Flux growth of doped lanthanum silicate oxyapatite crystals with hexagonal tabular morphology

Koichiro FUKUDA¹, Yuki TSUNODA¹, Daisuke URUSHIHARA¹, Toru ASAKA¹ and Hideto YOSHIDA²

¹Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Nagoya 466-8555, Japan
²Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan

We have for the first time succeeded in the preparation of thin tabular crystals of K₂O- and F-doped lanthanum silicate oxyapatite, which were grown by the high-temperature solution technique using KF as solvent. The crystals were characterized using microscopy, energy dispersive X-ray spectroscopy, electron probe microanalysis (EPMA), and X-ray diffractometry (XRD). The atomic compositions determined by EPMA showed the significant correlations among the numbers of atoms (N) for La, Si, and F. They were well expressed by the two linear equations of \( N_{\text{La}} = 17.52 - 1.426N_{\text{Si}} \) and \( N_F = -1.20 + 0.243N_{\text{Si}} \), which enabled us to derive the general formula of \( [\text{La}_{8.964+1.426x}\text{Si}_{5.871-0.835x}\text{F}_{0.258x}]_2\{\text{O}_{25.742-0.243x}\text{F}_{0.818x}\}_2\text{O}_{25.77x}(0 \leq x \leq 0.134) \), where \( x \) represents the amount of silicon deficiency denoted by \( \square \). Based on the single crystal XRD data, the crystal structure was refined for one of the grains, the chemical formula of which was eventually determined to be \( [\text{La}_{9.11}\text{K}_{0.85}]_2[\text{Si}_{9.08}\square_{0.10}]_2\{\text{O}_{25.75}\text{F}_{0.21}\}_2\text{O}_{25.72}\text{F}_{0.10} \). The K and F ions preferentially occupied, respectively, the La and O (channel oxide-ion) sites, with the silicon site being deficient by ca. 1.7%. Since the tabular crystals showed the well-developed (001) faces with relatively high aspect ratios, they could act as satisfactory templates for the preparation of the c-axis-oriented polycrystals.

Key-words : Lanthanum silicate oxyapatite, Tabular crystals, Flux method, Crystal structure, Template particles

1. Introduction

The relatively high oxide-ion conductivity of rare-earth (RE) silicate oxyapatite (space group \( P6_3/m \)) has been discovered by Nakayama et al. in 1995. Among the nines-types of oxyapatite crystals with \( \text{RE} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Y}, \text{Ho}, \text{Er}, \text{and Yb}, \) the conductivity was the highest for the La silicate oxyapatite (LSO). The subsequent researchers have clarified the anisotropy of conduction for the crystals with \( \text{RE} = \text{La}, \text{Pr}, \text{Nd}, \text{and Sm}. \) The conductivity was much higher parallel to the \( c \)-axis than perpendicular to this direction. Thus, Fukuda et al. have prepared the highly \( c \)-axis-oriented LSO polycrystal by reactive diffusion technique using \( \text{La}_2\text{Si}_2\text{O}_7 \) diffusion couple. Since the conductivity has been effectively enhanced by the silicon deficiency in LSO, the grain-aligned polycrystal of \( \text{La}_9\text{Si}_7(\square_{0.10})_2\{\text{O}_{25.75}\}_2\text{O}_{25.72}\text{F}_{0.10} \) demonstrated, along the grain-alignment direction, the relatively high conductivity (e.g., \( 1.26 \times 10^{-1} \text{S/cm}^2 \) at 1073 K), where \( \square \) denotes a vacancy in Si site. The LSO polycrystals as obtained were necessarily composed of the hexagonal columnar crystals, the elongation directions of which were along the \( c \)-axis. The crystal structure of silicon-deficient LSO has recently been in more detail characterized by Fujii et al.

