

Hydrothermal Crystal Synthesis of Solid Solutions in the System $\text{SrF}_2\text{--LaF}_3$

Kwang Jin Kim, Masahiro Yoshimura
and Shigeyuki Sōmiya

Research Laboratory of Engineering Materials and Department of Materials Science,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama, 227 Japan

SUMMARY

The possibility of the hydrothermal crystal synthesis/growth of the SrF_2 -solid solutions by spontaneous nucleation is studied in the system $\text{SrF}_2\text{--LaF}_3$. The lattice parameters of the solid solutions synthesized at 750°C by solid state reaction for 23 days in vacuum, or by hydrothermal reaction for 1 day under 100 MPa in 10 wt% LiCl solution, were identical. The composition of the $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals could be controlled by the starting composition. Single cubic crystals ($x = 0.4$) about 0.2 mm in size were grown at 650°C for 7 days under 100 MPa in 10 wt% LiCl aqueous solution from the composition containing 50 wt% SrF_2 . Single hexagonal plate-like crystals of LaF_3 -solid solution were also obtained, being about 0.2 mm in size. Hydroxyl ions (OH^-) were not detected in the products by infrared spectroscopy.

1 INTRODUCTION

Fluorite type (MF_2 ; M = Ca, Sr, Ba or Pb) or tysonite type (RF_3 ; R = rare earth) fluorides and their solid solutions possess a high anionic conductivity at temperatures below 500°C . Many of them have been studied from the point of view of low temperature ionic conductors.^{1,2} We have previously reported on phase equilibria in the system $\text{SrF}_2\text{--LaF}_3$ above 500°C ,^{3,4} and also on hydrothermal growth of La^{3+} -doped SrF_2 single crystals.⁵ In the present work, we have studied the possibility of hydrothermal crystal synthesis/growth of the SrF_2 -solid solutions in the system $\text{SrF}_2\text{--LaF}_3$.

2 EXPERIMENTAL

The starting materials were mixtures of 99.9% SrF_2 (Tri Chemical Lab. Inc., Sagami-hara, Japan) and 99.9% LaF_3 (Shin-Etsu Chemical Co. Ltd, Tokyo, Japan) obtained after milling and mixing in ethanol at room temperature. Samples of mixtures which were heated for 4 h at 1300°C in a graphite crucible in a purified argon atmosphere with a flow of $2 \text{ litres min}^{-1}$, were also used for annealing experiments at lower temperatures (750°C) to ensure the attainment of the equilibrium state and also to select suitable mineralizer solutions. Solid state reactions were carried out at 750°C for 23 (= 7 + 7 + 9) days in quartz glass ampoules sealed in vacuum (10^{-2} Pa). In the case of hydrothermal synthesis/growth, it is necessary to investigate which solution acts as the most suitable mineralizer in the system studied. Re-distilled water and aqueous solutions of alkaline metal (Li, Na and K) fluorides, chlorides, bromides, carbonates, nitrates, sulfates and hydroxides were examined in this study. Water was prepared by redistillation, in a quartz distillator, of water which had been obtained from ion-exchanged and distilled water. The mixed or fired sample was placed in a platinum capsule of 2.7 mm inner diameter, 0.15 mm wall thickness and 35 mm length, containing a known amount of mineralizer solution. The capsule was then loaded into a Roy and Tuttle⁶ test-tube-type hydrothermal apparatus. A schematic illustration of hydrothermal synthesis/growth is shown in Fig. 1. A type-K thermocouple

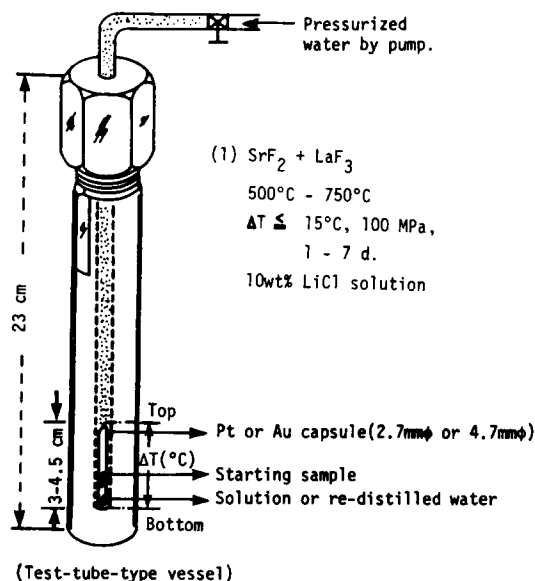


Fig. 1. A schematic illustration of the hydrothermal synthesis/growth apparatus (Test-tube-type vessel; Ref. 6).

