetic transition temperatures of some of the materials described here are listed [5-16]. The compounds containing Fe²⁺ or Fe³⁺ are especially useful for investigation by the Mössbauer method.

Of the compounds reported in this paper, $KMnF_3$ [17] is known to melt congruently and

TABLE I Magnetic transition temperatures of some complex fluorides

Formula	<i>T</i> _N (K)	Reference
KMnF ₃	275, 280, 253	[5-7]
RbFeF ₄	134	[8]
Rb ₂ FeF ₅	14.2	[9]
CsFeF ₄	159	[10]
$Rb_x FeF_3$ (0.18 < x < 0.29)	80,116	[11, 12]
$Cs_x FeF_3$ (0.18 < $x < 0.29$)	116	[12]
Na ₂ NiFeF ₇	90 (T _c)	[13]
Na ₂ NiAlF ₇	90	[14]
BaNiF ₄	150	[15]
BaCoF ₄	69.6	[16]

thus can be grown as crystals from the pure melt. This method produces large crystals relatively rapidly, but has two disadvantages: firstly, considerable amounts of pure, oxide-free starting materials are essential, and secondly, the dislocation density is usually of the order of 10^3 to 10^4 cm⁻² [18], as compared with 10^2 cm⁻² for flux-grown complex fluorides [19, 20]. Zone-refined MnF₂ and CoF₂ can be obtained, but commercially available FeF₂, FeF₃, CrF₃ and NiF₂ contain oxides as well as adsorbed water.

The flux growth of Na₂CoFeF₇ and Na₂NiFeF₇ from NaCl-MCl₂ has been reported [21]. However, the crystals were small, and in the present work alternative flux systems have been investigated. The other complex fluorides reported here containing FeF_2 , FeF_3 and CrF_3 have not previously been prepared as single crystals, with the exception of $RbFeF_4$ [4], for which a new starting composition is given. Many of these compounds cannot be grown from a pure melt because they melt incongruently. The flux method has, however, been shown to be suitable for such compounds since hydrofluorination of oxide impurities in the starting materials is readily accomplished by the addition of NH_4HF_2 [1-4, 22].

*Present address: Physics Department, Quaid-i-Azam University, Islamabad, Pakistan.

[†]Present address: Industrial Materials Research Laboratory, Tokyo Institute of Technology, Tokyo, Japan.

© 1979 Chapman and Hall Ltd. Printed in Great Britain.

TABLE II Starting compositions, cooling programmes and crystal products (a)

(u)							
Batch	Compounds	Starting	Crucible	Initial	Rate of	Final	Crystal products
no.	obtained	composition (g)	volume (cm ³)	temperature (° C)	cooling (K h ⁻¹)	temperature (° C)	
1	KAIF_4	$3.6 \text{ AIF}_3, 6.1 \text{ KHF}_2, 10.7 \text{ PbCI}_2, 4 \text{ NH}_4 \text{ HF}_2$	20	750	Ş	350	Transparent colourless plate- lets up to 4 mm × 4 mm × 2 mm (Fig. 1)
3	KMnF ₃	9.7 MnF ₂ , 11.6 KF, 38.5 PbCl ₂ , 3.5 NH ₄ HF ₂	50	950	m	415 ("hot drained")	Transparent, rectangular, pale pink, up to $8 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$
б	RbFeF4	$12.8 { m FeF}_3$, 20.3 RbF, 26.8 PbCl ₂ , 10.7 NH ₄ HF ₂	50	740	S	300	Colourless to orange trans- lucent plates up to 15 mm X
4	Rb ₂ FeF ₅ and Rb ₃ FeF ₆	9.4 FeF ₃ , 20.9 RbF 20 PbCl ₂ , 7 NH ₄ HF ₂	50	680	1.8	340 ("hot drained" at	15 mm \times 0.3mm Faceted colourless rods of Rb ₂ FeF ₅ , transparent, up to 3.5 mm \times 2 mm \times 1 mm
Ś	CsFeF ₄	13.5 FeF ₃ , 20.2 CsCl, 14.7 PbF ₂ , 9.3 PbCl ₂ 7 NH ₄ HF ₂	50	630	4	300	Milky crystals. 1.5 mm on edge, at crucible walls Purplish or brownish plates, up to $7 \text{ mm} \times 7 \text{ mm} \times 0.2 \text{ mm}$
و	$CsFeF_4$ and $Cs_3Fe_2F_9$	9 FeF ₃ , 25 Cl, 16.5 PbF ₂ , 7 NH ₄ HF ₂	50	640	2.6	300	C_{1} , C_{2} , C
٢	$CsFe_2F_7$	6 FeF ₂ , 4.8 CsCl, 18 PbF ₂ , 5.3 NH ₄ HF ₂	20	950	L	350	Large black plates, up to 8 mm \times 6 mm \times 0.5 mm, at melt surface, and 2 mm octahedra on wall and base of crucible
œ	Rb _x FeF ₃ (0.18 < $x < 0.29$)	5.7 FeF_3 , 2.1 RbF, 21.8 PbCl ₂ , 3.0 NH ₄ HF ₂	20	870	Ś	520 ("hot drained")	Black, shiny, brittle hexagonal rods, up to 2 mm × 2 mm × 8 mm (Fiz. 3)
6	$C_{3x}FeF_{3}$ (0.18 < x < 0.29)	5.9 FeF ₃ , 3.2 CsF, 21.8 PbCl ₂ , 2.0 NH ₄ HF ₂	20	840	10	450 ("hot drained)	Black, shiny, brittle hexagonal rods, up to 1 mm × 1 mm × 5 mm

