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Flux growth of crystals of some transition metal fluorides

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The flux growth of crystals of the following complex fluorides is reported: $KFeF_4$, K_2FeF_5, $K_2Fe_5F_{17}$, $RbFeF_4$, FeF_3, $K_{0.25}FeF_3$, K_2CrF_5, $KCrF_4$, $K_2Cr_5F_{17}$, K_2NiF_4, $KNiF_3$ and $LiRF_4$ (R = Er to Gd). Triangular composition diagrams for the metal fluoride, KF, and KCl or $PbCl_2$ are given.

1. Introduction

Complex fluorides of the transition metals are of interest on account of their magnetic properties, as indicated in Table I which lists transition temperatures of some iron and nickel compounds [1-17]. Data for the corresponding chromium compounds are not available. These complex fluorides are difficult to prepare as single crystals by growth from the melt, since the transition metal fluorides are not commercially available as oxide-free, anhydrous materials of high purity. Therefore, for growth by this method, those of the compounds which melt congruently ($KFeF_4$, $RbFeF_4$, $KNiF_3$ and some of the $LiRF_4$ series) must be purified, and preferably melted, under HF in platinum equipment. Some of the compounds melt incongruently but these, as well as the congruently melting compounds, can be grown at relatively low temperatures by the flux method [18-20]. NH_4HF_2 or KHF_2, incorporated in the flux, fluorinates most oxide material present; it is observed that the high melting oxide phases crystallize out first, and the growing crystals can reject any remaining oxygen ions during the growth process, which is slow relative to growth from the melt. When growth takes place in air, as in the experiments here described, a balance has to be struck between a desirably slow growth rate and contamination of the melt by hydrolysis or oxidation during growth. Of the compounds listed here, only the $LiRF_4$ series oxidized so readily that a relatively fast growth rate was required, limiting the crystal size to 1 to 1.5 mm.

TABLE I Transition temperatures of some complex fluoride compounds.

Formula	T_N	Reference
$KFeF_4$ (planar antiferromagnet)	230, 137	1, 2
K_2FeF_5	60	1
$RbFeF_4$ (planar antiferromagnet)	190, 50–60	1, 3
FeF_3 (canted antiferromagnet)	364, 362, 362	4, 5, 6
K_2NiF_4 (planar antiferromagnet)	102, 200, 97, 97	7, 8, 9, 10
$KNiF_3$	275, 253.5, 275, 250, 235.3	11, 12, 13, 14, 15
$LiHoF_4$	1.1	16
$LiTbF_4$	2.86	17

Growth from the pure melts of crystals of $KFeF_4$ [21] and $LiYF_4$ [22, 23] have been reported. K_2NiF_4 [24] and $KNiF_3$ [19] have been grown from KF and (KF + KCl) as flux, and FeF_3 has been produced as very small crystals from the vapour [25]. The other materials have been reported as powders only.

For identification purposes, X-ray powder pattern data for compounds in the systems $MF–FeF_2–FeF_3$ (M = Li, Na, K, Rb, Cs, Tl) were obtained from a thesis by Tressaud [1], who prepared powder specimens by reacting the components in sealed tubes of platinum or gold. He determined the melting points and crystallographic transition temperatures by differential thermal analysis.

2. Materials and equipment

The chemicals used were: Koch-Light CrF_3,

FeF_3 and RbCl; Johnson Matthey Grade 2 PbF_2; Lindsay Rare Earth Chemicals $HoCl_3$; BDH Optran NiF_2 and RbF; BDH "Analar" KCl; BDH Laboratory Reagent grade KHF_2 and $PbCl_2$; and BDH 99.9% RF_3.

Platinum crucibles of 0.5 mm wall thickness with close-fitting lids were used. The control equipment has been described [26]. The furnaces had Crusilite elements at each side, protected from the reactive flux vapours by D-shaped sillimanite muffles [27].

3. Experimental

The starting compositions and furnace programmes which produced the best crystals are given in Table II. The materials were weighed out to ± 0.05 g, mixed together, put into crucibles and the lids closely fitted. 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 at 100 K h^{-1} to the maximum temperature of the run and slow cooling was commenced at once.