(IEC Standard) calibrated against the melting point of zinc (419.6°C) was attached to the outside of the pressure vessel of a commercial alloy (Stellite 25, Union Carbide Corp., New York) for the measurement of temperature. The pressure in the space surrounding the capsule inside the vessel was raised to 10 MPa by using a water-pressure pump before the hydrothermal runs. The temperature was then increased at $15^{\circ}\text{C min}^{-1}$ to the operating temperature. The temperature and pressure were controlled to within $\pm 3^{\circ}\text{C}$ and ± 5 MPa of the desired value during runs. At the completion of the experiment the vessel was quenched in cold water. The capsule was weighed for observation of loss in weight. The hydrothermal runs were carried out at a temperature of 650°C for 1–14 days under 100 MPa in 10 wt% LiCl solution. The temperature at the bottom of the capsule was 650°C ; the temperature at the top was $0\text{--}15^{\circ}\text{C}$ lower than that at the bottom ($\Delta T = 0\text{--}15^{\circ}\text{C}$). The crystals grown by transportation at the top of the capsule were washed with distilled water and ethanol, and examined by an X-ray powder diffractometer (XRD), a scanning electron microscope (SEM), an energy dispersive spectroscopy (EDS) and a Fourier transform infrared spectrophotometer (FT-IR).

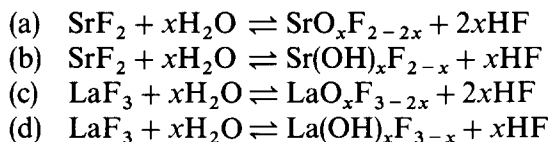
3 RESULTS AND DISCUSSION

3.1 Effect of mineralizers solutions on the synthesis of SrF_2 -solid solutions

The mineralizer solution must not change the phases or equilibria of products but accelerate their formation. In the system $\text{SrF}_2\text{--LaF}_3$, at about 500°C , the SrF_2 -solid solution has a solubility of 57 wt% (46 mol%) LaF_3 , and the LaF_3 -solid solution has a solubility of 1 wt% (2 mol%) SrF_2 .^{3,4} Both solid solutions are produced from the composition containing 70 wt% LaF_3 . Table 1, p. 238, shows the phases produced after hydrothermal reaction in the indicated solutions at 500°C for 1 day under 100 MPa. Consideration of these results suggests the following explanations.

- (1) SrF_2 might be contaminated by potassium ion (K^+) in the crystallization process in aqueous solution of KF.
- (2) LaF_3 formed NaLaF_4 in aqueous solution of NaF.
- (3) By-products such as LiLaO_2 and LaCO_3OH were formed under alkaline conditions, such as in the solutions of carbonates and hydroxides. It is also considered that in alkaline solutions the products were readily contaminated by hydroxyl ions (OH^-).
- (4) SrF_2 was decomposed in a strong acidic solution (6N HCl).
- (5) The same products were obtained in almost neutral solutions, such as chlorides, bromides, sulfates or nitrates.

Neutral or mildly acidic solutions are best for the synthesis of SrF_2 -solid solutions. If the hydrolysis reaction of fluorides or the substitution of hydroxyl ion (OH^-) for fluoride ion (F^-) occurred, a small amount of HF might be produced by the following reactions:



Therefore, the formation of these oxyfluorides or hydroxyfluorides have been studied as described below.

