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Hydrothermal crystal growth of mixed crystals in the $KMnF_3$–$KCoF_3$ system

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Single crystals up to 2.0 mm in length of solid solutions in the $KMnF_3$—$KCoF_3$ system were grown, under hydrothermal conditions from 400 to 600° C under 100 MPa. The effect of growth conditions on shape and surface structure of the single crystals was studied. The measurements of lattice parameter and magnetic susceptibility demonstrated that the composition of the crystals was the same as that of the starting mixture of $KMnF_3$ and $KCoF_3$ powders. The distribution of Mn^{2+} and Co^{2+} ions in a single crystal of the solid solution was investigated and it appeared to be homogeneous.

1. Introduction

Mixed crystals in the $KMnF_3$—$KCoF_3$ system are of interest because of their structural and magnetic properties [1–6]. Single crystals have been grown by several methods [1–7]: Svensson *et al.* [2] grew single crystals by the Stockbarger method and Skrzypek *et al.* [7] used the Bridgman method. In these methods, anhydrous pure fluorides were used as starting materials and these had to be melted down at temperatures above 1000° C. In order to prevent oxidation of fluorides, these methods require an argon or nitrogen atmosphere. The crystals had different compositions, far from those of the starting materials, because the solid crystallized along the solidus line, not the liquidus line.

The flux method [3, 6] has also been used to grow these single crystals but little information has been given. This method might have problems similar to the Stockbarger and Bridgman methods.

The hydrothermal method has been used to grow single crystals of the perovskite-type fluorides without particular difficulties [8, 9]. The uptake of OH^- ion in the crystal seems to be negligible because the crystal of $KCoF_3$ produced by this method showed no OH absorption in the infra-red spectrum [9]. This method has been developed to grow crystals of mixed perovskite-type fluorides in the present work.

2. Experimental procedure

Chemicals used were guaranteed reagent-grade KCl, KF, $MnCl_2 \cdot 4H_2O$ (Wako Pure Chemical Ind. Ltd, Tokyo, Japan) and $CoCl_2 \cdot 6H_2O$ (Kanto Chemical Co. Inc., Tokyo, Japan). $KMnF_3$ and $KCoF_3$ powders were separately synthesized by co-precipitation from KF and divalent metal chloride solutions. The precipitates were filtered, washed with water and dried at 110° C in air for 24 h. They were confirmed to be pure $KMnF_3$ and $KCoF_3$, respectively, by X-ray powder diffraction. Thermogravimetric analysis showed that the moisture content in the powders was within 0.1%. Powders were mixed by a wet blending method with ethanol to get the desired compositions. The mixed powder was moulded and isostatically pressed at 200 MPa into rods 1.5 mm in diameter.

The solvents used were aqueous solutions of KCl with 1.0, 2.0 and 4.0 molality and of KF with 2.57 molality. The calculated amount of solution, by which the inside pressure could be balanced with the outside pressure on the capsule at the growth temperature, was injected into a gold capsule, 3.0 mm in outer diameter, 0.15 mm in thickness and 50 mm in length. A few rods of the mixed powder, about 70 mg, were put into the solution. The capsule was closed by welding with an electric arc.

The sealed capsule was put into a test-tube-type

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pressure vessel of Stellite 25 and heated at 25° C $\min^{-1}$ in an electric furnace. Temperatures were measured on the wall of the pressure vessel by two platinel thermocouples calibrated against the melting point of zinc (419.5° C), at two positions corresponding to the top and the bottom of the capsule. The temperature at the top, that is the growth temperature, T_g, was adjusted to 400, 500 and 600° C by an electric controller. The temperature at the bottom, that is the dissolution temperature, T_d, was adjusted to be 20 or 50° C higher than at the top by using the temperature gradient in the furnace. The pressure was measured by a calibrated Heise pressure gauge and adjusted to 100 MPa. The duration of crystal growth experiments was 4 or 7 days.