						د د ډ	•	
othered component component <thcomponent< th=""> <thcomponent< th=""> <thco< th=""><th>ontaned composition (g) composition (g) composition composition Na, OfFer 1.3 CoF1, 1.5 Fer, 1.7 MaHF, 1 20 870 10 Na, NiAF 5.3 FbC1, 2.5 AIF, 8.5 MaHF, 1 20 870 10 Na, NiAF 5.3 FbC1, 2.5 AIF, 8.5 MaHF, 1 20 957 4 Na, NiAF 6.5 MF, 5.5 AIF, 8.5 MaHF, 1 20 957 4 Na, NiAF 6.5 MF, 5.5 AIF, 8.5 MaHF, 1 20 957 4 Na, ZiCF, 6.5 ZiF, 7.5 CiF, 8.5 MaHF, 20 957 4 Na, ZiCF, 6.7 ZiF, 7.5 CiF, 8.5 MaHF, 20 957 4 Na, ZiCF, 6.7 ZiF, 7.5 CiF, 8.5 MaHF, 20 9 957 4 Na, ZiCF, 6.7 ZiF, 7.5 CiF, 8.5 MaHF, 20 9 957 4 Na, CiF, 6.6 CiF, 5.1 MaHF, 20 9 9 9 9 Rb, CiF, 6 8.0 HF, 117 20 9 9 9 9 Rb, CiF, 6 3.2 Mi, HF, 3 9 9 9 9 9 9</th><th>Compounds</th><th>Starting</th><th>Crucible</th><th>Initial</th><th>Rate of</th><th>Final</th><th>Crystal products</th></thco<></thcomponent<></thcomponent<>	ontaned composition (g) composition (g) composition composition Na, OfFer 1.3 CoF1, 1.5 Fer, 1.7 MaHF, 1 20 870 10 Na, NiAF 5.3 FbC1, 2.5 AIF, 8.5 MaHF, 1 20 870 10 Na, NiAF 5.3 FbC1, 2.5 AIF, 8.5 MaHF, 1 20 957 4 Na, NiAF 6.5 MF, 5.5 AIF, 8.5 MaHF, 1 20 957 4 Na, NiAF 6.5 MF, 5.5 AIF, 8.5 MaHF, 1 20 957 4 Na, ZiCF, 6.5 ZiF, 7.5 CiF, 8.5 MaHF, 20 957 4 Na, ZiCF, 6.7 ZiF, 7.5 CiF, 8.5 MaHF, 20 957 4 Na, ZiCF, 6.7 ZiF, 7.5 CiF, 8.5 MaHF, 20 9 957 4 Na, ZiCF, 6.7 ZiF, 7.5 CiF, 8.5 MaHF, 20 9 957 4 Na, CiF, 6.6 CiF, 5.1 MaHF, 20 9 9 9 9 Rb, CiF, 6 8.0 HF, 117 20 9 9 9 9 Rb, CiF, 6 3.2 Mi, HF, 3 9 9 9 9 9 9	Compounds	Starting	Crucible	Initial	Rate of	Final	Crystal products
Na, CoFeF List, J.S. PRC, J.S. PRH, J. 20 870 10 300 Lage platishow organish mergeom Na, Nire F, 5.3 ReC, J.S. PRH, J. S. P. 50 957 4 300 Lage platishow organish mergeom Na, Nire F, 6.5 NF, J.S. PRH, J. S. P. 50 957 4 300 Lage platishow organish mergeom Na, Nire F, 6.5 NF, J.S. PRH, J. S. P., J. S. PR, J. S. P., J. S. P., J. S. P., J. S. PR, J. S. P., J. S. P. P., J. S. P. P., J. S. P. P., J. P. S. P., J. S. P. P., J. S. P. P., J. P. P. S. P. P., J. P. S. P. P., J. P. S. P., J. S. P. P., J. S. P., J. S.	Na, CoFef, 1.3 CoF, 1.5 Fef, 1.7 NaHF, 20 870 10 Na, Nief, 5.3 NPC, 2.00 N14, HF, 50 957 4 Na, Nief, 5.5 NF, 5.5 AHF, 8.5 NaHF, 50 957 4 Na, NiAF, 6.5 NF, 5.5 AHF, 8.5 NaHF, 50 957 4 Na, NiAF, 6.5 NF, 5.5 AHF, 8.5 NaHF, 50 957 4 Na, ZnCF, 6.5 NF, 7.5 AHF, 8.5 NaHF, 20 957 4 Na, ZnCF, 6.5 NF, 7.5 AHF, 8.5 NaHF, 20 957 4 Na, ZnCF, 6.5 NF, 7.5 AHF, 8.5 NaHF, 20 957 4 Na, ZnCF, 6.5 NF, 7.5 AHF, 1.200 PbCl_3, 20 957 4 Na, DicF, 6.5 CF, 4.5 NHF, 1.7 20 957 4 Na, DicF, 6.5 CH, 4.2 NHF, 1.7 20 957 4 Na, DicF, 6.5 CH, 4.2 NHF, 1.7 20 957 4 Na, CF, 6.5 CF, 4.2 NHF, 1.7 20 957 4 <td< th=""><th>obtained</th><th>composition (g)</th><th>volume (cm³)</th><th>temperature (°C)</th><th>$(K h^{-1})$</th><th>temperature (°C)</th><th></th></td<>	obtained	composition (g)	volume (cm ³)	temperature (°C)	$(K h^{-1})$	temperature (°C)	
Ns, MB-Ef, 5.5 NB, 7.18 MHF, 50 957 4 300 Cares, third, tark,	Na, NiFeF, 5.3 FOL; J. JOM4, HF; 50 957 4 Na, NiAIF, 6.5 NiF, J. SA, SAFF, 8.5 NaHF, 50 957 4 Na, NiAIF, 6.5 NiF, J. SAFF, 8.5 NaHF, 50 957 4 Na, ZMCF, 6.5 NiF, J. SCFF, 8.5 NaHF, 40 957 4 Na, ZMCF, 6.7 ZnF, 7.5 CF, 8.5 NaHF, 40 957 4 Na, ZMCF, 6.7 ZnF, 7.5 OF b0L, 20 957 4 Na, CF, 6.7 ZnF, 7.5 OF b0L, 20 957 4 Na, CF, 6.6 CF, J. NH, HF, 20 957 4 Na, CF, 6.6 CF, J. SNH, HF, 20 957 4 Na, CF, 6.6 CF, J. SNH, HF, 20 957 4 Nb, C, F, N 6.6 CF, J. SNH, HF, 20 957 4 (Ba, Pb) N(F, C), 3.0 NH, HF, 20 957 4 (Ba, Pb) CG, F, N 6.6 CF, J. SNH, HF, 20 957 4 (Ba, Pb) CG, F, N 3.0 NH, HF, 30 1000 4 <td>$Na_2 CoFeF_7$</td> <td>1.3 CoF₂, 1.5 FeF₃, 1.7 NaHF₂,</td> <td>20</td> <td>870</td> <td>10</td> <td>300</td> <td>Large, pinkish-brown</td>	$Na_2 CoFeF_7$	1.3 CoF ₂ , 1.5 FeF ₃ , 1.7 NaHF ₂ ,	20	870	10	300	Large, pinkish-brown
	Na, NHFEF, 6.5 MFr, 7.8 FFr, 8.5 NaHF, 50 957 4 Na, ZmCrF, 6.5 MFr, 7.8 FFr, 8.5 NaHF, 50 957 4 Na, ZmCrF, 6.5 MFr, 7.5 CFr, 8.5 NaHF, 90 957 4 Na, ZmCrF, 6.5 MFr, 7.5 CFr, 8.5 NaHF, 90 957 4 Na, ZmCrF, 6.7 MFr, 7.5 CFr, 8.5 NaHF, 90 957 4 Na, ZmCrF, 6.7 MFr, 7.5 CFr, 8.5 NaHF, 90 957 4 NacrE, 0.7 Tesped, 8.1 MHFr, 20.0 PbCl, 20 957 4 NacrE, 6.6 CFr, 5.1 RbCl, 4.2 RbF, 20 957 4 $\beta RbCrF,$ 6.8 CFr, 5.1 RbCl, 4.2 RbF, 20 957 4 $\beta RbCrF,$ 6.8 CFr, 5.1 RbCl, 4.2 RbF, 20 957 4 $\beta RbCrF,$ 6.6 CFr, 6.3 RbF, 20.0 PbCl, 1 20 957 4 $\beta Rb,$ Cr, Fr, 6.6 CFr, 6.3 RbF, 20.0 PbCl, 1 20 957 4 $\beta Rb,$ Cr, Fr, 6.6 CFr, 6.3 RbF, 20.0 PbCl, 1 20 957 4 $\beta Rb,$ Cr, Fr, <		$3.5 \text{ PbCl}_2, 2.0 \text{ NH}_4 \text{HF}_2$					crystals, intergrown
17.5 PGC1, 8 NH, HF, 50 957 4 300 Continue Science Na, NAJEr, 6.5 NF, 5.5 AF, 5.5 AHF, 5.5	$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Na ₂ NiFeF,	6.5 NiF_2 , 7.8 FeF ₃ , 8.5 NaHF ₂	50	957	4	300	Large, shiny, dark-
	Na, NiAJE, 6.5 NF, 5.5 AF, 8.5 AHF, 1 5.6 AHF, 1 5.5 AHF, 8.7 MaHF, 1 5.0 957 4 Na, ZhCrF, 6.7 ShC1, 8 NH, HF, 17.5 PhC1, 8 MH, HF, NaCrF, 6.7 ShC1, 8.5 MHF, 1 40 957 4 Na, ZhCrF, 6.7 ShC1, 8.5 MHF, 120.0 PbC1, 20 957 4 NaCrF, 5.3 NaHF, 20.0 PbC1, 20 20 957 4 NaCrF, 5.6 CrF, 3.7 NaHF, 20.0 PbC1, 20 20 957 4 Rb, CrF, 6.6 CrF, 5.1 RbC1, 4.2 RbF, 20.0 PbC1, 20 20 970 10 Rb, CrF, 6.6 CrF, 6.3 RbF, 20.0 PbC1, 20 20 957 4 Rb, Cr, F, 6.6 CrF, 6.3 RbF, 20.0 PbC1, 20 20 957 4 Rb, Cr, F, 6.6 CrF, 6.3 RbF, 20.0 PbC1, 20 20 957 4 Rb, Cr, F, 6.6 CrF, 6.3 RbF, 20.0 PbC1, 20 20 957 4 (Ba, Pb)N(F, C)a, 5.0 NF, 114, Br, 20 20 957 4 (Ba, Pb)Cr, CJ, 5.0 NF, 14, Br, 25 NH, 4Fr, 20 20 957 4 (Ca, Pb), Cr, F, 7.9 CrF, 12.08 CsG1, 8 Br)C1, 20		17.5 PbCl_2 , 8 NH, HF					brown, intergrown