4. Results

With $PbCl_2$, KF and KCl as the flux components, transport of Si and Al from the muffle into the fluxed melts, which had been

TABLE II Starting compositions, furnace programmes and crystal products

Composition of mixture	Crucible volume (cm^3)	t_{max} (°C)	Rate of cooling (K h^{-1})	Final temperature (°C)	Crystal products
15 g FeF_3, 6.7 g KCl, 4.7 g KHF_2, 8 g NH_4HF_2	100	870	2	300	Flattened prisms of $KFeF_4$ up to $(4 \times 4 \times 2)mm^3$
5.4 g FeF_3, 8.9 g $PbCl_2$, 1.6 g KHF_2, 3 g NH_4HF_2	20	1020	7	300	Black shiny K_xFeF_3
12.8 g FeF_3, 26.8 g $PbCl_2$, 15.2 g KHF_2, 4.6 g NH_4HF_2	50	640	1.5	330	Colourless transparent K_2FeF_5 up to $(4 \times 3 \times 3)mm^3$
5.9 g FeF_3, 21.8 g $PbCl_2$, 1.7 g KHF_2, 2 g NH_4HF_2	20	850	2	450	Black, brittle crystals of $K_2Fe_5F_{17}$
4 g FeF_3, 3.6 g RbCl, 2.1 g RbF, 6 g NH_4HF_2	20	870	3	350	Plates of transparent, brownish $RbFeF_4$ up to $(1 \times 1)cm^2$
27.2 g FeF_3, 36 g $PbCl_2$, 8 g PbF_2, 10 g NH_4HF_2	100	1020	7	300	Platelets of FeF_3 up to $(2 \times 2 \times 0.5)mm^3$, above melt on walls. Larger plates in melt
6.6 g CrF_3, 20 g $PbCl_2$, 4.7 g KHF_2, 1.5 g NH_4HF_2	20	870	2	300	Fibrous rods of $\alpha KCrF_4$ up to $(12 \times 1.5 \times 1.5)mm^3$ and prisms of $K_2Cr_5F_{17}$ up to $(3 \times 2 \times 2)mm^3$
7.9 g CrF_3, 15.6 g $PbCl_2$, 5.6 g KHF_2	20	930	6	350	Fibres of $\alpha KCrF_4$ up to 10 mm in length and $(2 \times 2)mm^2$ platelets of K_2CrF_5
10 g NiF_2, 7.5 g KCl, 21 g KHF_2	50	960	2	300	Platelets of K_2NiF_4 up to $(3 \times 3 \times 1)mm^3$
12.6 g NiF_2, 17.9 g KCl, 10.2 g KHF_2, 4 g NH_4HF_2	50	960	2	300	Transparent crystals of $KNiF_3$ up to $(4 \times 4 \times 4)mm^3$
9.7 g NiF_2, 38.5 g $PbCl_2$, 11.6 g KF, 3.5 g NH_4HF_2	50	900	4	340	$KNiF_3$ up to $(5 \times 5 \times 5)$ mm^3
10.9 g $HoCl_3$, 0.9 g LiF, 20.1 g $PbCl_2$, 10 g PbF_2, 5 g NH_4HF_2	20	870	3	350	Yellow pyramidal crystals of $LiHoF_4$. Flux evaporated completely
7.5 g DyF_3, 0.9 g LiF, 18 g $PbCl_2$, 1.4 g PbF_2, 5 g NH_4HF_2	20	870	2	300	Clear yellow crystals of $LiDyF_4$ Evaporation of flux almost complete