3.2 Analysis of hydroxyl ions in synthetic SrF_2 -solid solutions

It is of great importance to analyze for the presence of water molecules and/or hydroxyl ion (OH^-) in the products synthesized in solution, although it is very difficult to distinguish between fluorides and hydroxyfluorides. The presence of water molecules and/or hydroxyl ions (OH^-) in the products which were synthesized by solid state or hydrothermal reaction was

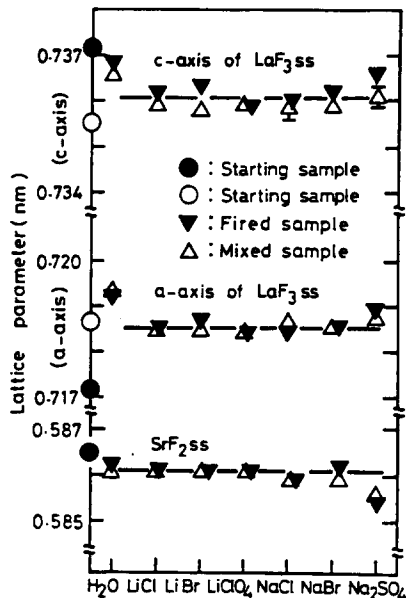


Fig. 2. The lattice parameters of SrF_2 - and LaF_3 -solid solutions synthesized hydrothermally from the composition containing 70 wt% LaF_3 at 750°C for 1 day under 100 MPa in the indicated solutions, \circ , starting sample of SrF_2 or LaF_3 ; \bullet , starting sample fired at 1300°C before the above treatments; \triangle , samples from mixed sample ($\text{SrF}_2 + \text{LaF}_3$); \blacktriangledown , samples from fired sample.

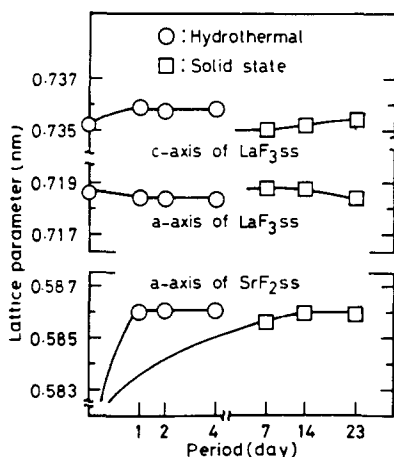


Fig. 3. The lattice parameters of SrF₂- and LaF₃-solid solutions synthesized by hydrothermal and solid state reactions from the composition containing 70 wt% LaF₃ at 750°C for the indicated periods in 10 wt% LiCl solution and vacuum, respectively.

determined by FT-IR and by measurement of the lattice parameters of the solid solutions. Figure 2 shows the lattice parameters of synthetic solid solutions produced from the composition containing 70 wt% LaF₃ after hydrothermal reaction at 750°C for 1 day under 100 MPa in re-distilled water, or in 10 wt% solutions such as LiCl,* LiBr,† LiClO₄,‡ NaCl,§ NaBr,† and Na₂SO₄† (all reagent grade). The 10 wt% solutions of LiCl, LiBr, LiClO₄, NaCl and NaBr produced identical solid solutions with the same lattice parameters. The larger lattice parameters of LaF₃-solid solution, synthesized in re-distilled water or 10 wt% solution of Na₂SO₄, suggests water molecule or hydroxyl ion (OH⁻) contamination in the solid solutions. An aqueous solution of LiCl seems to be the best mineralizer for the system studied because of the following results. The products had identical lattice parameters in both SrF₂- and LaF₃-solid solutions from the mixed samples and the fired samples. These lattice parameters of the products coincided with those synthesized at 750°C by the solid state reaction in vacuum (10⁻² Pa) after long treating periods (Fig. 3). Furthermore, the presence of water molecules and/or hydroxyl ions (OH⁻) was not detected by FT-IR in the products synthesized hydrothermally at 750°C under 100 MPa in 10 wt% LiCl solution (Fig. 4). The EDS analysis detected neither chlorine nor any other cation contamination in the products using 10 wt% LiCl solution.

* Kanto Chemical Co. Inc., Tokyo, Japan.

† Koso Chemical Co. Ltd, Tokyo, Japan.

‡ Nakarai Chemical Co. Ltd, Kyoto, Japan.

§ Wako Pure Chemical Indus. Ltd, Osaka, Japan.