At the completion of the experiments, the vessel was quenched in cold water. The capsule was cut open to reveal the contents, which were washed with water. The shape and surface structure of the crystals were observed with an optical microscope (VANOX, Olympus Optic Ind. Ltd, Tokyo, Japan) and a scanning electron microscope (SEM) (JSM-T200, JEOL Ltd, Tokyo, Japan), and the crystals were identified by X-ray powder diffraction (RU-200, Rigaku Denki Co. Ltd, Tokyo, Japan). Lattice parameters were calculated from high-angle diffraction lines with a slow scan rate (0.25° $\min^{-1}$), using Si (99.999% pure) as an internal standard. The compositional change of the solid solution was checked by the measurement of the lattice parameter. This method allows changes within 1 wt% to be detected, which is more precise than electron probe micro-analysis (EPMA). The magnetic susceptibility was measured by a Faraday-type magneto-balance (MB-1A, Shimadzu Seisakusho Ltd, Kyoto, Japan). The distribution of metal ions in the single crystals was measured by EPMA (EMX 11 A, Shimadzu Seisakusho Ltd, Kyoto, Japan).

3. Results and discussion

3.1. Hydrothermal reaction in the $KMnF_3$–$KCoF_3$ system

The rate of the hydrothermal reaction in the $KMnF_3$–$KCoF_3$ system was studied by quenching samples of 50 mol% $KMnF_3$ after heating in 2 M-KCl solution at 500° C under 100 MPa for 0, 1, 3, 6, 12 or 24 h.

The sample quenched as soon as the temperature reached 500° C showed a diffuse diffraction peak (Fig. 1b) between those of $KMnF_3$ and $KCoF_3$. It showed that $KMnF_3$ and $KCoF_3$ powders had already reacted and produced solid solutions between them during heating up to 500° C. As the duration of heating at 500° C was increased, the peak of the solid solution became gradually sharper. The solid solutions were considered to have homogeneous compositions after 12 h (Fig. 1d). No oxides were detected by X-ray powder diffraction. It is probable that the compositions of the solid solutions produced by this hydrothermal method are essentially equal to the starting compositions, because the solubilities of

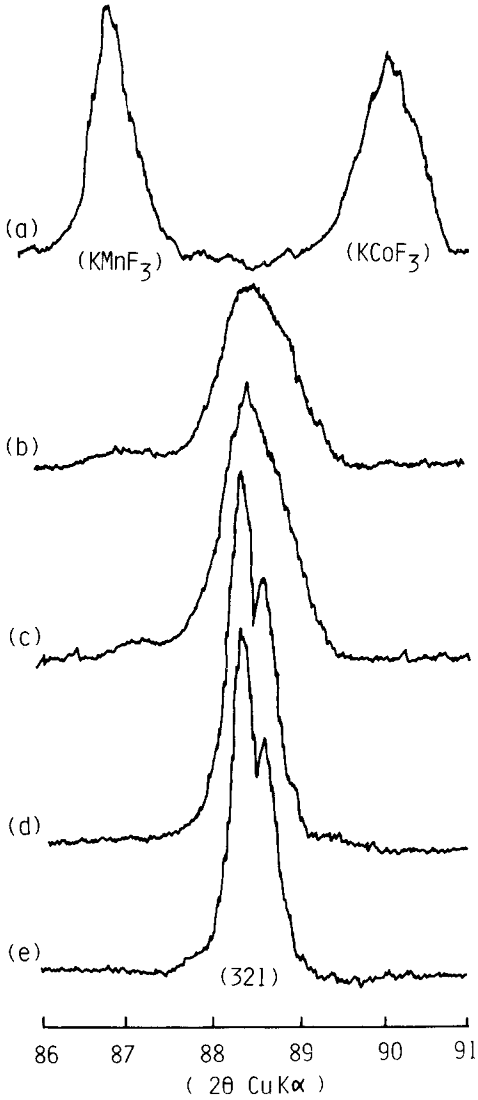

Figure 1 Peak profile of (3 2 1) diffraction line of $KMn_{0.5}Co_{0.5}F_3$ synthesized at 500° C in 2 M KCl solution under 100 MPa. (a) Starting material, (b) after 0 h, (c) after 1 h, (d) after 12 h, (e) crystals grown for 7 days.