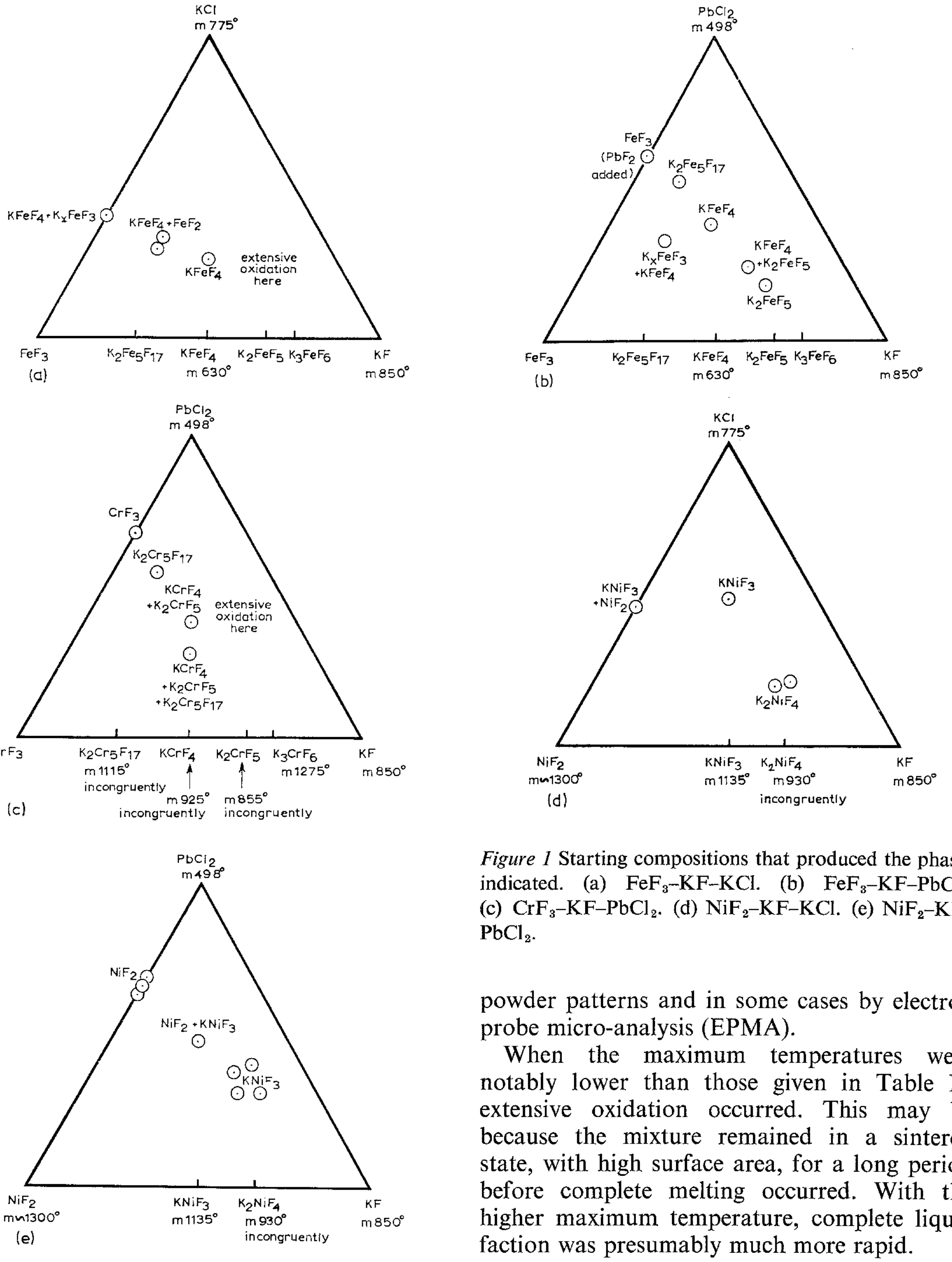

Figure 1 Starting compositions that produced the phases indicated. (a) FeF_3–KF–KCl. (b) FeF_3–KF–$PbCl_2$. (c) CrF_3–KF–$PbCl_2$. (d) NiF_2–KF–KCl. (e) NiF_2–KF–$PbCl_2$.

observed with PbF_2 as flux [27, 28], did not occur. The triangular composition diagrams of the metal fluoride, KF, and KCl or $PbCl_2$, are given in Fig. 1 and show the starting compositions that produced the crystals indicated.

The crystals were identified by their X-ray powder patterns and in some cases by electron probe micro-analysis (EPMA).

When the maximum temperatures were notably lower than those given in Table II, extensive oxidation occurred. This may be because the mixture remained in a sintered state, with high surface area, for a long period before complete melting occurred. With the higher maximum temperature, complete liquefaction was presumably much more rapid.