The natural apatite crystals with chemical formula \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH, F, CI}) \) often occur in wide varieties of crystal habit, which is usually hexagonal columnar or hexagonal tabular. Similarly, the single crystals of RE-bearing silicate oxyapatite, which were grown by the high-temperature solution technique, showed two distinct outer shapes. The crystals of \( \text{SrPr}_4\text{Si}_3\text{O}_{13} \) (1373–923 K and \( \text{SrCl}_2 \)), \( \text{Pb}_0.2\text{Dy}_4.8\text{Si}_2.8\text{O}_{13} \) (1543–1403 K and \( \text{PbF}_2/\text{PbO}_2 \)), \( \text{Pr}_9\text{KSi}_6\text{O}_{26} \) (1273–1073 K and \( \text{KF} \)), and \( \text{NaNd}_9\text{Si}_6\text{O}_{26} \) (1623–1653 K and \( \text{Na}_2\text{MoO}_4 \)) were columnar in morphology, and those of \( \text{LiEu}_5\text{Si}_6\text{O}_{26} \) (1653–1193 K and \( \text{Li}_2\text{MoO}_3 \)) and \( \text{Na}_2\text{La}_8\text{Si}_6\text{O}_{24}\text{F}_2 \) (1623–1223 K and \( \text{NaF} \)) were thick tabular, where parentheses indicate the soaking-temperature ranges and solvents used. Setoguchi, who synthesized the crystals of \( \text{NaNd}_9\text{Si}_6\text{O}_{26} \) and \( \text{LiEu}_5\text{Si}_6\text{O}_{26} \), speculated that the crystal morphology would be mostly controlled by the compositions of crystal and/or flux as well as the soaking temperatures. It is well known for snow and hydrothermally grown pyrite that the growth temperature, together with degree of supersaturation, strongly affects the morphology of crystals. Furthermore, with hydroxyfluorapatite \( [\text{Ca}_{10}(\text{PO}_4)_6(\text{F, OH})_2] \), the fluorine concentration in solution has influenced on the morphologic variations; the crystal habit was tabular at
relatively high concentration of fluorine, and it was needle-like at relatively low fluorine concentration.\(^\text{18}\)

In the present study, we have for the first time succeeded in the preparation of thin tabular crystals of K\(_2\)O- and F-doped LSO, which have been grown at a relatively low temperature by the KF flux method. Because the resultant crystal grains exhibited relatively high aspect ratios with well-developed [001] faces, they could be appropriately used for the template particles of the templated grain growth (TGG) method\(^\text{19}-\text{21}\) for the synthesis of highly c-axis-oriented polycrystals.

### 2. Experimental procedures

#### 2.1 Material

We prepared the powder mixture of reagent-grade chemicals of La\(_2\)O\(_3\) (99.99\%, Mitsuwa Chemicals Co. Ltd., Osaka, Japan), SiO\(_2\) (99.0\%, Mitsuwa Chemical Co. Ltd., Osaka, Japan), and KF (99.0\%, Kishida Chemical Co. Ltd., Osaka, Japan), the [La\(_2\)O\(_3\)SiO\(_2\)KF] molar ratios of which were [1:1.29:42.64]. It was subsequently heated in Pt crucible (capacity 10 mL) with lid at 1173 K for 72 h, then slowly cooled to 1073 K at 1 K/h, and followed by rapid cooling to ambient temperature by cutting furnace power. During the slow cooling process, silicate crystals up to 160 \(\mu\)m in size grew in the presence of KF flux. The upper part of the solidified material in the crucible was mainly composed of KF, and the lower part was mostly consisting of silicate crystals, suggesting that the crystal growth occurred under the heterogeneous conditions in chemical composition. We washed the overall sample with distilled water to remove the flux material, and eventually obtained the silicate crystals.