$ \begin{split} N_{4} NiAF, & 5 NiF_{4} S S AFF_{4} S S AFF_{4} & 50 & 57 & 4 & 300 & 72 Bag prominingrown \\ N_{4} ZnCF_{7} & 57 ZnF_{4} S S AHF_{7} & 0 & 957 & 4 & 300 & 7948 (Fig.5) \\ N_{4} ZnCF_{7} & 57 ZnF_{7} S S AHF_{7} & 200 PbC1_{3} & 201 PbC1_{3} & 201 PbC1_{4} & 200 PbC1_{3} & 201 PbC1_{4} & 200 PbC1_{3} & 201 PbC1_{4} & 201 PbC1_{3} & 201 PbC1_{4} &$	Na, NiAIF, 6.5 NF, 5.5 AF, 8.5 MHF, 50 957 4 Na, ZiaCF, 1.75 P6CI, 8 NH, HF, 0.72 KF, 8.5 MHF, 0.957 4 Na, ZiaCF, 6.72 kF, 7.5 CFF, 8.5 MHF, 0.957 4 NaCF, 6.72 kF, 7.5 CFF, 8.5 NH, HF, 0.957 4 NaCF, 6.72 kF, 7.5 CFF, 8.5 NH, HF, 0.957 4 NaCF, 6.6 CFF, 5.3 NHF, 7.00 PbCl, 20 957 4 g RbCF, 3.2 NH, 4 FF, 20 957 4 g RbCF, 3.0 NH, 4 FF, 20.0 PbCl, 20.957 4 g RbCF, 5.1 RbCI, 4.2 RbF, 20.9 957 4 g RbCF, 5.1 RbCI, 4.2 RbF, 20.9 957 4 g RbCF, 5.1 RbCI, 4.0 RbCI, 20.957 4 4 g RbCF, 5.1 RbCI, 4.0 RbF, 5.00 957 4 g RbCG, 5.0 RbCI, 5.0 RbCI, 5.0 RbCI, 5.0 RbCI, 5.0 957 4 g RbDC, 6.0 CFF, 14.0 BaF, 8.8 PbCI, 5.0 SCG RbF, 5.0 50 4 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td>crystals, up to 10 mm</td></t<>							crystals, up to 10 mm
	Na, NiAJF, 6.5 MF, 5.5 AJF, 8.5 MHF, 50 957 4 Na, ZhC/F, 6.7 MH, HF, 8.0 MH, HF, 9.0 9.7 4 Na, ZhC/F, 6.7 MH, HF, 8.0 MH, HF, 9.7 4 Na, ZhC/F, 6.7 MH, HF, 9.0 PbCl, 9.7 4 NaCrF, 6.7 CF, 3.7 NaHF, 20.0 PbCl, 20 957 4 NaCrF, 6.6 CF, 3.7 NaHF, 20.0 PbCl, 20 957 4 BC/F, 6.8 CF, 5.1 RbCl, 4.2 RbF, 20 870 10 $\beta RbCrF_A$ 6.8 CF, 5.1 RbCl, 4.2 RbF, 20 957 4 $\beta RbCrF_A$ 6.8 CF, 5.1 RbCl, 4.2 RbF, 20 957 4 $\beta RbCrF_A$ 6.8 CF, 6.3 RbF, 20.0 PbCl, 20 957 4 $\beta Rb, CI, F_A$ 6.6 CF, 1.6.3 RbF, 20.0 PbCl, 20 957 4 $\beta Rb, CI, F_A$ 6.6 CF, 1.6.3 RbF, 20.0 PbCl, 20 957 4 $\beta Rb, CI, F_A$ 6.6 CF, 1.6.3 RbF, 20.0 PbCl, 20 957 4 $\beta Rb, CI, F_A$ 6.6 CF							\times 10 mm \times 6 mm
	Na, ZnCrF, 17.5 PbCl , 8 NH, HF, 6.7 ZnF, 15. GrF, 8.5 NaHF, 12.00 PbCl, 17.5 NaHF, 12.00 PbCl, 20 957 4 NaCrF, 6.7 ZnF , 15. GrF, 8.5 NaHF, 12.00 PbCl, 20 957 4 NaCrF, 6.5 CrF , 3.7 NaHF, 12.00 PbCl, 20 957 4 7.2 NH , HF, 5.3 NH , HF, 20 870 10 $\beta \text{ RbCrF}_4$ 6.8 CrF , 5.1 RbCl, 4.2 RbF, 20 870 10 $\beta \text{ RbCrF}_4$ 6.8 CrF , 5.1 RbCl, 4.2 RbF, 20 870 10 $\beta \text{ RbCrF}_4$ 6.8 CrF , 6.3 RbF, 20.0 PbCl, 1 20 957 4 $\beta \text{ Rb}$, Ca, Fi, $3.1 \text{ NH}_4 \text{ HF}_3$ 20 957 4 $\beta \text{ Rb}$, Ca, Fi, 6.5 Rb , 3.0 NF_5 , 10.0 BaT_5 , 8.6 PbT_5 , 200 PbC_1 , 200 Pb_1 , $200 P$	$Na_2 NiAlF_7$	6.5 NiF ₂ , 5.5 AlF ₃ , 8.5 NaHF ₂ ,	50	957	4	300	Pale green intergrown
	Na, ZnCrF, 6.7 ZnF, 7.5 CrF, 8.5 NaHF, 40 957 4 NaCrF, 6.7 ZnF, 7.5 CrF, 8.5 NaHF, 120.0 PbCl, 20 957 4 NaCrF, 6.5 CrF, 5.1 NaHF, 120.0 PbCl, 20 957 4 8.6 CrF, 5.1 NbCl, 4.2 RbF, 20 870 10 $8.b$ CrF, 5.1 NbCl, 4.2 RbF, 20 870 10 $8.b$ Cr, F_1 6.6 CrF, 6.3 RbF, 20.0 PbCl, 20 870 10 $8.b$ Cr, F_1 6.6 CrF, 6.3 RbF, 20.0 PbCl, 20 957 4 $8.b$ Thi, 10.0 BaF, 8.6 PbF, 20 957 4 8.6 Cr, 16.3 NH, $4.F_3$ 20 957 4 8.6 PbCl, 3.3 NH, $4.F_3$ 20 957 4 8.6 PbCl, 13.5 NH, $4.F_3$ 20 957 4 8.6 PbCl, 13.5 NH, $4.F_3$ 50 1000 4 8.6 PbCl, 13.5 NH, $4.F_3$ 50 860 4 8.8 PbCl, 13.5 NH, $4.F_3$ 50 860 4 8.6 PbCl, 13.5 NH, $4.F_3$ 50		17.5 PbCl ₂ , 8 NH ₄ HF ₂					crystals (Fig. 5)
NG/F, $5.2 \mathrm{NH}_{\mathrm{s}} \mathrm{Hr}_{\mathrm{s}}^{2}$ $9.3 \mathrm{NH}_{\mathrm{s}} \mathrm{Hr}_{\mathrm{s}}^{2}$ $1.0 \mathrm{mot} \mathrm{NG} \mathrm{S} \mathrm{cm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{s}}^{2}$ $1.0 \mathrm{NG} \mathrm{S} \mathrm{cm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{s}}^{2}$ $1.0 \mathrm{NG} \mathrm{S} \mathrm{cm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{s}}^{2}$ $1.0 \mathrm{NG} \mathrm{S} \mathrm{cm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{sm}}^{2} \mathrm{sm}_{\mathrm{s}}^{2} \mathrm{sm}_{\mathrm{sm}}^{2} \mathrm{sm}_{\mathrm{sm}}^{2} $	NaCFF ₄ 17.5 PbC1, 8 NH ₄ HF ₄ 20.0 PbC1 ₂ , 20 957 4 3.2 NH ₄ HF ₄ 5.6 CrF ₃ , 3.7 NaHF ₄ , 20.0 PbC1 ₄ 20 870 10 β RbCrF ₄ 6.8 CrF ₃ , 5.1 RbCi, 4.2 RbF, 20.0 870 10 β RbCrF ₄ 6.8 CrF ₁ , 6.3 RbF, 20.0 PbC1 ₃ 20 870 10 β Rb ₂ Cr ₄ F ₁ 6.6 CrF ₁ , 6.3 RbF, 20.0 PbC1 ₃ 20 957 4 β Rb ₂ Cr ₄ F ₁ 6.6 CrF ₁ , 6.3 RbF, 20.0 PbC1 ₃ 20 957 4 β Rb ₂ Cr ₄ F ₁ 6.6 CrF ₁ , 6.3 RbF, 20.0 PbC1 ₃ 20 957 4 β Rb ₂ Cr ₄ F ₁ 6.6 CrF ₁ , 6.3 RbF, 20.0 PbC1 ₃ 20 957 4 β Rb PbC ₁ 3.1 NH ₄ HF ₃ 50 50 1000 4 β Rb PbC ₁ 50 NiF ₄ , 10.0 RaF ₁ , 8.6 PbF ₂ 50 860 4 β St PbC ₁ , 5.0 NH ₄ HF ₃ 50 50 50 50 60 4 β St PbC ₂ , 4.0 NH ₄ HF ₃ 5	$Na_2 ZnCrF_{\gamma}$	6.7 ZnF ₂ , 7.5 CrF ₃ , 8.5 NaHF ₂ ,	40	957	4	300	Dark green pseudocubes
MaCrF ₄ 66 CrF ₁ , 3.7 MaHF ₁ , 20.0 PbC1, 20 957 4 300 Face drangement frageration $3.2 NH_4 HF_3$ $3.2 NH_4 HF_3$ $3.2 NH_4 HF_3$ $20 NH_4 HF_3$ $10 mm X O_5$ mm, and platelets $\beta RbCrF_4$ $68 CrF_3$, $5.3 RbC1, 4.2 RbF_4$ $20 $ 957 4 300 $Pacent fitnous$ $\beta Rb_3 Cr_4 Fr,$ $66 CrF_1$, $6.3 RbF_2 O_3 D^3 Cr_4$ $20 $ 957 4 300 $Pacent fitnous$ $3.1 NH_4 HF_3$ $3.1 NH_4 HF_3$ $3.1 NH_4 HF_3$ $3.0 NF_3$, $10.0 BaF_2$, $8.6 PbF_3$, $20 $ 957 4 300 $Caceo fitnom toplatelets (B_4, Pb)N(F, C)_4 50 NF_3, 10.0 BaF_2, 8.6 PbF_3, 50 1000 4 600 Careo fitnom x 2.0 mm X (B_4, Pb)N(F, C)_4 50 NF_3, 10.0 BaF_3, 8.6 PbF_3, 50 1000 4 600 20 mm X 2.0 mm X (B_4, Pb)N(F, C)_4 50 NF_3, 10.0 BaF_3, 8.6 PbF_3, 50 1000 4 50 100 10 mm X 2.0 mm X (B_4, Pb)CoF_4, C)_4 50 NF_3, 10.0 M_4 HF_5 50 $	NaCrF ₄ 6.6 CrF ₁ , 3.7 NaHF ₁ , 20.0 PbCl ₃ , 20 957 4 B. BbCrF ₄ 5.2 NH ₄ , HF ₃ β Rb ₄ Cr, F ₁ 6.8 CrF ₃ , 5.1 RbCl, 4.2 RbF, 20 870 10 β Rb ₄ Cr, F ₁ 6.6 CrF ₁ , 6.3 RbF, 20.0 PbCl ₃ , 20 957 4 Rb ₄ Cr, F ₁ 6.6 CrF ₁ , 6.3 RbF, 20.0 PbCl ₃ , 20 957 4 (Ba, Pb)N(F, Cl) ₄ 5.0 NiF ₄ , 10.0 BaF ₂ , 8.6 PbF ₃ , 20 20 957 4 $(Ba, Pb)N(F, Cl)_4$ 5.0 NiF ₄ , 10.0 BaF ₂ , 8.6 PbF ₃ , 50 860 4 $(Ba, Pb)Co(F, Cl)_4$ 6.0 CoF ₂ , 14.0 BaF ₂ , 8.6 PbF ₃ , 50 860 4 $(Ba, Pb)Co(F, Cl)_4$ 6.0 CoF ₂ , 14.0 BaF ₂ , 8.6 PbF ₃ , 20 954 7 $(Ca, Pb)Cr4, F1, 2.5 PbCl3, 3.5 NH4, HF3 (Ca, Pb)_{2}Cr4,6F1, 2.6 CrF4, 4.0 NH4, HF3$		17.5 PbCl ₂ , 8 NH ₄ HF ₂					at surface of melt
$ \begin{array}{cccccc} 3.2 \operatorname{Nit}_{4}\operatorname{HF}_{7} & & & & & & & & & & & & & & & & & & &$	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$NaCrF_4$	6.6 CrF_3 , 3.7 NaHF_2 , 20.0 PbCl_2 ,	20	957	4	300	Faceted transparent