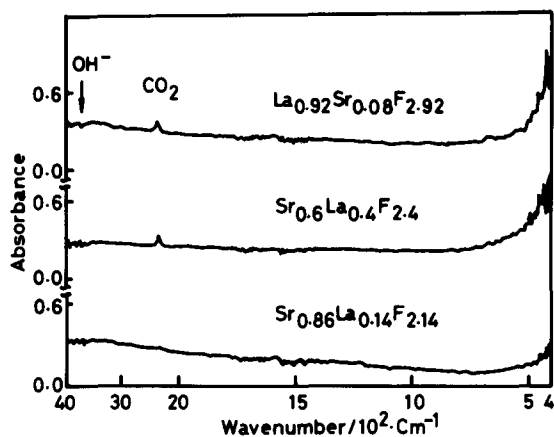


Fig. 4. The infrared spectra of SrF_2 - and LaF_3 -solid solutions synthesized hydrothermally at 750°C for 1 day under 100 MPa in 10 wt% LiCl solution (KBr used as a standard).

These results revealed the possibility of hydrothermal synthesis in the system SrF_2 - LaF_3 . The LiCl or LiBr solutions were preferable to NaCl for the growth of $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals.⁵

3.3 Hydrothermal crystal synthesis/growth of the SrF_2 -solid solutions

An aqueous solution of LiCl seemed to be the best mineralizer for the system studied. We therefore carried out the hydrothermal synthesis in 10 wt% LiCl solution for various compositions. The solid solutions of both SrF_2 and LaF_3 could be synthesized as equilibrium phases by hydrothermal reaction at 750°C for 1 day under 100 MPa in 10 wt% LiCl solution (Fig. 5). Crystals having the composition of $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ ($x = 0 - 0.47$) were synthesized without a temperature difference, and were controllable by the starting compositions, because a linear relationship was established between the starting compositions and the lattice parameters of the products. This is similar to the case of the solid state reactions where the product compositions are the same as the starting compositions. However, the product composition was different from the starting composition in the crystal growth with a temperature difference. Optimal conditions to grow larger crystals appeared to be in the regions around 650°C with a temperature difference of about 5°C .⁵ Figure 6 shows the lattice parameters of solid solution crystals of SrF_2 and LaF_3 , grown at the top and the bottom of the capsule, after hydrothermal growth at a dissolution temperature of 650°C ($\Delta T = 5 - 10^\circ\text{C}$) for 3 days under 100 MPa in 10 wt% LiCl solution. Almost pure SrF_2 single crystals, about 0.3 mm in size, were grown at the top from starting compositions containing up to 30 wt% LaF_3 . The crystals of

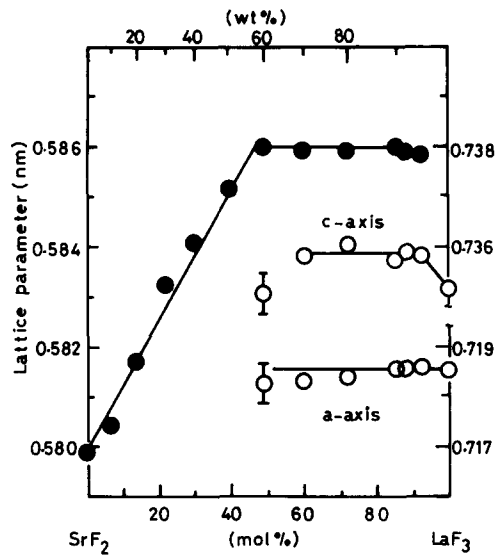


Fig. 5. The lattice parameters of SrF₂- and LaF₃-solid solutions synthesized hydrothermally at the bottom of the capsule from the composition containing indicated LaF₃ contents at 750°C ($\Delta T = 0^\circ\text{C}$) for 1 day under 100 MPa in 10 wt% LiCl solution.