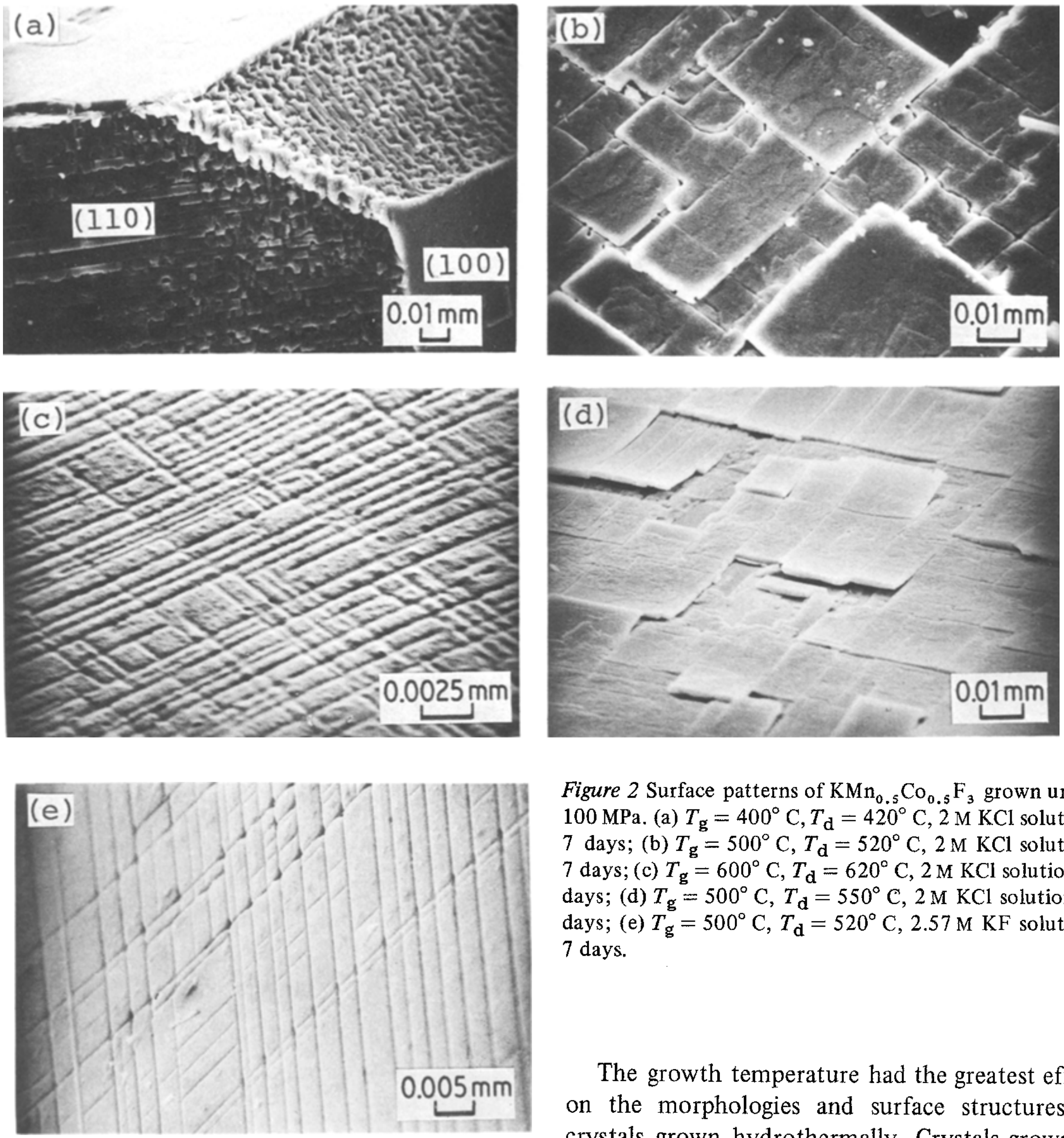

Figure 2 Surface patterns of $KMn_{0.5}Co_{0.5}F_3$ grown under 100 MPa. (a) $T_g = 400°$ C, $T_d = 420°$ C, 2 M KCl solution, 7 days; (b) $T_g = 500°$ C, $T_d = 520°$ C, 2 M KCl solution, 7 days; (c) $T_g = 600°$ C, $T_d = 620°$ C, 2 M KCl solution, 7 days; (d) $T_g = 500°$ C, $T_d = 550°$ C, 2 M KCl solution, 4 days; (e) $T_g = 500°$ C, $T_d = 520°$ C, 2.57 M KF solution, 7 days.

$KMnF_3$ and $KCoF_3$ are small in comparison with the amount of undissolved solid under hydrothermal conditions.

3.2. Crystal growth

Mixed crystals of $K(Mn, Co)F_3$ were grown at the top of the capsule under hydrothermal conditions between 400 and 600° C under 100 MPa. Mixed crystals of $KMn_{0.5}Co_{0.5}F_3$ (Fig. 1e) grown for 7 days shows a diffraction peak at the same position as that of the solid solution (Fig. 1d) produced by the hydrothermal reaction under the same conditions. This result revealed that the mixed crystals had the same compositions as the starting compositions.

The growth temperature had the greatest effect on the morphologies and surface structures of crystals grown hydrothermally. Crystals grown at 400° C had (100) and (110) surfaces (Fig. 2a). Small and rough (110) surfaces were observed on the edges of cubic or rectangular prism crystals. Their growth rate is probably faster than (100) surfaces. Crystals grown above 500° C were surrounded only (100) surfaces with chequered patterns (Fig. 2b, c). Growth patterns and difference of height on surfaces of crystals grown at 600° C (Fig. 2c) were much smaller than at 500° C (Fig. 2b).

The increase of the temperature gradient caused rough surfaces (Fig. 2d). Increasing the concentration of KCl solution used also had similar effects. When KF solution was used as a solvent, the crystals had flatter surfaces with linear patterns (Fig. 2e).