5. Notes on the crystals

5.1. $KFeF_4$

The melting point of this orthorhombic material has been reported as 630 ± 10°C [1]. A relatively rapid cooling rate (7 K h^{-1}) resulted in sheets of crystal, whereas when cooled at 2 to 3 K h^{-1}, tabular prisms (4 × 4 × 2) mm^3, shown

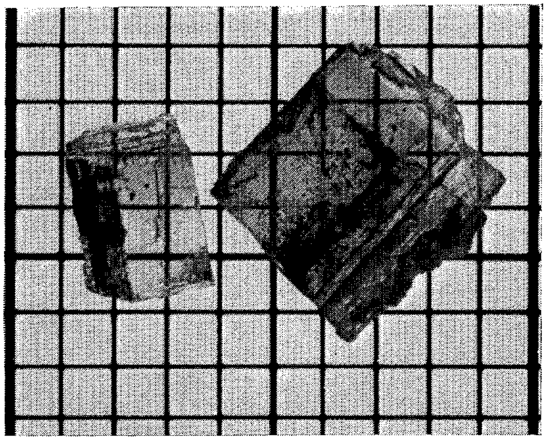

Figure 2 Platelets of $KFeF_4$ (1 mm grid).

in Fig. 2, were produced. The crystals were glossy, transparent, amber or pale mauve in colour. They showed simultaneous extinction and cleaved very readily especially when grown at the faster rate. They were soft, and thin slices could be bent in a rather fibrous manner. They reacted with cold water, precipitating $Fe(OH)_3$, but did not appear to be hygroscopic.

5.2. K_2FeF_5

K_2FeF_5 is said to decompose into $KFeF_4$ and KF on heating [1]. Crystals 3 to 4 mm on edge grew from $PbCl_2$ + KF as flux. They were colourless, without facets, the cleavage was vitreous, and they showed simultaneous extinction. The X-ray powder pattern, as reported for K_2FeF_5 [1], was very similar to those of K_2CrF_5 and K_2GaF_5 [29, 30]. The crystals reacted with cold water precipitating $Fe(OH)_3$.

5.3. $K_2Fe_5F_{17}$

The crystals grew as prisms with facets up to $(6 \times 6)\ mm^2$. They were black, shiny, extremely brittle, and hydrolyzed in water. The X-ray powder pattern agreed with published data [1]. (Note: see K_xFeF_3, Section 5.6.)

5.4 $\alpha RbFeF_4$

This material has been reported to melt at 690°C and to undergo a crystallographic transition at 650°C [1, 31]. The crystals grew as transparent sheets, brownish or amber in colour, up to 1 cm on edge. Under the polarizing microscope, twin domains were apparent. The crystals resembled $KFeF_4$ as regards cleavage and reaction with H_2O. The X-ray powder pattern indicated that this was the low-temperature (α) form of $RbFeF_4$ [1].

5.5. FeF_3

To lower the liquidus temperature, and avoid undue dissociation to FeF_2 [32], PbF_2 was added to $PbCl_2$ flux as shown in Table II. Well-formed rods and platelets $(2 \times 2 \times 1)\ mm^3$ grew just above the melt on the crucible walls, the melt having presumably reached these sites by a creeping process followed by evaporation of the flux. Thin platelets were transparent, green, and showed almost simultaneous extinction. Like AlF_3, this material is cubic at the growth temperature and becomes rhombohedral at 402°C [25]. This results in twinning of the larger crystals. In the melt, larger, more opaque FeF_3 material occurred.

5.6. K_xFeF_3 (x = 0.18 to 0.25) or
$KF.Fe\ F_2.3\ FeF_3$

This hexagonal phase is reported to exist as a solid solution with $x = 0.18$ to 0.25 [33-35] and was produced as black, shiny, polycrystals in melts, intended to result in $KFeF_4$, which were heated to about 1000°C; FeF_3 is known to decompose near this temperature [32] and it appears that K_xFeF_3 is the product of its partial decomposition in the presence of KF. Similarly, FeF_2 occurred as dark brown rods with FeF_3 and with $KFeF_4$ and K_xFeF_3 in melts heated to about 1000°C.

Hexagonol K_xFeF_3 (x=0.18 to 0.25) and $K_2Fe_5F_{17}$ have very similar X-ray powder patterns, differing only in the intensities of the weaker lines. Tressaud [1] suggests that the structures of both derive from the tungsten bronze, K_xWO_3. The fact that free FeF_2 occurred with the phase described here, in addition to the agreement of the X-ray powder pattern data with that published, substantiates the probability that this material is K_xFeF_3 (or $KF.FeF_2.3FeF_3$ approximately).

