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Hydrothermal crystal growth of perovskite-type fluorides

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Single crystals of perovskite-type fluorides were grown from potassium fluoride and di-valent metal chloride solutions by a hydrothermal method under a temperature gradient, at maximum temperature 600° C and pressure 98 MPa. Single-crystal cubes of $KMnF_3$, $KFeF_3$, $KCoF_3$ and $KZnF_3$, of cube edge sizes ranging from 0.2 to 2.0 mm, were grown. Crystals of $KNiF_3$ grew in rectangular prisms and those of $KCdF_3$ in anhedral form. Single crystals of $KCuF_3$ were grown in pure water from co-precipitated $KCuF_3$ powder. $KMgF_3$ crystals were not grown by this method.

1. Introduction

Perovskite-type fluorides have very interesting magnetic and optical properties [1–8], and several methods have been employed to grow single crystals suitable for measurements of their properties [1–15].

Leckebusch [9] grew small crystals of $KMnF_3$ by a gel method. Hirakawa *et al.* [1] grew $KCuF_3$ crystals from aqueous HF solution by evaporating the solvent. However, crystals grown from aqueous solution are seldom stoichiometric [2].

Garrard *et al.* [10] grew crystals of $KCoF_3$ and $KFeF_3$ by a flux method. Nitrogen gas prevented oxidation of the fluorides. The starting mixture was heated to 500° C with a small amount of NH_4HF_2 for purification and dehydration.

Both Bridgeman–Stockbargar and Czochralski methods have been used to grow crystals of perovskite-type fluorides [4–8, 13, 14]. The starting materials had to be purified and dehydrated before use and both were carried out in an atmosphere of nitrogen or inert gas.

The hydrothermal method [15] has been developed to grow single crystals of $KCoF_3$ and $KFeF_3$, and is reported here for the growth of other perovskite-type fluorides.

2. Experimental procedure

For the production of perovskite-type fluorides, the following reaction was used:

$$MCl_2 + 3KF \xrightarrow{H_2O} KMF_3 + 2KCl, \qquad (1)$$

where M is di-valent metal ion. KMF_3 produced by this reaction is somewhat soluble in the resulting KCl solution under hydrothermal conditions and may be transported by a temperature gradient to crystallize in the low temperature region.

The starting materials were KF, $MnCl_2 \cdot 4H_2O$, $FeCl_2 \cdot nH_2O$, $CoCl_2$ (anhydrous), $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 2.5H_2O$ (all of reagent grade from Wako Pure Chemical Industries Co., Ltd, Tokyo, Japan) $ZnCl_2$ (anhydrous) and $MgCl_2 \cdot 6H_2O$ (of reagent grade from Koso Chemical Co., Ltd, Tokyo, Japan). Water was twice distilled.

Aqueous solutions of potassium fluoride of three concentrations were used: concentrated (35 g/65 g H_2O, 9.27 m), medium (40 g/100 g H_2O, 3.07 m) and dilute (15 g/85 g H_2O, 3.07 m). Potassium fluoride solution was injected into a gold capsule of outside diameter 3.0 mm, of thickness 0.2 mm and of length 50 mm. The amount of solution was calculated to balance the pressure outside and inside the capsule at the growth tem-

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TABLE I The best experimental conditions for crystal growth of perovskite-type fluorides at a pressure of 98 MPa

KMF_3	Solution (m)	Growth temperature (° C)	Temperature difference (° C)	Growth period (days)	Results
$KMnF_3$	Dil*	500	20	4	Partly aggregated. Pink cubes with smooth surfaces (see Fig. 1). Largest is of edge size 1 mm.
$KFeF_3$	Dil	500	20	7	Pale yellow cubic crystals of $KFeF_3$ of edge size up to 2 mm.
$KCoF_3$	Dil	500	20	7	Partly aggregated. Cubic or rectangular prism form.
$KNiF_3$	Dil	600	20	7	Aggregates of rectangular prism crystals. Largest is of length 0.5 mm (see Fig. 2).
$KCuF_3$	Med*	500	20	2	A few plate-like crystals of $KCuF_3$. Largest is 0.5 mm × 0.5 mm × 0.1 mm. Also produced are crystals of CuO and Au.
$KZnF_3$	Dil	500	20	4	A few cubic $KZnF_3$ crystals with rough surfaces. Largest is of edge size 1 mm (see Fig. 3).
$KCdF_3$	Dil	500	20	4	A transparent $KCdF_3$ crystal without any particular faces.
$KMgF_3$	Med	500	50	4	Suspended. Very small crystals of sizes from 0.02 to 0.05 mm (see Fig. 5).

*Dil: 3.07 m KF solution; Med: 6.89 m KF solution.

perature. The equivalent amounts of chlorides according to Equation 1 were added to the solution. For $KFeF_3$, the calculated amount of solid KF was added to $FeCl_2$ solutions, which were prepared from a saturated solution at 10° C. The capsule was welded shut with an electric arc.