$ \beta \text{ RbCrE}_{4} = (3 \text{ CrE}_{7}, 5 \text{ I RbCl}, 4.2 \text{ RbF}, 20 = 870 = 10 = 300 = 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, \text{ and } 0.0 \text{ mm} \times 0.5 \text{ mm}, 0.5 \text{ mm} \times 0.5 \text$	$ \beta \text{ RbCrF}_{4} = \begin{cases} 6.8 \text{ CrF}_{3}, S.1 \text{ RbCI}, 4.2 \text{ RbF}, & 20 & 870 & 10 \\ 3.0 \text{ NH}_{4} \text{ HF}_{3} \\ \text{Rb}_{3} \text{ Cr}_{4} \text{ F}_{1}, & 6.6 \text{ CrF}_{3}, 6.3 \text{ RbF}, 20.0 \text{ PbCI}_{1}, & 20 & 957 & 4 \\ 3.1 \text{ NH}_{4} \text{ HF}_{3} \\ (Ba, Pb) \text{ Ni}(F, C)_{4} = \begin{cases} 5.0 \text{ NiF}_{3}, 10.0 \text{ BaF}_{2}, 8.6 \text{ PbF}_{3}, & 50 & 1000 & 4 \\ 4.25 \text{ PbCI}_{1}, 3.5 \text{ NH}_{4} \text{ HF}_{3} \\ (Ba, Pb) \text{ Co}(F, C)_{4} = \begin{cases} 6.0 \text{ CoF}_{3}, 14.0 \text{ BaF}_{3}, 8.6 \text{ PbF}_{3}, & 50 & 860 & 4 \\ 3.5 \text{ NH}_{4} \text{ HF}_{3} \\ (Cs, Pb) \text{ CrF}_{4} & 3.8 \text{ PbF}_{2}, 4.0 \text{ NH}_{4} \text{ HF}_{3} \\ (Cs, Pb)_{2} \text{ Cr}_{4.6} \text{ F}_{17} \\ (Cs, Pb)_{2} \text{ Cr}_{4.6} \text{ F}_{17} \end{cases} $		3.2 NH HF 3					rods, up to 3.5 mm X
$ \beta \text{ BCF}_{\text{c}} = 6.8 \text{ CF}_{\text{c}}, 5.1 \text{ BC}, 4.2 \text{ Rb}, 20 \text{ B7}, 0 = 300 300 5 results of the mititions and the set if the se$	$\beta \text{ RbCrF}_{4} = 6.8 \text{ CrF}_{3}, 5.1 \text{ RbCI}, 4.2 \text{ RbF}, = 20 = 870 = 10$ $3.0 \text{ NH}_{4} \text{ HF}_{3} = 3.0 \text{ NH}_{4} \text{ HF}_{3} = 3.0 \text{ NH}_{4} \text{ HF}_{3} = 20.0 \text{ PbCI}, = 20 = 957 = 4$ $Rb_{3} \text{ Cr}_{5} \text{ F}_{1}, = 6.6 \text{ CrF}_{3}, 6.3 \text{ RbF}, 20.0 \text{ PbCI}_{1}, = 20 = 957 = 4$ $(Ba, Pb) \text{ Ni}(F, C)_{4} = 5.0 \text{ NiF}_{3}, 10.0 \text{ BaF}_{2}, 8.6 \text{ PbF}_{3}, = 50 = 1000 = 4$ $(Ba, Pb) \text{ Co}(F, C)_{4} = 5.0 \text{ NiF}_{3}, 10.0 \text{ BaF}_{2}, 8.6 \text{ PbF}_{3}, = 50 = 860 = 4$ $(Ba, Pb) \text{ Co}(F, C)_{4} = 6.0 \text{ CoF}_{3}, 14.0 \text{ BaF}_{2}, 8.6 \text{ PbF}_{2}, = 50 = 860 = 4$ $(Cs, Pb) \text{ CrF}_{4} = 7.9 \text{ CrF}_{3}, 12.08 \text{ CsCI}, 8.8 \text{ PbC}_{1}, = 20 = 954 = 7$ $(Cs, Pb)_{2} \text{ Cr}_{4.6} \text{ F}_{1}, = 8.8 \text{ PbF}_{2}, 4.0 \text{ NH}_{4} \text{ HF}_{3} = 20 = 954 = 7$							$1.0 \text{ mm} \times 0.5 \text{ mm}$, and
$ \begin{tabular}{lllllllllllllllllllllllllllllllllll$	$ \beta \text{RbCrF}_{4} = 6.8 \text{CrF}_{3}, 5.1 \text{RbCl}, 4.2 \text{RbF}, = 20 = 870 = 10 \\ 3.0 \text{ MH}_{4}\text{HF}_{2} = 6.6 \text{CrF}_{3}, 6.3 \text{RbF}, 20.0 \text{PbCl}_{3}, = 20 = 957 = 4 \\ 3.1 \text{ NH}_{4}\text{HF}_{3} = 3.0 \text{ NH}_{3} = 3.0 \text{ NH}_{4}\text{HF}_{3} = 3.0 \text{ NH}_{4}\text{HF}_{3} = 3.0 \text{ NH}_{4} $							platelets
	$\begin{array}{lcl} 3.0 \ \mathrm{NH}_4 \mathrm{HF}_2 \\ \mathrm{Rb}_2 \mathrm{Cr}_5 \mathrm{F}_1, & 6.6 \ \mathrm{CrF}_1, 6.3 \ \mathrm{RbF}, 20.0 \ \mathrm{PbCI}_1, & 20 & 957 & 4 \\ & 3.1 \ \mathrm{NH}_4 \mathrm{HF}_2 \\ & 3.1 \ \mathrm{NH}_4 \mathrm{HF}_2 \\ \mathrm{(Ba, \ Pb) \ Ni(F, \ C)}_4 & 5.0 \ \mathrm{NiF}_4, 10.0 \ \mathrm{BaF}_7, 8.6 \ \mathrm{PbF}_5, & 50 & 1000 & 4 \\ & 42.5 \ \mathrm{PbCI}_2, 3.5 \ \mathrm{NH}_4 \mathrm{HF}_2 \\ & 42.5 \ \mathrm{PbCI}_2, 3.5 \ \mathrm{NH}_4 \mathrm{HF}_2 \\ \mathrm{(Ba, \ Pb) \ Co}_6 (F, \ C)_4 & 6.0 \ \mathrm{CoF}_7, 14.0 \ \mathrm{BaF}_2, 8.6 \ \mathrm{PbF}_2, & 50 & 860 & 4 \\ & 4 & 38.5 \ \mathrm{PbCI}_2, 3.5 \ \mathrm{NH}_4 \mathrm{HF}_2 \\ & (G^*, \ Pb) \ \mathrm{CrF}_4 & 7.9 \ \mathrm{CrF}_4, & 12.08 \ \mathrm{CsC}_1, 8.8 \ \mathrm{PbCI}_1, & 20 & 954 & 7 \\ & 4 & 38.5 \ \mathrm{PbF}_2, 4.0 \ \mathrm{NH}_4 \mathrm{HF}_2 \\ & (G^*, \ Pb)_2 \ \mathrm{Cr}_{4,6} \mathrm{F}_1, & & & & & & & & & & \\ \end{array}$	$\beta \text{ RbCrF}_{4}$	$6.8 \mathrm{CrF}_3, 5.1 \mathrm{RbCl}, 4.2 \mathrm{RbF},$	20	870	10	. 300	Green, fibrous
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$Rb_{2}Cr_{6}F_{1,1}$ 6.6 CrF_{1,6.3} RbF, 20.0 PbCl_{1} 20 957 4 $(Ba, Pb)Ni(F, Cl)_{4}$ $5.0 NiF_{4}, 10.0 BaF_{2}, 8.6 PbF_{3}, 8.0$ 50 1000 4 $(Ba, Pb)Ni(F, Cl)_{4}$ $5.0 NiF_{4}, 10.0 BaF_{2}, 8.6 PbF_{3}, 8.0$ 50 1000 4 $(Ba, Pb)Ni(F, Cl)_{4}$ $5.0 NiF_{4}, 14F_{3}$ 50 80 4 $(Ba, Pb)Co(F, Cl)_{4}$ $6.0 CoF_{3}, 14.0 BaF_{2}, 8.6 PbF_{2}, 50$ 800 4 $(Ba, Pb)Co(F, Cl)_{4}$ $6.0 CoF_{3}, 14.0 BaF_{2}, 8.6 PbF_{2}, 50$ 800 4 $(Ba, Pb)Co(F, Cl)_{4}$ $6.0 CoF_{3}, 14.0 BaF_{2}, 8.6 PbF_{2}, 70$ 50 860 4 $(Cs, Pb)Co(F, Cl)_{4}$ $6.0 CoF_{3}, 14.0 BaF_{2}, 8.6 PbF_{2}, 70$ 50 860 4 $(Cs, Pb)_{2}Cr_{4.6}F_{1,1}$ $8.8 PbF_{2}, 4.0 NH_{4}HF_{2}$ 20 954 7 $(Cs, Pb)_{2}Cr_{4.6}F_{1,1}$ $8.8 PbF_{2}, 4.0 NH_{4}HF_{2}$ 20 954 7		$3.0 \text{ NH}_{4} \text{HF}_{2}$					β RbCrF ₄ covering the
$ Rb_{2}Cr_{4}F_{1}, \qquad 6.6CrF_{1}, 6.3RbF, 20.0PbCl_{1}, \qquad 20 \qquad 957 \qquad 4 \qquad 300 \qquad Clumps of brownish \\ 3.1NH_{4}HF_{3} \\ \qquad 3.1NH_{4}HF_{3} \\ (B_{4},P)N(F,C)_{4} \qquad 5.0NF_{4}, 10.0BaF_{2}, 8.6PbF_{3}, \qquad 50 \qquad 1000 \qquad 4 \qquad 600 \qquad Clumps of brownish \\ (B_{4},P)N(F,C)_{4} \qquad 5.0NF_{4}, 10.0BaF_{2}, 8.6PbF_{3}, \qquad 50 \qquad 1000 \qquad 4 \qquad 600 \qquad 8mm (Fig. 6) \\ (B_{4},P)Co(F,C)_{4} \qquad 5.0NF_{4}, 14,P_{3} \\ (B_{4},P)Co(F,C)_{4} \qquad 6.0CoF_{3}, 14.0BaF_{2}, 8.6PbF_{3}, \qquad 50 \qquad 1000 \qquad 4 \qquad 600 \qquad 8mm (Fig. 6) \\ (B_{4},P)Co(F,C)_{4} \qquad 6.0CoF_{3}, 14.0BaF_{2}, 8.6PbF_{3}, \qquad 50 \qquad 1000 \qquad 4 \qquad 600 \qquad 8mm (Fig. 6) \\ (B_{4},P)Co(F,C)_{4} \qquad 6.0CoF_{3}, 14.0BaF_{3}, 8.6PbF_{3}, \qquad 50 \qquad 860 \qquad 4 \qquad 300 \qquad 8mm (Fig. 6) \\ (C_{5},P)C(F_{6} \qquad 7,9Cr_{5},12.08CSC, 8.8PbC(_{3},2,3NH_{4},HF_{3} \qquad 0 \\ (C_{5},P)C(F_{6} \qquad 7,9Cr_{6},F_{1}, \qquad 20 \qquad 954 \qquad 7 \qquad 350 \qquad 1000 \qquad 1000 \\ (C_{5},P)C(F_{6},F_{1}, \qquad 0,2mm \times 0.5mm $	Rb ₂ Cr ₅ F ₁ , 6.6 CrF ₃ , 6.3 RbF, 20.0 PbCl ₃ , 20 957 4 (Ba, Pb)Ni(F, Cl) $3.1 NH_4 HF_3$ $3.1 NH_4 HF_3$ $4.6 FF_3$, $8.6 PbF_3$, $8.6 PbF_3$, $8.0 1000$ 4 (Ba, Pb)Cq(F, Cl) ₄ $5.0 NiF_3$, $10.0 BaF_2$, $8.6 PbF_3$, 50 50 1000 4 (Ba, Pb)Cq(F, Cl) ₄ $6.0 CoF_2$, $14.0 BaF_2$, $8.6 PbF_3$, 50 860 4 (Ba, Pb)Cq(F, Cl) ₄ $6.0 CoF_2$, $14.0 BaF_2$, $8.6 PbF_3$, 50 860 4 (Ba, Pb)Cq(F, Cl) ₄ $6.0 CoF_2$, $14.0 BaF_2$, $8.6 PbF_3$, 50 860 4 (Cs, Pb)Cq, F_1 , $7.9 CrF_3$, $12.08 CsCl, 8.8 PbCl_3$, 20 954 7 (Cs, Pb) ₂ Cr _{4,6} F ₁ , $8.8 PbF_2$, $4.0 NH_4 HF_2$ 20 954 7							surface of the melt