#### 2.2 Characterization

We preliminarily examined the powder specimen on a stereo microscope (M205C, Leica Microsystems GmbH, Wetzlar, Germany), and found that it was composed of minute euhedral crystals. The outer shape of each crystal grain was observed at the higher magnification using a scanning electron microscope (SEM; JSM-6010LA, JEOL Ltd., Tokyo, Japan), equipped with an energy dispersive X-ray spectrometer (EDX; JED-2300, JEOL Ltd., Tokyo, Japan).

The chemical compositions of the crystals were semi-quantitatively investigated using the EDX. We also used an electron probe micro-analyzer (EPMA, model JXA-8900L, JEOL, Tokyo, Japan) to quantitatively determine the chemical compositions of K\(_2\)O- and F-doped LSO crystals by measuring one point for each of the nine crystal grains. The accelerating voltage, probe current, and electron probe diameter were, respectively, 15 kV, 20 nA, and ca. 1 \(\mu\)m. We corrected the characteristic X-ray intensities by ZAF routines using the standard materials of synthetic La\(_2\)Si\(_2\)O\(_7\) for La and Si, natural adularia (KA\(_2\)Si\(_3\)O\(_8\)) for K, and synthetic CaF\(_2\) for F.

We selected two tabular LSO crystals, and fixed them onto glass slides with epoxy resin. The developed (001) plane was almost parallel to the slide surface for one crystal grain (sample 1), and the corresponding plane was almost perpendicular to it for the other one (sample 2). These orientation-defined crystal grains were mirror finished by buff polishing after being polished using a #1500 waterproof emery paper. The SEM images, together with concentration distribution maps for La\(_2\)O\(_3\), K\(_2\)O, and SiO\(_2\), were obtained using the EPMA on these crystal grains. The analysis areas were 70 \(\times\) 70 \(\mu\)m with 70 \(\times\) 70 pixels for sample 1 and 70 \(\times\) 100 \(\mu\)m with 70 \(\times\) 100 pixels for sample 2, with the dwell time being 20 ms. The accelerating voltage, probe current, and electron probe diameter were, respectively, 15 kV, 0.010 \(\mu\)A, and ca. 2 \(\mu\)m.

We picked up single crystals with different morphology, and mounted each of them on the end of a soda glass capillary. The single-crystal X-ray diffraction (XRD) data were collected on a Bruker D8 VENTURE diffractometer using Mo K\(\alpha\) radiation (50 kV and 1 mA). We refined the unit-cell parameters and extracted the observed structure factors using a program package APEX3 Suite.\(^\text{22}\) We refined the structural parameters on a computer program JANA2006,\(^\text{23}\) and validated the significance of the final structural model by the difference Fourier maps using the same program. The crystal structure model was visualized with a computer program VESTA.\(^\text{24}\)

We collected the X-ray powder diffraction data from the powder specimen in the 2\(\theta\) range from 12.5 to 64.6\(^\circ\) using a diffractometer (X’Pert PRO Alpha-1, PANalytical B.V., Almelo, The Netherlands) in the Bragg-Brentano geometry, which was equipped with an incident-beam Ge(111) Johansson monochromator to obtain Cu K\(\alpha_1\) radiation and a high-speed detector. The X-ray generator was operated at 45 kV and 40 mA. Based on a Brindley’s procedure,\(^\text{25}\) we determined the phase composition using the whole-pattern-fitting method on a computer program RIETAN-FP.\(^\text{26}\)