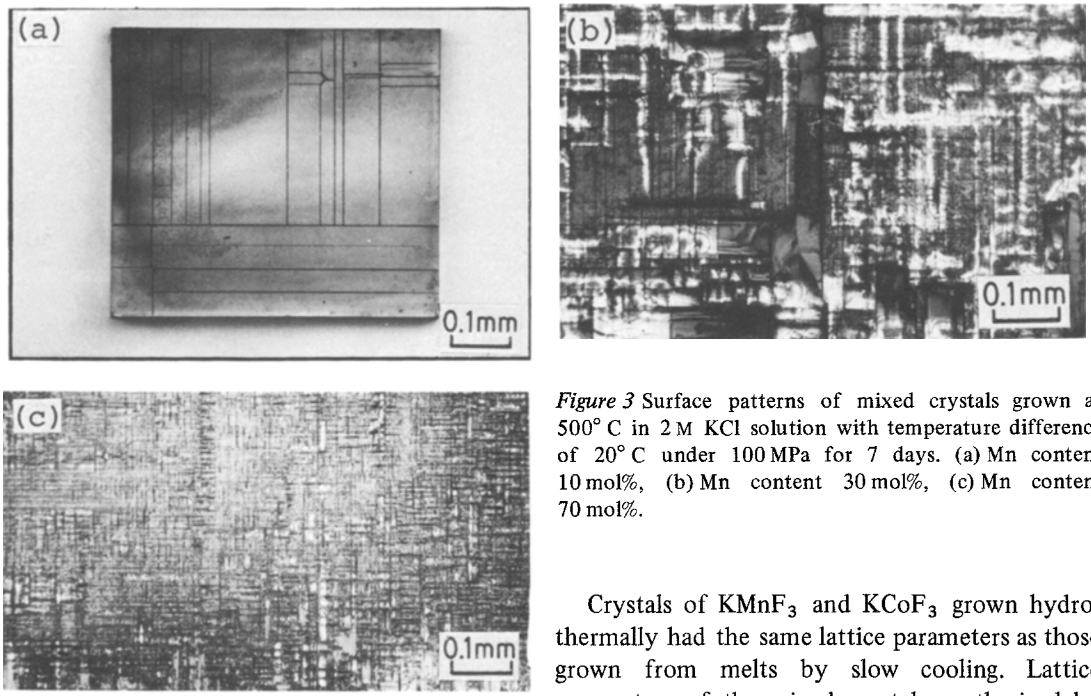

Figure 3 Surface patterns of mixed crystals grown at 500° C in 2 M KCl solution with temperature difference of 20° C under 100 MPa for 7 days. (a) Mn content 10 mol%, (b) Mn content 30 mol%, (c) Mn content 70 mol%.

Crystals with smooth surfaces were grown at the high growth temperature with a small gradient in diluted KCl solution or in KF solution. The surface structures were considered to be affected by the crystal growth rate, which depended on the supersaturation at the surface and on the deposition rate. The increased growth temperature gave an increased deposition rate. The decrease of the gradient resulted in decrease of the supersaturation. The solubility of $K(Mn, Co)F_3$ seemed to be lower in the diluted KCl solution or in KF solution. The low solubility might result in smaller supersaturation. It was concluded that the smooth crystal surfaces were achieved when the deposition rate was larger than the feed rate by the supersaturation.

Growth patterns on the crystal surfaces changed with starting compositions. Crystals with 10 mol% $KMnF_3$ had a few linear lines on the surface (Fig. 3a). As the concentration of manganese increased, the growth patterns became gradually smaller (Fig. 3b, c).

3.3. Characterization of crystals

3.3.1. *Lattice parameter*

Lattice parameters of hydrothermally grown crystals are shown against composition in Fig. 4. The lattice parameter–composition curve deviates slightly upward from Vegard's law.

Crystals of $KMnF_3$ and $KCoF_3$ grown hydrothermally had the same lattice parameters as those grown from melts by slow cooling. Lattice parameters of the mixed crystals synthesized by cooling melts quickly are shown with crosses in Fig. 4. They too showed the slight deviation from Vegard's law.

3.3.2. *Magnetic susceptibility*

Magnetic susceptibilities of mixed crystals synthesized under hydrothermal condition are shown in Fig. 5. The temperature of the maximum value of the susceptibility changes from 80 to 125 K with the decrease of manganese contents. The values of susceptibility measured in this work were identical with those reported previously [6, 10]. This means that the hydrothermal method as well as the flux

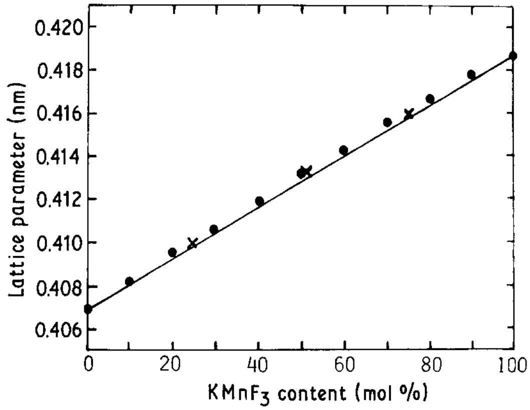

Figure 4 Lattice parameters of mixed crystal grown at 500° C in 2 M KCl solution under 100 MPa for 7 days.