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		$Rb_2Cr_5F_{17}$	6.6 CrF ₃ , 6.3 RbF, 20.0 PbCl ₃ ,	20	957	4	300	Clumps of brownish
$ (Ba, Pb)Ni(F, CI)_4 S.ONiF_3, 10.0 BaF_3, 8.6 PbF_3, S0 P1, 1000 P1, 8.6 PbF_3, S0 P1, 1000 P1, 8.0 P1, 9.0 P1, 1000 $	(Ba, Pb)Ni(F, Cl)_45.0 NiF_3, 10.0 BaF_2, 8.6 PbF_3, 42.5 PbCl_2, 3.5 NH_4 HF_35010004(Ba, Pb)Co(F, Cl)_46.0 CoF_3, 14.0 BaF_3, 8.6 PbF_3, 38.5 PbCl_2, 3.5 NH_4 HF_3508604(Ba, Pb)Co(F, Cl)_46.0 CoF_3, 14.0 BaF_3, 8.6 PbF_3, 38.5 PbCl_2, 3.5 NH_4 HF_3508604(Cs, Pb) CrF_47.9 CrF_3, 12.08 CsCl, 8.8 PbCl_2, 3.8.8 PbF_2, 4.0 NH_4 HF_3209547(Cs, Pb)_2 Cr4.6 F_1, (Cs, Pb)_2 Cr4.6 F_1,8.8 PbF_2, 4.0 NH_4 HF_3209547		3.1 NH ^A HF ₂					green fibres at the
	(Ba, Pb)Ni(F, Cl),5.0 NiF ₂ , 10.0 BaF ₂ , 8.6 PbF ₂ ,5.010004(Ba, Pb)Co(F, Cl),5.0 NiF ₂ , 14.0 BaF ₂ , 8.6 PbF ₂ ,508604(Ba, Pb)Co(F, Cl),6.0 CoF ₂ , 14.0 BaF ₂ , 8.6 PbF ₂ ,508604(Cs, Pb) CrF ₄ 7.9 CrF ₃ , 12.08 CsCI, 8.8 PbCl ₂ ,509547and $(Cs, Pb)_2 Cr_{4.6} F_{17}$ 8.8 PbF ₂ , 4.0 NH ₄ HF ₂ 209547							melt surface. At the
	(Ba, Pb)Ni(F, Cl),5.0 NiF ₄ , 10.0 BaF ₄ , 8.6 PbF ₂ ,5010004(Ba, Pb)Co(F, Cl),6.0 CoF ₂ , 14.0 BaF ₄ , 8.6 PbF ₂ ,508604(Ba, Pb)Co(F, Cl),6.0 CoF ₂ , 14.0 BaF ₄ , 8.6 PbF ₂ ,508604(Cs, Pb)CrF ₄ 7.9 CrF ₁ , 3.5 NH ₄ HF ₃ 508604(Cs, Pb)CrF ₄ 7.9 CrF ₁ , 12.08 CsCl, 8.8 PbCl ₂ ,209547andand8.8 PbF ₂ , 4.0 NH ₄ HF ₂ 209547							crucible walls, dark
$ (Ba, Pb)Ni(F, C)_{4} 5.0NiF_{4}, 10.0 BaF_{4}, 8.6 PbF_{4}, 50 1000 4 600 2.0 \text{mm} \times 2.0 \text{m} \times 2.0 \text{mm} \times 2.0 \text{mm} \times 2.0 \text{m} \times 2.0$	(Ba, Pb)Ni(F, Cl)_45.0 NiF_3, 10.0 BaF_2, 8.6 PbF_3,5010004(Ba, Pb)Co(F, Cl)_46.0 CoF_3, 14.0 BaF_2, 8.6 PbF_2,508604(Ba, Pb)Co(F, Cl)_46.0 CoF_3, 14.0 BaF_2, 8.6 PbF_2,508604(Cs, Pb) CrF_47.9 CrF_3, 12.08 CsCl, 8.8 PbCl_2,309547(Cs, Pb) CrF_47.9 CrF_3, 4.0 NH_4 HF_2209547(Cs, Pb)_2 Cr_4, F_1,8.8 PbF_2, 4.0 NH_4 HF_2209547							green crystals which
	(Ba, Pb)Ni(F, Cl),5.0 NiF_3, 10.0 BaF_2, 8.6 PbF_3,5010004(Ba, Pb)Cq(F, Cl),42.5 PbCl_2, 3.5 NH_4 HF_3508604(Ba, Pb)Cq(F, Cl),6.0 CoF_2, 14.0 BaF_2, 8.6 PbF_2,508604(Ba, Pb)Cq(F, Cl),6.0 CoF_3, 14.0 BaF_2, 8.6 PbF_2,508604(Cs, Pb) CrF_47.9 CrF_3, 12.08 CsCl, 8.8 PbCl_2,209547and8.8 PbF_2, 4.0 NH_4 HF_2209547							cleaved easily, up to
	(Ba, Pb)Ni(F, Cl)_45.0 NiF_2, 10.0 BaF_2, 8.6 PbF_3,5.010004(Ba, Pb)Cq(F, Cl)_46.0 CoF_2, 14.0 BaF_2, 8.6 PbF_2,5.08604(Ba, Pb)Cq(F, Cl)_46.0 CoF_2, 14.0 BaF_2, 8.6 PbF_2,5.08604(Cs, Pb) CrF_47.9 CrF_3, 12.08 CsCl, 8.8 PbCl_2,2.09547and8.8 PbF_2, 4.0 NH_4 HF_22.09547(Cs, Pb) 2Cr4.6 F178.8 PbF_2, 4.0 NH_4 HF_22.09547							$2.0 \text{ mm} \times 2.0 \text{ mm} \times$
	(Ba, Pb)Ni(F, Cl)_45.0 NiF_2, 10.0 BaF_2, 8.6 PbF_3,5010004(Ba, Pb)Cq(F, Cl)_46.0 CoF_2, 14.0 BaF_2, 8.6 PbF_2,508604(Ba, Pb)Cq(F, Cl)_46.0 CoF_2, 14.0 BaF_2, 8.6 PbF_2,508604(Cs, Pb) CrF_47.9 CrF_3, 12.08 CsCl, 8.8 PbCl_2,209547and8.8 PbF_2, 4.0 NH_4 HF_2209547(Cs, Pb) $_2$ Cr4.6 F178.8 PbF_2, 4.0 NH_4 HF_2209547							8 mm (Fig. 6)
		$(Ba, Pb)Ni(F, Cl)_a$	5.0 NiF, 10.0 BaF, 8.6 PbF,	50	1000	4	600	A layer of light
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	(Ba, Pb)Co(F, Cl)_4 $6.0 \operatorname{CoF}_3, 14.0 \operatorname{BaF}_2, 8.6 \operatorname{PbF}_2, 50$ 860 4 $38.5 \operatorname{PbCl}_3, 3.5 \operatorname{NH}_4 \operatorname{HF}_3$ $38.5 \operatorname{PbCl}_3, 3.5 \operatorname{NH}_4 \operatorname{HF}_3$ $79 \operatorname{CrF}_3, 12.08 \operatorname{CsCl}, 8.8 \operatorname{PbCl}_2, 20$ 954 7 $(Cs, Pb) \operatorname{CrF}_4$ $7.9 \operatorname{CrF}_3, 12.08 \operatorname{CsCl}, 8.8 \operatorname{PbCl}_2, 20$ 954 7 and $8.8 \operatorname{PbF}_2, 4.0 \operatorname{NH}_4 \operatorname{HF}_2$ $(Cs, Pb)_2 \operatorname{Cr}_4, 6 \operatorname{F}_1, 7$ $79 \operatorname{Cr}_4, 6 \operatorname{F}_1, 7$		42.5 PbC1 ₂ , 3.5 NH ₄ HF ₂					green rods at the
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{llllllllllllllllllllllllllllllllllll$							melt surface, up to
$ \begin{array}{cccccc} (Ba, Pb)Co(F, CI)_4 & 6.0 CoF_2, 14.0 BaF_2, 8.6 PbF_2, & 50 & 860 & 4 & 300 & Small purple rods, up \\ & 38.5 PbCl_2, 3.5 NH_4 HF_3 & & & & & & & & & & & & & & & & & & &$	$\begin{array}{llllllllllllllllllllllllllllllllllll$							$6 \text{ mm} \times 2 \text{ mm} \times 0.5 \text{ mm}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$(Ba, Pb)Co(F, CI)_4$	6.0 CoF_2 , 14.0 BaF ₂ , 8.6 PbF ₂ ,	50	860	4	300	Small purple rods, up
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{llllllllllllllllllllllllllllllllllll$		38.5 PbCl,, 3.5 NH, HF,					to $3 \text{ mm} \times 0.5 \text{ mm} \times$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{llllllllllllllllllllllllllllllllllll$		с -					0.2 mm
and $8.8 \text{ PbF}_2, 4.0 \text{ NH}_4 \text{HF}_2$ (Cs, Pb) $_2 \text{CJ}_4, 6 \text{F}_{17}$ B.8 PbF}2, 4.0 NH_4 HF}2 brownish-gradent, brownish-gradent, brownish-gradent platelets	and 8.8 PbF ₂ , 4.0 NH ₄ HF ₂ (Cs, Pb) ₂ Cr _{4.6} F _{1.7}	(Cs, Pb) CrF ₄	7.9 CrF ₃ , 12.08 CsCl, 8.8 PbCl ₂ ,	20	954	7	350	Long, brownish-green
(Cs, Pb) ₂ Cr _{4.6} F ₁₇ Irregular, dark, brownish-green platelets	(Cs, Pb) ₂ Cr _{4.6} F ₁₇	and	8.8 PbF_2 , $4.0 \text{ NH}_4 \text{ HF}_2$					needles
brownish-green platelets		$(Cs, Pb)_2 Cr_{4.6} F_{17}$						Irregular, dark,
platelets								brownish-green
								platelets