The sealed capsule containing the reactants was put into a Stellite 25 test-tube-type pressure vessel. These were heated in a temperature gradient furnace. Temperatures were measured on the wall of the pressure vessel by two Platinel (Engelhard) thermocouples at two positions, corresponding to the top and the bottom of the capsule. The temperature at the top, that is at the growth temperature zone, was adjusted to 400, 500 or 600° C. The temperature difference between the growth temperature and the dissolution temperature was either 20 or 50° C higher. The pressure was adjusted to 98 MPa (1000 kg cm^{-2}). The duration of the crystal growth experiments was 2, 4 or 7 days.

At the conclusion of a run, the pressure vessel was quenched in cold water. The capsule was cut apart with a knife, the contents were washed in water, and identified from X-ray powder diffraction study patterns and from microscopic observations.

3. Results and Discussion

3.1. Crystal growth

The composition corresponding to Equation 1 was used in the growth experiments. The conditions are summarized in Table I.

Crystals of $KMnF_3$, $KFeF_3$, $KCoF_3$, $KNiF_3$ and $KZnF_3$ were aggregated when the temperature difference between the growth temperature and the dissolution temperature was 50° C and the concentration of the KF solution was 9.27 or 6.87 m. The morphology was improved by reducing the temperature difference to 20° C and reducing the concentration of KF solution to 3.07 m (see Figs 1 and 2). These results indicate that the number of crystals grown decreases in the dilute solution with a small temperature gradient. Increase of the growth temperature to 600° C was effective to grow single crystals, especially for $KNiF_3$ (see Fig. 3).

Growth experiments on $KCuF_3$ gave only a small yield of $KCuF_3$ crystals and crystals of cupric oxide were also formed in the low tempera-

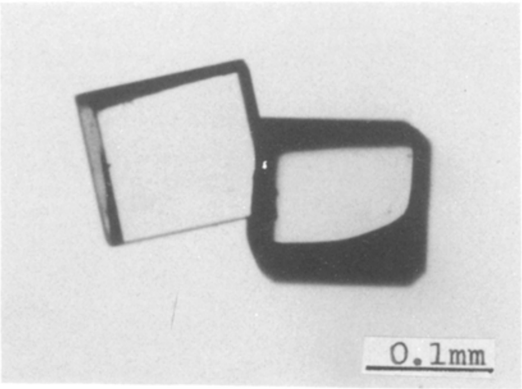

Figure 1 $KMnF_3$ single crystals.

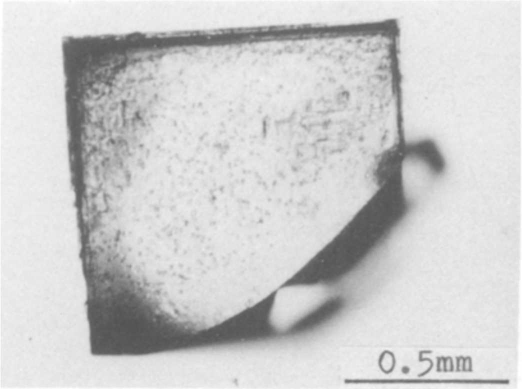

Figure 2 $KZnF_3$ single crystal.

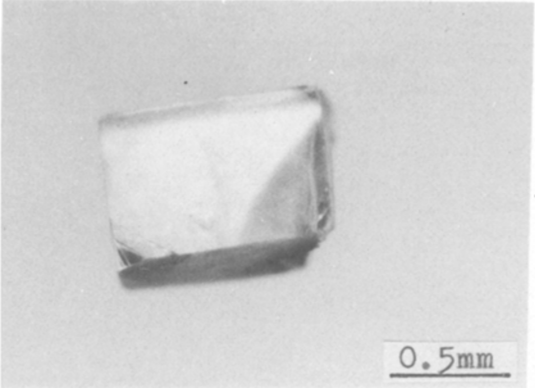

Figure 4 $KCuF_3$ single crystal.

ture region. The gold capsule was corroded at the dissolution zone and gold crystals grew at the top of the capsule. A few larger single crystals of $KCuF_3$, however, were grown from co-precipitated $KCuF_3$ using pure water instead of KCl solutions as a solvent. Fig. 4 shows the product.

Anhedral crystals of $KCdF_3$ were formed under any of the conditions tried in this work. $KMgF_3$ crystals were suspended in the solution but were not grown by transportation to the low temperature region (see Fig. 5).

3.2. Effect of the starting composition on phases synthesized by the hydrothermal reaction

The starting compositions studied were, corresponding to (a) Equation 1, $KF/MCl_2 = 3$; (b) KF excess, $KF/MCl_2 = 6$; (c) MCl_2 excess, $KF/MCl_2 = 1.5$. The experimental conditions and the phases produced in these experiments are summarized in Table II.