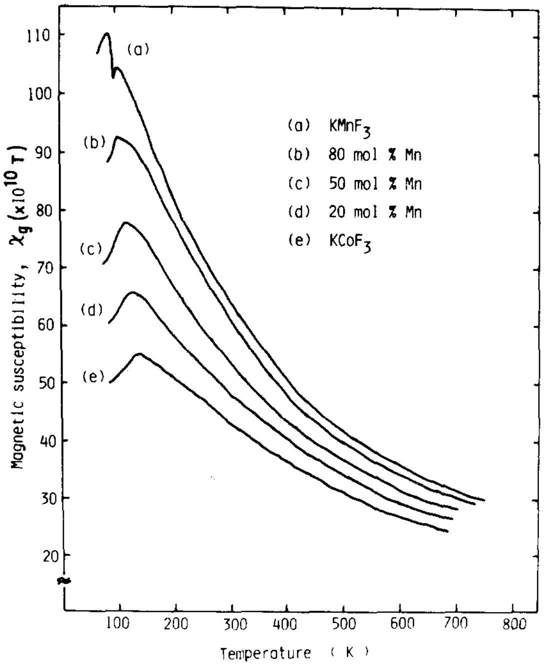

Figure 5 Magnetic susceptibility of mixed crystals synthesized at 500° C in 2 M KCl solution under 100 MPa for 1 day.

method [6] can be employed to synthesize mixed crystals in the $KMnF_3$–$KCoF_3$ system.

3.3.3. *Distribution of metal ions*

The distribution of metal ions in the single crystal was examined by EPMA with linear scanning of the beam on polished surfaces. As shown in Fig. 6, no significant variations were observed in manganese or cobalt intensities in both horizontal and vertical scanning for a single crystal of $KMn_{0.5}Co_{0.5}F_3$.

It was concluded that the distribution of manganese and cobalt in the single crystal is constant within the limits of experimental error. When the beam was fixed on a point of the crystal surface, diffraction intensities of K, Mn and Co changed slightly with time. Experimental errors were estimated to be about 3%. Some changes in intensity resulted from small cracks on the surface made during polishing.

4. Conclusions

The hydrothermal method has been applied to the growth of single crystals of solid solutions in the $KMnF_3$–$KCoF_3$ system. The co-precipitated $KMnF_3$ and $KCoF_3$ powders, used as starting materials, reacted rapidly under hydrothermal condition at 500° C and produced solid solutions. Crystals grown hydrothermally had the same compositions as the starting mixtures. The formation of continuous solid solutions at 500° C was revealed by the measurement of lattice parameters and magnetic susceptibilities. The results of EPMA showed homogeneous distribution of metal ions in the single crystals.

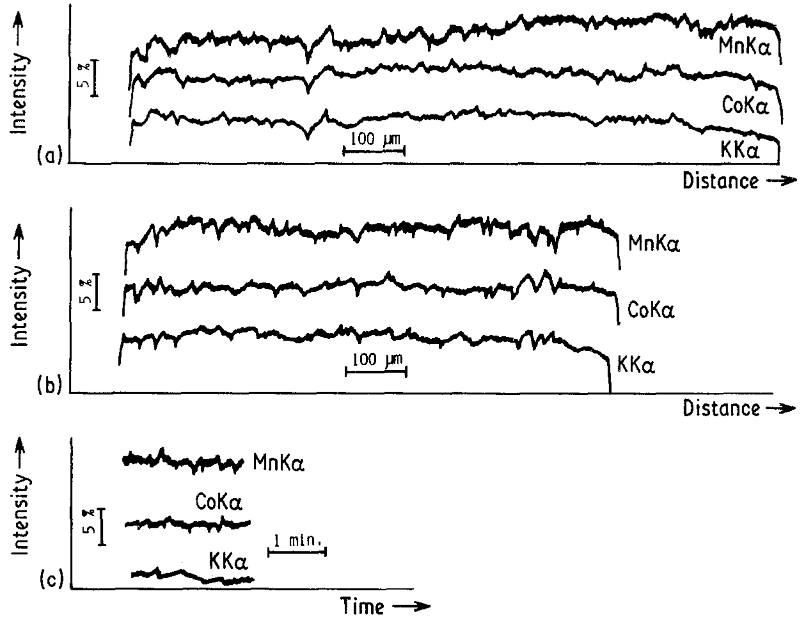

Figure 6 EPMA result for a single crystal of $KMn_{0.5}Co_{0.5}F_3$ grown at 500° C in 2 M KCl solution under 100 MPa for 7 days. (a) Horizontal scan, (b) vertical scan, (c) steady beam.

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