For identification purposes, a thesis by Tressaud [23] has been particularly helpful. He prepared powder specimens by reacting the purified components in sealed tubes of platinum or gold, and characterized the compounds by X-ray powder patterns. He also determined melting points and, in some cases, magnetic transition temperatures.

2. Chemicals and equipment

The chemicals used were: Koch Light FeF_3 and MnF_2 ; BDH Laboratory Reagent grade $NaHF_2$, BaF_2 , KHF_2 , CsF, CsCl, RbF, NH_4 HF_2 and $PbCl_2$; BDH "Optran" AlF₃, CoF₂, NiF₂ and ZnF₂; BDH "Analar" CsCl; BDH "Extra Pure" PbF₂; and Cambrian Chemicals CrF₃. Platinum crucibles of 0.5 mm wall thickness with close-fitting lids were used. The crucibles were heated in D-shaped sillimanite muffles to protect the crusilite elements from attack by flux vapours [24].

3. Experimental details

The materials were weighed, mixed, placed in crucibles and the lids fitted as closely as possible. The crucibles were placed on a layer of alumina powder in the sillimanite muffle and the entrance was blocked with refractory brick. The furnace was heated to the desired initial temperature and slow cooling was commenced at once.

The starting compositions and furnace programmes which produced the best crystals are given in Tables IIa and b.

4. Results

X-ray powder patterns of the crystals were compared with published data. When crystals could not be identified in this way, an empirical formula was derived from EPMA. The more reactive fluorides of the transition metals proved to be difficult subjects for EPMA since they did not polish well, had poor conductivity, and hydrolysed readily on exposure to air.

All the compounds contained iron hydrolysed in water, and mechanical methods of separation from the flux were thus necessary; accordingly, the crystals were broken out of the solid flux and scraped clean with a razor-blade, or the flux was "hot-drained" from the crucible while molten, by inverting the crucible and heating to a temperature above the eutectic.



Figure 1 Platelet of $KAlF_4$ (mm grid).

5. Notes on the crystals 5.1. KAIF₄

The crystals were colourless, transparent plates up to $4 \text{ mm} \times 4 \text{ mm} \times 2 \text{ mm}$, and were soft and easy to bend, like KFeF₄ [4]. Viewed perpendicularly to the surfaces, they were optically isotropic. They reacted with water, forming Al(OH)₃. One is shown in Fig. 1.

5.2. KMnF₃

The crystals were transparent, pale pink, with rectangular facets. The larger crystals contained flux inclusions, but some smaller ones (e.g. $2 \text{ mm} \times 2 \text{ mm} \times 3 \text{ mm}$) showed no strain and were free from visible inclusions.

5.3. Compounds in the system $FeF_3 - RbF - PbCl_2$

The starting compositions that produced the crystals indicated are shown in the triangular composition diagram (Fig. 2a). The crystals are described below.

5.3.1. RbFeF4

The previously reported composition for flux growth of RbFeF₄ contained FeF₃, RbCl and RbF [4]. The composition reported here contains FeF₃, RbF and PbCl₂, and yielded thin plates up to $15 \text{ mm} \times 15 \text{ mm}$, which were larger in area than those obtained earlier. They appeared twinned under the polarizing microscope, and this was



Figure 2 (a) Triangular composition diagram for the system $FeF_3 - RbF - PbCl_2$, showing starting compositions that produced the compounds indicated. (b) Triangular composition diagram for the system $FeF_3 - CsF - PbCl_2$, showing starting compositions that produced the compounds indicated.

confirmed by Laue back-reflection photographs. The twinning results from crystallographic transitions below the growth temperature [25].

5.3.2. Rb₂FeF₅

 Rb_2FeF_5 was obtained from composition 5, Table IIa, which produced also Rb_3FeF_6 . The crucible was "hot-drained" at 520°C. The crystals of Rb_2FeF_5 were faceted rods with rough surfaces, up to $3.5 \text{ mm} \times 2 \text{ mm} \times 1 \text{ mm}$. The rods were colourless and transparent; carefully selected crystals showed simultaneous extinction. The Mössbauer spectrum showed no sign of Fe^{2+} .

5.3.3. Rb₃FeF₆

This material could easily be distinguished from the transparent rods of $Rb_2 FeF_5$, which were also present, since it formed a layer of closely packed, milky crystals, each about 1.5 mm in all dimensions, at the crucible wall. Apparently, $Rb_3 FeF_6$ crystallized first, followed at a later stage by $Rb_2 FeF_5$. Under the polarizing microscope, it could be seen that extinction occurred. No crystallographic facets were evident.

EPMA indicated that the Rb:Fe molar ratio was 2.99:1, in good agreement with the formula Rb_3FeF_6 . X-ray powder pattern data are given in Table III.

5.3.4 αRb_x FeF₃ (0.18 < x < 0.29) The structure of this material is very similar to

TABLE III X-ray powder pattern data for Rb₃FeF₆

Intensity, estimated	$d_{\mathbf{obs}}(\mathbb{A})$	
VW	5.9	_
W	3.59	
VW	3.49	
VW	3.27	
VS	3.15	
VW	2.896	
VW	2.700	
W	2.571	
VW	2.337	
S	2.227	
S	1.823	
VW	1.776	

that of $\text{Rb}_2 \text{Fe}_5 \text{F}_{17}$ [26], and both closely resemble that of the tungsten bronze $\alpha M_x WO_3$. Thus it is very difficult to distinguish between $\alpha \text{Rb}_x \text{FeF}_3$ and $\text{Rb}_2 \text{Fe}_5 \text{F}_{17}$ by X-ray methods. The powder patterns have identical *d*-values and similar intensities except for a few of the weaker lines [26, 27].

The Rb_x FeF₃ crystals were obtained as black, shiny, brittle hexagonal rods (Fig. 3) when the starting temperature was 870° C, while lower starting temperatures (near 650° C) gave a platy habit. Mössbauer experiments showed that crystals of both habits contained Fe²⁺ and Fe³⁺ in a ratio corresponding to the formula Rb_xFeF₃ (0.18 < x < 0.29), or approximately RbF·FeF₂·3FeF₃. The X-ray powder pattern was in close agreement with that of Rb₀₂₈FeF₃ [27].



Figure 3 Rods of $Rb_x FeF_3$ (mm grid).

5.4. Compounds in the system FeF_3 -CsF-PbCl₂

The starting compositions that produced the crystals indicated are shown in the triangular composition diagram (Fig. 2b). Notes on the crystals follow.

5.4.1. CsFeF₄

Large, thin plates resulted from starting composition 5. They were transparent, purplish or brownish, and cleaved less readily than KFeF₄ and RbFeF₄. Thicker crystals of CsFeF₄, transparent and up to 1.5 mm thick, resulted from composition 6. Some are shown in Fig. 4. The X-ray powder pattern data are given in Table IV. Mössbauer experiments showed that no Fe²⁺ was present in the crystals.

5.4.2. Cs₃Fe₂F₉

Composition 7 produced a second phase in the form of colourless, triangular or hexagonal platelets up to $4 \text{ mm} \times 4 \text{ mm} \times 0.5 \text{ mm}$ at the melt surface, and also large thin sheets throughout the melt.



Figure 4 Platelets of CsFeF₄ (mm grid). 1452

TABLE IV X-ray powder patter data for CsFeF₄

Intensity, estimated	hkl	d_{obs} (Å)	d _{calc.} (A)
VW	010	6.580	6.56
VS	012	3.345	3.345
М	020	3.275	3.278
М	202	2.748	2.740
MW	212	2.539	2.533
MW	220	2.503	2.498
W	222	2.099	2.102
MW	004	1.944	1.944
MW	230	1.903	1.902
MW	214	1.682	1.680
VW	040	1.645	1.640
VW	234	1.360	1.360
$a_0 = 7.73 \text{ Å}, b_0 =$	6.56 Å,	$c_0 = 7.78 \text{\AA}$	

Since they reacted with water and were fragile, it was not possible to recover the sheets intact. EPMA (Table V) was in good agreement with the formula $Cs_3Fe_2F_9$ and showed very low impurity levels. This material had previously been prepared only as a powder, and the published unit cell dimensions and space group [28] were used to index the X-ray powder pattern obtained from single crystal material, which is given in Table VI. Mössbauer experiments showed that Fe^{2+} was almost certainly absent.