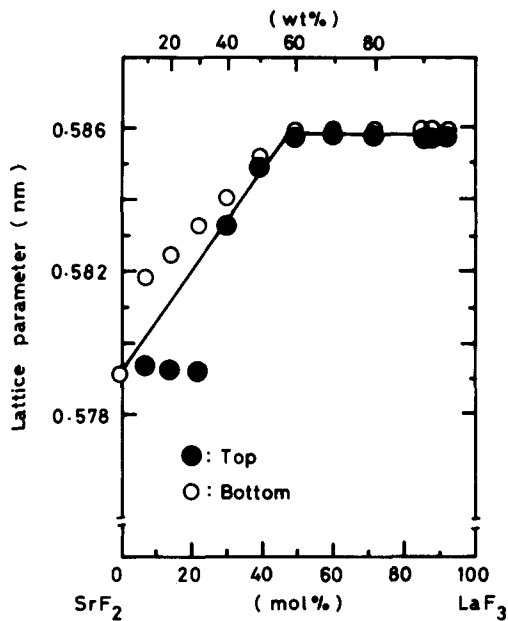


Fig. 6. The lattice parameters of SrF₂- and LaF₃-solid solution crystals grown at the top and the bottom of the capsule hydrothermally at 650°C ($\Delta T = 5\text{--}10^\circ\text{C}$) for 3 days under 100 MPa in 10 wt% LiCl solution.

SrF₂-solid solution at the bottom of the capsule had larger lattice parameters; they contained more LaF₃ than the equilibrium phases. The solubilities of SrF₂ and LaF₃ in 100 ml water at room temperature are 11 mg and 0 mg, respectively.⁷ SrF₂ is more soluble in dilute acids and decomposed by strong acids; for example, a by-product was formed in 6N HCl (Table 1). The large difference between solubilities of SrF₂ and LaF₃ causes decomposition of each pure phase. Therefore SrF₂ is preferentially

TABLE 1

The Phases Produced Hydrothermally from the Composition Containing 70 wt% LaF₃ at 500°C for 1 day Under 100 MPa in the Indicated Solution

<i>Solution</i>	<i>SrF₂</i>	<i>LaF₃</i>	<i>Other phases</i>
H ₂ O (re-distilled)	○	○	none
LiF 8 wt%	○	○	none
NaF 8 wt%	×	×	NaLaF ₄ ; 10-153 ^a
KF 8 wt%	#	○	none
NH ₄ F 8 wt%	○	○	phase?
LiCl 10 wt%	○	○	none
NaCl 10 wt%	○	○	none
KCl 8 wt%	○	○	none
NH ₄ Cl 7 wt%	○	○	none
HCl 6N	×	○	phase?
LiBr 10 wt%	○	○	none
NaBr 10 wt%	○	○	none
Na ₂ CO ₃ 10 wt%	×	×	phase?
K ₂ CO ₃ 8 wt%	○	△	LaCO ₃ OH; 26-815, ^a 20-1097 ^a
LiOH 8 wt%	○	△	LiLaO ₂ ; 19-722 ^a
NaOH 10 wt%	○	△	phase?
KOH 8 wt%	○	×	phase?
LiNO ₃ 10 wt%	○	○	none
NaNO ₃ 10 wt%	○	○	none
KNO ₃ 8 wt%	○	○	none
Li ₂ SO ₄ 10 wt%	○	○	phase?
Na ₂ SO ₄ 10 wt%	○	○	none
K ₂ SO ₄ 8 wt%	○	○	none
LiClO ₄ 10 wt%	○	○	none
(CH ₃ COO)Li 10 wt%	○	○	phase?

○, that phase is found by XRD; △, that phase is weak by XRD; ×, that phase is not found by XRD; Phase?, unidentified phase; #, K⁺ contamination.

^a Powder diffraction file number of ASTM or JCPDS.

transported from the bottom to the top of capsule. An excess of LaF_3 may be required in the starting samples in this region.

Single crystals of SrF_2 -solid solution, about 0.2 mm in size, grown at the top of the capsule from the composition containing 40 wt% LaF_3 , had only slight deviation from the starting composition. The composition containing 50 wt% SrF_2 yielded single crystals of SrF_2 -solid solution, being about 0.2 mm in size and having the same lattice parameters as those of the equilibrium phase. Figure 7(a) shows a single cubic crystal of SrF_2 -solid