5.7. K_2CrF_5

The crystals were identified by single crystal X-ray analysis which showed that they were orthorhombic with $a_0 = 7.36$ Å, $b_0 = 12.82$ Å, $c_0 = 20.30$Å, space group *Pbcn*, in close agreement with the unit cell reported by de Kozak for K_2CrF_5 [36], who also reported that this compound melts incongruently at 855°C. The powder pattern agreed closely with that reported for K_2GaF_5 [29, 30].

K_2CrF_5 crystals occurred together with

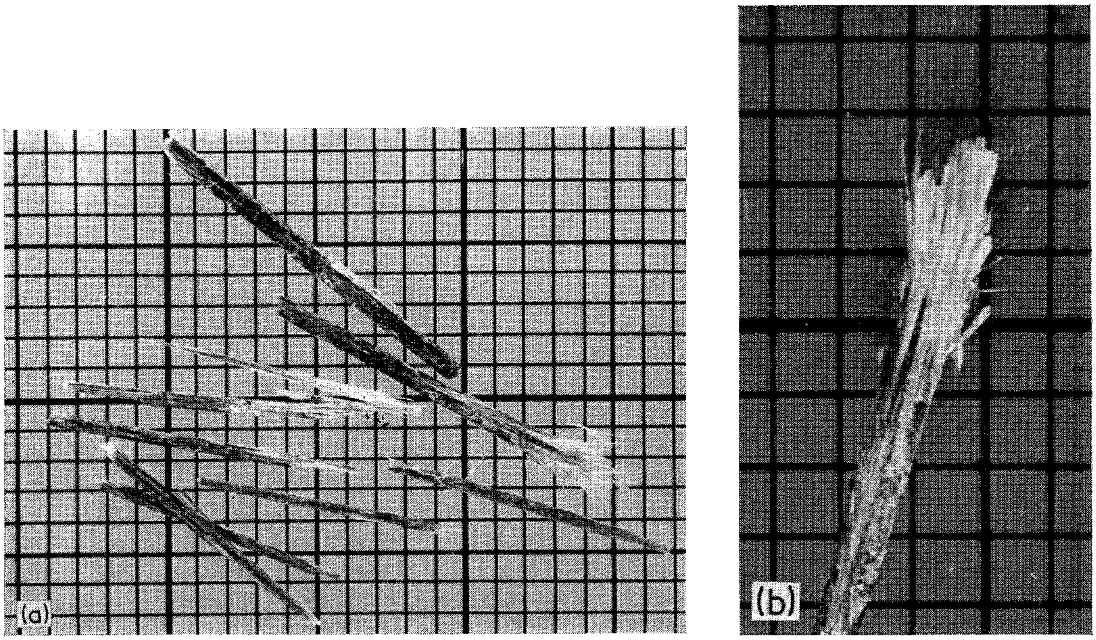

Figure 3 (a) and (b) Rods of $\alpha KCrF_4$ (1 mm grid).

$KCrF_4$ fibres. They were separated mechanically from the flux and cleaned by soaking overnight in hot 1:15 HNO_3 solution. They grew as fragile dark emerald green platelets approximately $(2 \times 2 \times 0.2)$ mm^3, and under the polarizing microscope they showed extinction parallel to an edge.

5.8. $\alpha KCrF_4$

The X-ray powder pattern of the dark green fibres which occurred with K_2CrF_5 agreed closely with that given for $\alpha KCrF_4$ by de Kozak [36, 37], and EPMA was consistent with this formula. He also reported that $KCrF_4$ melts incongruently at 925° C and undergoes a structural transition at 786° C to the low temperature form, $\alpha KCrF_4$. These hexagonal fibres differ both in structure and in habit from the other compounds KMF_4 ($M = Fe^{3+}, V^{3+}, Ga^{3+}, Al^{3+}$), which have tetragonal or orthorhombic structures and plate-like habits.

The fibrous rods were cleaned by soaking overnight in hot 1:15 HNO_3 solution. They showed extinction parallel to the axis. Pressure on the rods revealed their fibrous nature: the rods divided into a brush-like structure, the units of which were so fine that it was difficult to obtain single crystal X-ray photographs. The fibres bent readily without cracking. Fig. 3 shows some of the rods.

EPMA indicated that the crystals contained 0.6% Pb.