TABLE V Composition of $Cs_3Fe_2F_9$ confirmed by EPMA

	Formula requires (%)	EPMA indicates (%)
Cs	58.5	57.2
Fe	16.4	16.4
F	25.1	24.2
Pb		0.03
Cl		0.01

T.	A]	ΒL	Е	VI	X-ray	powder	pattern	data	for	$Cs_3Fe_2F_9$,
----	------------	----	---	----	-------	--------	---------	------	-----	---------------	---

hkil	d_{obs} (Å)	$d_{\text{calc}}(A)$
1013	3.66	3.66
1120	3.16	3.17
1014	3.06	3.06
0006	2.462	2.462
2023	2.395	2.397
1016	2.249	2.246
1017	1.974	1.970
$11\bar{2}6$	1.941	1.944
2133	1.910	1.911
3030	1.828	1.829
2240	1.585	1.584
3143	1.455	1.454
	$\begin{array}{c} h k il \\ \hline 1 0 \overline{1} 3 \\ 1 1 \overline{2} 0 \\ 1 0 \overline{1} 4 \\ 0 0 0 6 \\ 2 0 \overline{2} 3 \\ 1 0 \overline{1} 6 \\ 2 0 \overline{2} 3 \\ 1 0 \overline{1} 6 \\ 1 0 \overline{1} 7 \\ 1 1 \overline{2} 6 \\ 2 1 \overline{3} 3 \\ 3 0 \overline{3} 0 \\ 2 2 \overline{4} 0 \\ 3 1 \overline{4} 3 \end{array}$	$\begin{array}{c cccc} hkil & d_{obs}(A) \\ \hline 10\bar{1}3 & 3.66 \\ 11\bar{2}0 & 3.16 \\ 10\bar{1}4 & 3.06 \\ 0006 & 2.462 \\ 20\bar{2}3 & 2.395 \\ 10\bar{1}6 & 2.249 \\ 10\bar{1}7 & 1.974 \\ 11\bar{2}6 & 1.941 \\ 21\bar{3}3 & 1.910 \\ 30\bar{3}0 & 1.828 \\ 22\bar{4}0 & 1.585 \\ 31\bar{4}3 & 1.455 \\ \end{array}$

 $a_0 = 6.335 (2) \text{ A} \quad c_0 = 14.77 (2) \text{ A} \quad (P\vec{6}2c [28])$

5.4.3. CsFe₂F₇

Large black plates grew at the melt surface and smaller black octahedra, 2 mm on edge, were found on the wall and base of the crucible.

The ratio Cs:Fe, determined by EPMA, was 1:1.9. The Mössbauer spectrum indicated that iron was present almost entirely as Fe^{3+} , and that two sites are present in the unit cell. The EPMA and Mössbauer spectrum are thus both in agreement with the formula $CsFe_2F_7$, with two sites for Fe^{3+} . A structure analysis has been undertaken [29]. Laue photographs showed that the octahedra examined were single crystals. X-ray powder pattern data have been indexed similarly to pyrochlore [30] and are given in Table VII.

5.4.4. $Cs_x FeF_3$ (0.18 < x < 0.29)

 $Cs_x FeF_3$ has a structure very similar to $Cs_2 Fe_5 F_{17}$ [14]; thus, like the Rb analogue, it closely resembles the tungsten bronze structure. It is similarly difficult to distinguish between these two forms on the basis of X-ray methods. The crystals gave an X-ray powder pattern which agreed closely with data obtained from a sintered sample [23]. The indexed powder pattern, obtained from single crystal material, is given in Table VIII.

5.5. Na₂ ABF₇

Crystals with A = Mn, Ni and Co, B = Fe, Al, have previously been prepared from NaCl + MCl₂ as flux, in sealed platinum crucibles [21]. In the present experiments, PbCl₂ was used as flux in crucibles with well-fitting lids. The yields were large and, because the crystals were intergrown, only a few were faceted. They were soft and rather fragile. Some of these compounds are described below.

TABLE VII X-ray powder pattern data for $CsFe_2F_7$

Intensity, estimated	hkl	d _{obs} (A)	$d_{\mathrm{calc}}\left(\mathrm{A} ight)$
M	220	3.66	3.66
VS	311	3.13	3.13
W	222	2.993	2.992
VW	400	2.591	2.591
W	331	2.377	2.378
VW	422	2.115	2.116
S	333	1.996	1.995
S	440	1.833	1.833
W	620	1.640	1.639
W	533	1.581	1.581
VW	622	1.562	1.563

 $a_0 = 10.37 \text{ A}$

TABLE VIII X-ray powder pattern data for Cs_xFeF_3 (0.18 < x < 0.29)

Intensity, es	timated hkil	d _{obs} (A) $d_{\text{calc}}(A)$
MW	0002	3.813	3.815
S	1012	3.286	3.286
VS	2020	3.246	3.235
М	1122	2.678	2.669
w	2130	2.445	2.445
W	2132	2.060	2.059
М	3032	1.872	1.867
MW	3033	1.654	1.654
VW	4042	1.486	1.489
VW	2244	1.338	1.334
VW	4153,4044	1.239	1.234

 $a_0 = 7.47$ Å, $c_0 = 7.63$ Å.

5.5.1. Na₂CoFeF₇

The crystals were brownish pink, translucent, and up to $5 \text{ mm} \times 4 \text{ mm} \times 3 \text{ mm}$ in size. Extinction was not simultaneous. The X-ray powder pattern agreed with published data [31] and EPMA was in good agreement with the formula, indicating only 0.1% Cl and 0.3% Pb in the crystal (Table IX). However, EPMA showed, in addition, many small precipitates of PbCl₂ throughout the crystal. Mössbauer experiments indicated the absence of Fe²⁺.

5.5.2. Na₂NiFeF₇

The shiny dark-brown crystals, up to $10 \text{ mm} \times 10 \text{ mm} \times 6 \text{ mm}$, cleaved easily. Under the polarizing microscope, smaller platelets appeared yellow and showed simultaneous extinction. Some small octahedra were also present. The X-ray powder pattern agreed with ASTM data [32]. Mössbauer experiments again indicated the absence of Fe²⁺.

5.5.3. Na2NiAIF7

The crystals were soft, brittle and pale green. Some were rod-shaped, while others were pseudocubic, and the smaller crystals showed simultaneous extinction. Some NiF₂ crystals grew at the crucible base; these were a brighter, yellowish green. X-ray powder pattern data for crystals of Na₂ NiAlF₇ are given in Table X, and some are shown in Fig. 5.

5.5.4 Na2ZnCrF7

A layer of dark green crystals grew at the surface of the melt and separate pseudocubic crystals up to $2 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$ were attached to the crucible walls. Under the polarizing microscope,

TABLE IX EPMA data for crystals of Na₂CoFeF₇

Na ₂ CoF	eF ₇ requires (%)	EPMA indicates (%)
Na	15.7	15.9
Co	19.0	19.4
Fe	20.1	20.9
F	45.3	43.9
C1		0.1
Pb		0.3

the crystals were seen to be intimately twinned. X-ray powder pattern data are given in Table X.

5.6. NaCrF₄

The crystals grew as dark green, faceted, platy rods up to $3.5 \text{ mm} \times 1.0 \text{ mm} \times 0.5 \text{ mm}$. Under the polarizing microscope, most showed simultaneous extinction but twinned regions were visible in some. The X-ray powder pattern was in good agreement with ASTM data [33].

5.7. $\beta RbCrF_4$

The surface of the solidified melt was covered with microscopic needles. The X-ray powder pattern of these needles agreed with ASTM data [34].

5.8. Rb₂ Cr₅ F₁₇

These crystals grew as brownish-green fibrous aggregates, up to $8 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$. Extinction was not uniform. Some are shown in Fig. 6.

TABLE X X-ray powder pattern data for Na_2NiAlF_7 and Na_2ZnCrF_7

Intensity, estimated	hkl	Na ₂ Ni	AlF,	Na ₂ Zn	CrF ₇
estimated		$d_{\rm obs}$	$d_{\rm calc}$	d_{obs}	d_{calc}
		(Å)	(Å)	(Å)	(Å)
vs	011	5.95	5.92	6.02	6.09
MS	101	5.10	5.09	5.20	5.20
MS	121	3.58	3.58	3.66	3.67
S	031,211	3.04	3.05	3.11	3.12
VS	022	2.962	2.962	3.00	3.04
VS	220	2.892	2.894	2.966	2.956
W	202	2.548	2.546	2.591	2.601
VW	040	2.515	2.515		
W	013	2.375	2.374		
VW	132	2.335	2.335		
W	103	2.311	2.309	2.374	2.369
W	222	2.273	2.271	2.322	2.325
М	113	2.249	2.251	2.305	2.309
VW	123	2.100	2.099		
W	042	2.075	2.074		
VW	321	2.050	2.050	2.096	2.092
MS	033	2.173	2.174	2.041	2.031
$a_{0} = 7.07$ $b_{0} = 10.0$ $c_{0} = 7.32$	$\begin{array}{rcrcr} 7 & A & a_0 &= 7 \\ 06 & A & b_0 &= 1 \\ 09 & A & c_0 &= 7 \end{array}$	7.198 Å .0.37 Å 7.526 Å			



Figure 5 Crystals of Na, NiAlF, (mm grid).



Figure 6 Needles of $Rb_2Cr_5F_{17}$ (mm grid).

The X-ray powder pattern resembled that of $K_2V_5F_{17}$ [35]. EPMA was in good agreement with the formula $Rb_2Cr_5F_{17}$, with only 0.9% Pb and 0.3% C in the crystal (Table XI).

5.9. (Cs, Pb) CrF₄

The crystals grew as dark green rods up to $6 \text{ mm} \times 0.5 \text{ mm} \times 0.5 \text{ mm}$, with hexagonal facets.

The X-ray powder pattern differed from that published for $CsCrF_4$ [36]. EPMA showed a considerable amount of Pb in the lattice, and was in good agreeement with the empirical formula $(Cs_{0.6}Pb_{0.2})$ CrF₄ (Table XII).