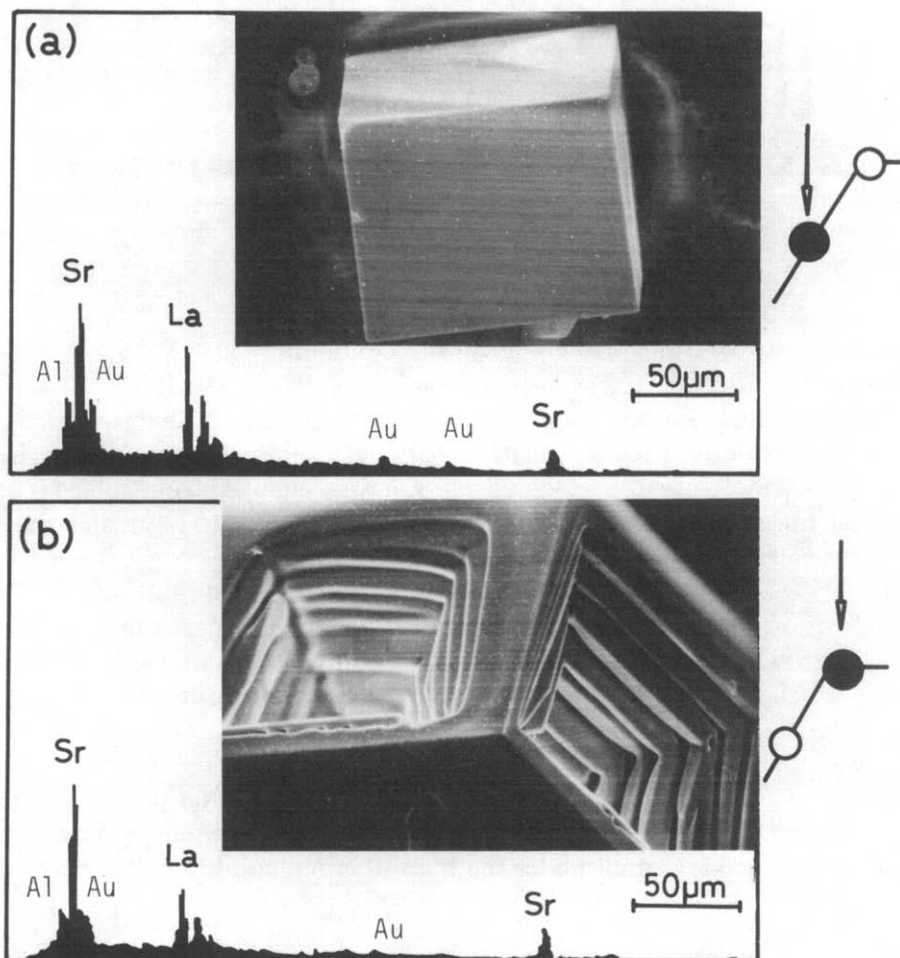


Fig. 7. Single crystals of SrF_2 -solid solution grown hydrothermally from the composition containing (a) 50 wt% and (b) 60 wt% LaF_3 at a temperature of 650°C ($\Delta T = 5\text{--}10^\circ\text{C}$ (a), and greater than 15°C (b)) for 7 and 3 days, respectively, under 100 MPa in 10 wt% LiCl solution (Au = Au sputtering, Al = substrate for sample). The sample compositions are indicated by the arrows on the right-hand side of the two photographs (see Fig. 6).

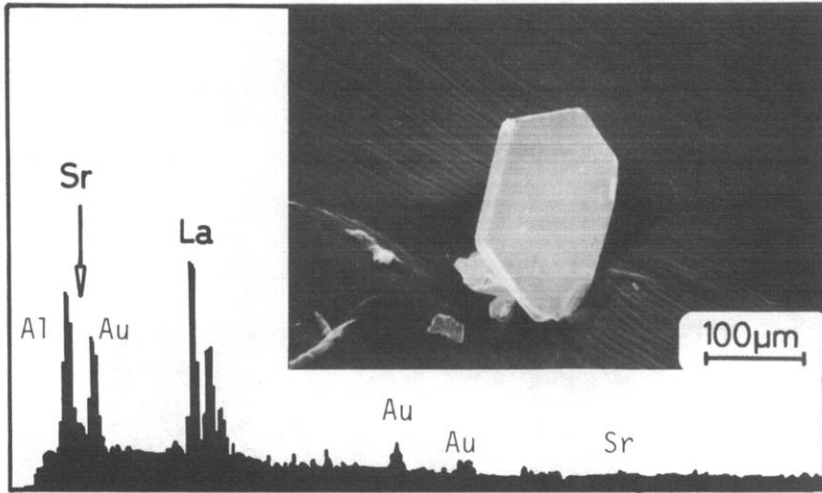


Fig. 8. The hexagonal plate-like single crystal of LaF_3 -solid solution grown hydrothermally from the composition containing 92 wt% LaF_3 at 650°C ($\Delta T = 5\text{--}10^\circ\text{C}$) for 7 days under 100 MPa in 10 wt% LiCl solution.