Some by-products were occasionally produced in these reactions. The amounts of oxides produced by the hydrothermal reaction were in the following order: manganese oxides (none) $< \gamma$-Fe_2O_3 (maghemite) $\simeq CoO < NiO \ll CuO$ (in accordance with atomic numbers). This suggests that the stability of the fluorides KMF_3 (where M = Mn, Fe, Co, Ni and Cu) under the hydrothermal condition tends to decrease with decreasing numbers on unpaired d-electrons.

With addition of excess KF, crystals of $KMnF_3$, $KFeF_3$, $KCoF_3$ and $KZnF_3$ were well-shaped in cubic or rectangular prism form of edge sizes up to 2 mm. An excess of di-valent metal chlorides seemed to be less effective in promoting crystal growth.

4. Conclusion

Crystals of KMF_3 (where M = Mn, Fe, Co, Ni, Cu, Zn and Cd) were grown by the hydrothermal method under pressure of 98 MPa at 500° C, with a temperature gradient of 20° C, using 3.07 m KF solution. Single crystals of $KCuF_3$ were grown in

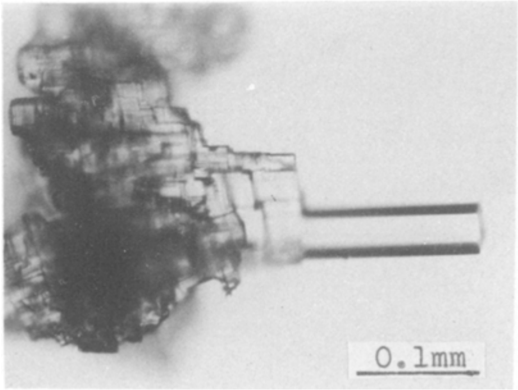

Figure 3 $KNiF_3$ crystals.

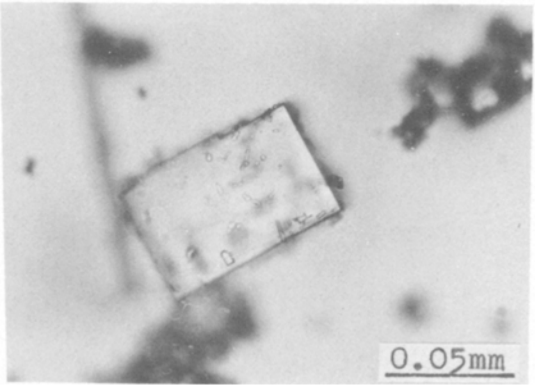

Figure 5 $KMgF_3$ crystals.

TABLE II Solid phases produced by the hydrothermal reaction with different starting compositions at a pressure of 98 MPa and 500° C in 7 days with a temperature difference of 20° C, using 6.89 M KF solution

KMF_3	MCl_2 excess $KF/MCl_2 = 1.5$	Equivalent (Equation 1) $KF/MCl_2 = 3$	KF excess $KF/MCl_2 = 6$
Mn	$KMnF_3 + MnF_2$	$KMnF_3$	$KMnF_3$
Fe	$KFeF_3 + \gamma\text{-}Fe_2O_3{}^*$	$KFeF_3 + \gamma\text{-}Fe_2O_3{}^*$	$KFeF_3 + \gamma\text{-}Fe_2O_3{}^*$
Co	$KCoF_3 + U_1$	$KCoF_3 + CoO^*$	$KCoF_3 + CoO^*$
Ni	$U_2{}^\dagger$	$KNiF_3 + NiO^*$	$KNiF_3{}^\dagger + NiO^*$
Cu	$KCuF_3{}^\dagger + CuO^\dagger$	$KCuF_3 + CuO$	CuO
Zn	$KZnF_3$	$KZnF_3$	$KZnF_3$
Cd	$KCdF_3 + CdOHF$	$KCdF_3 + CdOHF$	$KCdF_3$
Mg	$MgF_2{}^\dagger$	$KMgF_3{}^\dagger + MgF_2{}^\dagger$	$KMgF_3{}^\dagger$

*Precipitated.

†Suspended in the solution.

All others are transported to the top of the capsule. U_1 and U_2 are unidentified phases.

pure water using co-precipitated $KCuF_3$ powder. The infra-red spectra of $KCoF_3$ showed no evidence of the presence of hydroxyl ions [15]. Thus, the uptake of hydroxyl ions by crystals of perovskite-type fluorides appears to be negligible. The amount of oxide by-products increased with the decrease of unpaired 3d-electrons from Mn to Cu. Addition of excess KF promoted growth of crystals of $KMnF_3$, $KFeF_3$, $KCoF_3$ and $KZnF_3$ of cube edge size up to 2 mm. The increase of the growth temperature was also effective in growing crystals of $KNiF_3$. These results show the possibility of growing larger and higher quality single crystals of perovskite-type fluorides by a hydrothermal technique using KF solution at high temperatures above 600° C in a larger container, such as an autoclave.

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