5.9. $K_2Cr_5F_{17}$

This compound is said to melt incongruently at 1115°C [36]. Dark green, hexagonally faceted, shiny prisms approximately $(2 \times 2 \times 2)$mm^3 grew at the surface of the melt containing also $\alpha KCrF_4$ and K_2CrF_5. Some are shown in Fig. 4. The crystals cleaved readily parallel to the basal plane. Under the polarizing microscope, extinction was not quite uniform, possibly due to strain. After mechanical separation they were cleaned by soaking overnight in warm 1:15 HNO_3 solution. The X-ray powder pattern closely resembled those given for $K_2V_5F_{17}$ [38], $K_2Ga_5F_{17}$ [29] and $K_2Fe_5F_{17}$ [1], and EPMA of the crystals was consistent with the formula $K_2Cr_5F_{17}$. EPMA showed that they contained 0.1% Pb.

5.10. K_2NiF_4

K_2NiF_4 melts incongruently at 930°C [39]. Crystals were obtained from (KCl and KF) as flux. They grew as pseudo-cubes or platelets, a few mm on edge.

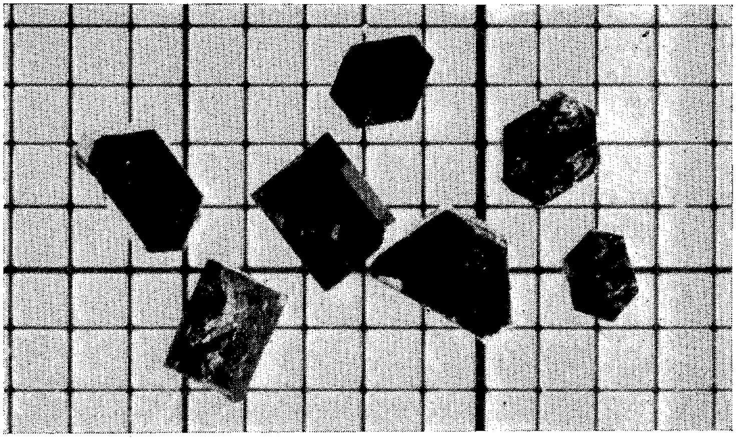

Figure 4 Transparent, dark green prisms of $K_2Cr_5F_{17}$ (1mm grid).

5.11. $KNiF_3$

A previous paper [19] reported the growth of $KNiF_3$ from a mixture of NiF_2 and KCl, which resulted also in crystals of NiF_2. A great degree of intergrowth took place which caused strain and deformation of the crystals.

Better quality $KNiF_3$ has been obtained from compositions in the three-component systems NiF_2–KF–$PbCl_2$ and NiF_2–KF–KCl, from both of which it was possible to obtain $KNiF_3$ in the absence of NiF_2. The crystals grew firmly attached to the crucible wall or base, and had to be separated mechanically and finally cleaned in dilute HNO_3 when (KF + $PbCl_2$) was used as flux, whereas (KF + KCl) dissolved in water. Those crystals which grew with only a small area of attachment to the crucible were found to be free from strain. They were up to 5 mm on edge. X-ray topographs showed that some of them were almost free from dislocations and of a high degree of perfection [40].

5.12. $LiRF_4$ (R = Tm, Er, Ho, Dy, Gd)

These compounds have the same tetragonal structure as the rare earth vanadates, phosphates and arsenates. $LiTbF_4$ has been reported to be ferrimagnetic [17] and small crystals of the compounds with R = Tm, Er, Ho, Dy and Gd were required for determination of magnetic susceptibilities.

$LiTmF_4$ melts congruently at 800° C but, with increasing ionic radius of the rare earth ion, the compounds melt incongruently [41]. While it is possible to pull the crystals from a non-stoichiometric melt, with excess LiF [22, 23], this requires purification of RF_3 under HF and relatively large batches. It was found possible to grow transparent crystals 1 to 1.5 mm in size by using ($PbCl_2$ + PbF_2) as flux, with either RF_3 or anhydrous RCl_3, plus LiF and NH_4HF_2 (see Table II). When $HoCl_3$ was used, it was interesting to note that the mixture became hot and fumed for several seconds, presumably owing to a reaction which produced NH_4Cl. The crystals were identified by comparison of their X-ray powder patterns with published data [42].

The melt appeared to hydrolyze appreciably in the furnace, and it was not possible to produce larger crystals since larger batches and slower cooling rates resulted in opaque material only.

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