solution grown from the composition containing 50 wt% SrF_2 at a temperature of 650°C ($\Delta T = 5\text{--}10^\circ\text{C}$) for 7 days under 100 MPa in 10 wt% LiCl solution. The composition of this single crystal by EDS analysis was the same as that derived from the lattice parameters measured by XRD. The crystal morphologies of SrF_2 -solid solution were changed from cubic (a) to skeletal (b) under conditions of temperature difference (ΔT) greater than 15°C at 650°C (Fig. 7).

In the two-phase region, the single crystals of SrF_2 -solid solution had the composition of the solubility limit, and were about 0.05 mm in size. The crystal growth of SrF_2 -solid solution was controlled by the solubility of LaF_3 which acts as a growth inhibitor. From the composition containing more than 70 wt% LaF_3 , single crystals of LaF_3 -solid solution were grown as hexagonal plates, about 0.1–1 mm in size, at 650°C ($\Delta T = 5\text{--}10^\circ\text{C}$) for 7 days under 100 MPa in 10 wt% LiCl solution at the top and bottom of the capsule, due to the low solubility of LaF_3 (Fig. 8). The solubility gradient of LaF_3 might be very small under the hydrothermal condition studied.

4 CONCLUSIONS

- (1) Crystal synthesis of SrF_2 -solid solutions in the system $\text{SrF}_2\text{--LaF}_3$ was possible under hydrothermal conditions at about 650°C and under 100 MPa by spontaneous nucleation.

- (2) An aqueous solution of LiCl was found to be the best mineralizer.
- (3) The solid solutions synthesized at 750°C by solid state reaction for 23 days in vacuum, or by hydrothermal reaction for 1 day under 100 MPa in 10 wt% LiCl solution, had the same lattice parameters.
- (4) The crystal composition of SrF₂-solid solution was controllable by the starting composition.
- (5) Hydroxyl ions (OH⁻) in the products were not detected by FT-IR.
- (6) Single crystals of SrF₂-solid solution about 0.2 mm in size were grown from the composition containing 50 wt% SrF₂ at 650°C for 7 days under 100 MPa in 10 wt% LiCl solution.
- (7) Hexagonal plate-like single crystals of LaF₃-solid solution, about 0.1–1 mm in size, were grown at 650°C for 7 days.

REFERENCES

1. Portier, J., Reau, J. M., Matar, S., Soubeyroux, J. L. and Hagemuller, P., Advances on fluorine ion conductors, basic and applied research, *Solid State Ionics*, **11** (1983) 83–90.
2. Schoonman, J., Oversluizen, G. and Wapenaar, K. E. D., Solid electrolyte properties of LaF₃, *Solid State Ionics*, **1** (1980) 211–21.
3. Yoshimura, M., Kim, K. J. and Sōmiya, S., Phase diagram of the system SrF₂–LaF₃, *Yogyo-Kyokai-Shi (J. Ceram. Soc., Japan)*, **93** (1985) 130–6.
4. Yoshimura, M., Kim, K. J. and Sōmiya, S., Revised subsolidus phase diagram of the system SrF₂–LaF₃, *Solid State Ionics*, **18/19**, Part II (1986) 1211–16.
5. Yoshimura, M., Kim, K. J. and Sōmiya, S., Hydrothermal growth of La³⁺-doped SrF₂ single crystal, *J. Mater. Sci. Lett.*, **3** (1984) 1097–8.
6. Roy, R. and Tuttle, O. F., in *Physics and Chemistry of the Earth*. Eds L. H. Ahrens, K. Rankama and S. K. Runcorn, Vol. 1, Pergamon Press, Oxford, 1956, pp. 138–80.
7. *Lange's Handbook of Chemistry*. 13th edn, Eds John A. Dean and Norbert Adolph Lange. Physical constants of inorganic compounds, McGraw Hill Inc., New York, 1985, 12–133.

Received 20 November 1986; revised version received 12 March 1987; accepted 6 May 1987