5.10. (Cs, Pb)₂ Cr_{4.6} F₁₇

The batch which produced (Cs, Pb) CrF_4 also yielded irregularly shaped, brownish-green platelets, typically $2 \text{ mm} \times 3 \text{ mm} \times 0.5 \text{ mm}$. They were transparent and highly twinned. The X-ray powder pattern data differed from that published for $Cs_2 Cr_5 F_{17}$ [37], and EPMA showed the presence of a large amount of Pb in the lattice (Table XII).

It thus appears that flux systems containing lead are not suitable for the complex fluorides of caesium and chromium. This is unexpected, since

TABLE XI EPMA data for crystals of $Rb_2Cr_5F_{17}$

$Rb_2Cr_5F_{17}$	requires (%)	EPMA indicates (%)		
Rb	22.6	23.6		
Cr	34.4	34.4		
F	42.8	44.1		
Рb		0.9		
Cl		0.3		

as shown in Sections 5.4.1 to 5.4.4, there is little substitution of lead in the caesium iron flourides.

5.11. BaMF₄

Attempts to produce crystals of BaNiF₄ and BaCoF₄ were made, using as fluxes $PbCl_2$, PbF_2 , LiBr and CaF₂-CaCl₂. Only PbCl₂ produced crystals with compositions approximating to BaMF₄, as shown in Table XIII. EPMA data indicated that the incorporation of Cl⁻ and Pb²⁺ were both unusually high, approximately 6% and 3%, respectively. The high chloride content was unexpected, since Cl⁻ has a much larger ionic radius than F⁻ (1.8 Å and 1.3 Å, respectively), and the chloride content of fluorides previously grown from PbCl₂ or KCl as flux has been very low, as shown in Table XIV. The rather high Pb content was, however, not unexpected since the ionic radius of $Ba^{2+}(1.4 \text{ Å})$ is not very different from that of $Pb^{2+}(1.3 \text{ Å})$.

5.11.1 (Ba, Pb) Ni (F, Cl)4

A layer of yellow-green, transparent rods up to $6 \text{ mm} \times 2 \text{ mm} \times 0.5 \text{ mm}$ grew at the melt surface. The crystals showed simultaneous extinction. The X-ray powder pattern data for (Ba, Pb) Ni (F, Cl)₄ showed fair agreement with ASTM data for BaCoF₄ [42] but not with ASTM data for BaNiF₄ [43].

5.11.2 (Ba, Pb) Co (F, Cl)₄

Scarlet rods, up to $3 \text{ mm} \times 0.5 \text{ mm} \times 0.2 \text{ mm}$, were obtained and these showed simultaneous extinction. The X-ray powder pattern of (Ba, Pb) Co (F, Cl)₄ was in fair agreement with ASTM data for BaCoF₄ [42].

Acknowledgements

The authors are grateful to Dr S. H. Smith and Mr B. J. Garrard for helpful discussions and technical assistance, and to the Mössbauer Group of Liverpool University for information on the Mössbauer spectra of the crystals containing iron. The work was supported in part by the SRC. A. M. and K. Y. wish to thank the British Council and the Japanese Government, respectively, for financial support.

References

- 1. G. GARTON and B. M. WANKLYN, J. Crystal Growth 1 (1967) 49.
- 2. B. M. WANKLYN, *ibid* 5 (1969) 279.
- 3. B. M. WANKLYN and B. J. GARRARD, *ibid* 33 (1976) 165.
- 4. B. M. WANKLYN, J. Mater. Sci. 10 (1975) 1487.
- R. V. COLVIN and S. ARAJS, J. Phys. Chem. Solids 26 (1965) 435.
- 6. A. OKAZAKI, J. Phys. Soc. Japan 14 (1959) 1823.
- 7. P. R. LOCHER, Solid State Commun. 5 (1967) 185.
- J. D. RUSH, A. SIMOPOULOS, M. F. THOMAS and B. M. WANKLYN, Solid State Commun. 18 (1976) 1039.
- 9. G. HEGER and H. DACHS, Solid State Commun. 10 (1972) 1299.
- 10. D. BABEL, F. WALL and G. HEGER, Z. Naturforsch. 29b (1974) 139.
- 11. A. MAQSOOD and G. P. GUPTA, unpublished work.
- A. TRESSAUD, F. MENIL, R. GEORGES, J. PORTIER and P. HAGENMULLER, *Mat. Res. Bull.* 7 (1972) 1339.

TABLE XII EPMA data for crystals of (Cs, Pb) CrF_4 and (Cs, Pb)₂ $Cr_{4.6}F_{17}$

$(Cs_{0.6} Pb_{0.2}) CrF_4$	requires (%)	EPMA indicates (%)	$(Cs_{1.55} Pb_{0.45})_2 Cr_{4.6} F_{17}$	requires (%)	EPMA · indicates (%)	
Cs	30.3	31.7	Cs	23.9	23.5	
Pb	17.0	17.1	РЪ	10.8	10.9	
Cr	21.4	21.0	Cr	27.8	29.0	
F	31.3	31.2	F	37.5	37.1	
Cl		0.1	C1		0.4	

ГАВLЕ XIII EPMA da	a for crystals of (B	a, Pb) Ni(F, Cl) ₄	and (Ba, Pb)Co($F, Cl)_4$
--------------------	----------------------	-------------------------------	-----------------	------------

	$(Ba_{0.95}Pb_{0.05})Ni(F_{0.89}Cl_{0.11})_4$ requires (%)	EPMA indicates (%)		$(Ba_{0.95}Pb_{0.05})Co(F_{0.89}Cl_{0.11})_4$ requires (%)	EPMA indicates (%)
Ba	46.1	44.7	Ba	46.1	46.9
Pb	3.7	3.8	Pb	3.7	3.0
Ni	20.7	20.9	Co	20.8	20.8
F	24.0	26.3	F	23.9	28.8
Cl	5.5	6.1	Cl	5.5	5.9

TABLE XIV Substitutional flux impurities in fluoride crystals

Crystal formula	Flux	Substitutional Imp	Substitutional Impurity (%)	
	KC1	Cl	K	
CoF,		< 0.03	< 0.05	[38]
KCoF.		< 0.03		[38]
FeF,		< 0.03	< 0.05	[38]
KFeF.		< 0.03		[38]
KV F		0.02		[38]
2 - 6	PbCl,		Pb	
FeF.	4	0.07	< 0.02	[39]
(Co, Fe) F.		0.03	< 0.02	[39]
KFeF.			0.12	[39]
α KCrF.			0.6	[4]
K _o Cr _e F _e			0.1	[4]
KVF.			0.03	[39]
K.V.F.			< 0.01	[40]
ZrFeF.		< 100 ppm	600 ppm	[41]
Na. CoFeF.		0.1	0.3	present work
Rb, Cr. F.		0.3	0.9	present work
$(Cs. Pb) CrF_4$		0.1	17.1	present work
$(Cs, Pb) Ct \in F_{1,2}$		0.4	10.9	present work
(Ba, Pb) Ni(F, Cl).		6.1	3.8	present work
$(Ba, Pb)Co(F, Cl)_4$		5.9	3.0	present work

- R. COSIER, A. WISE, A. TRESSAUD, J. GRANNEC, R. OLAZMAGA and J. PORTIER, Compt. Rend. 271 (1970) 142.
- 14. G. HEGER, Int. J. Magn. 5 (1973) 119.
- D. E. COX, M. EIBSCHÜTZ, H. J. GUGGENHEIM and L. HOLMES, J. Appl. Phys. 41 (1970) 943.
- 16. K. P. BELOV, et. al., Fiz. Tverd. Tela. 14 (1970) 2155.
 M. EIBSCHÜTZ, L. HOLMES, H. J. GUGGENHEIM, D. E. COX, Phys. Rev. B6 (1972) 2677.
- 17. I. N. BELYAEV, O. YA. REVINA, Russ. J. Inorg. Chem. (1966) 774.
- D. ELWELL and H. J. SCHEEL, "Crystal Growth from High Temperature Solutions" (Academic Press, London, 1975).
- 19. M. SAFA, B. K. TANNER, H. KLAPPER and B. M. WANKLYN, *Phil. Mag.* 35 (1977) 811.
- M. SAFA, B. K. TANNER, B. J. GARRARD and B. M. WANKLYN, J. Crystal Growth 39 (1977) 243.
- A. TRESSAUD, J. M. DANCE, J. M. PARENTEAU,
 J. C. LAUNAY, J. PORTIER and P. HAGENMULLER, *ibid* 32 (1976) 211.
- 22. B. M. WANKLYN, in "Crystal Growth", edited by B. Pamplin (Pergamon, London, 1975).
- 23. A. TRESSAUD, Thesis Faculte des Sciences de l'Université de Bordeaux, October (1969).
- 24. G. GARTON, S. H. SMITH and B. M. WANKLYN, J. Crystal Growth 13/14 (1972) 588.
- 25. M. HIDAKA, I. G. WOOD, B. M. WANKLYN and B. J. GARRARD, J. Phys. Chem. (in press).

- A. TRESSAUD, J. PORTIER, R. DE PAPE and P. HAGENMULLER, J. Solid State Chem. 2 (1970) 269.
- 27. A.S.T.M. 27-532.
- I. MITTEILUNG, F. WALL, G. PAUSEWANG and V. D. BABEL, J. Less Common Metals 25 (1971) 257.
- 29. V. D. BABEL.
- 30. A.S.T.M. 13-254.
- 31. A.S.T.M. 24-1079.
- 32. A.S.T.M; 24-1115.
- 33. A.S.T.M. 33–673.
- 34. A.S.T.M. 27-513.
- 35. A.S.T.M. 26-927.
- 36. A.S.T.M. 26–364.
- 37. A.S.T.M. 26-365.
- 38. B. J. GARRARD, B. M. WANKLYN and S. H. SMITH, J. Crystal Growth 22 (1974) 169.
- 39. W. DAVISON and B. M. WANKLYN, unpublished.
- 40. B. M. WANKLYN, B. J. GARRARD and F. R. WONDRE, J. Crystal Growth 33 (1976) 165.
- 41. B. J. GARRARD and B. M. WANKLYN, J. Crystal Growth (in press).
- 42. A.S.T.M. 21-65.
- 43. A.S.T.M. 21-79.

Received 15 August and accepted 2 October 1978.