### 3. Results and discussion

#### 3.1 Crystal morphology and phase composition

The powder specimen as obtained was found to be composed of two-types of euhedral crystals; one was hexagonal plate-like (tabular), and the other was columnar (Fig. 1). The former crystals, ranging up to 160 \(\mu\)m in size, mainly contained La, Si, O, and K, with a very small amount of F. The intensity distributions of single-crystal XRD patterns were in accord with those of LSO, hence we successfully refined the crystal structure starting from the structural model of La\(_{9.33}\)Si\(_6\)O\(_{26.27}\).\(^\text{27}\) The detailed procedure for the structural refinement of the K\(_2\)O- and F-doped LSO will be described later. The Miller indices were [001] for the well-developed faces of the thin tabular crystals, and [100] for the side faces [Fig. 1(a)]. The hexagonal tabular morphology indicates that the growth rate in the (001) direction was much slower than those in the orthogonal directions. The hexagonal base of each crystals was often distorted from a regular hexagon. Thus, we defined \(d\) for the diameter of a circle whose area is equal to the corresponding hexagonal base, and determined the aspect ratio
(= \(d/t\)) of each tabular crystal, where \(t\) is thickness. We randomly selected ten crystal grains to find that the \(d/t\)-value ranged from 4.5 to 13.7 (average = 9.8). On the other hand, we found that the crystals with columnar morphology, ranging up to \(65 \text{\mu m}\) in size, were of \(K_5La_4F(SiO_4)_{28}\) from the single-crystal XRD patterns as well as the EDX spectrum. The unit-cell dimensions refined by the XRD were \(a = 1.25402(9) \text{ nm}\) and \(c = 0.55300(5) \text{ nm}\) (space group \(I4\)), which were comparable with those reported in a previous study \((a = 1.2514 \text{ nm} and\ c = 0.5515 \text{ nm})\). The well-developed faces were indexed by \{100\}, \{111\}, and \{132\} based on the tetragonal lattice [Fig. 1(b)]. A series of faces belonging to \{100\} constitute a zone with the zone axis [001], which is parallel to the elongation direction. The phase composition of the powder specimen was, under the condition of effective particle radii being \(5.00 \text{\mu m}\), found to be \(62.7 \text{ mol}\% K_2O-\) and \(F-\) doped LSO and \(37.3 \text{ mol}\% K_5La_4F(SiO_4)_{28}\) (Fig. 2).

It is worthy of notice that we have, for the first time, successfully prepared the tabular crystals of doped LSO. This achievement would be considered significant in the physics and chemistry of crystal growth, since the crystal morphology reported so far has been necessarily columnar for both LSO and doped LSO.\(^{4,7,29}\) Because the \{001\} faces were well developed for the thin tabular crystals with high aspect ratio, they would be technologically useful as template particles of TGG method for the preparation of the \(c\)-axis-oriented polycrystal, which is expected to demonstrate the relatively high oxide-ion conductivity along the common \(c\)-axes. In anticipation of the TGG experiment, we have confirmed the thermal stability of the outer shape as well as crystal structure of the tabular crystals of \(K_2O-\) and \(F-\) doped LSO after the heat treatment at \(1873 \text{ K}\) for \(100 \text{ h}\).

Although, the reason why the tabular crystals of \(K_2O-\) and \(F-\) doped LSO grew from the KF solvent is still uncertain, the crystal morphology could be principally influenced by the growth temperature as in snow\(^{16}\) and

![Fig. 1. SEM images of (a) the thin tabular crystal of \(K_2O-\) and \(F-\) doped lanthanum silicate oxyapatite (doped LSO), and (b) the columnar crystal of \(K_5La_4F(SiO_4)_{28}\).](image)

![Fig. 2. Fitting result of the observed diffraction pattern (symbol: +) for the powder specimen, consisting of \(K_2O-\) and \(F-\) doped lanthanum silicate oxyapatite (doped LSO) and \(K_5La_4F(SiO_4)_{28}\). The calculated pattern and the positions of possible Bragg reflections are, respectively, indicated by the upper solid line and the lower vertical bars. The difference curve between the observed and calculated patterns is given in the lower part of the diagram.](image)
hydrothermally grown pyrite,17) and the presence of fluorine as in hydroxylfluorapatite.18) Actually, the maximum heating temperature (= 1173 K) of the present flux method was significantly lower than those (= 1273–1653 K) of the high-temperature solutions, from which the columnar and thick tabular crystals of RE-bearing silicate oxyapatite grew as reported in the previous studies.11–15

### Table 1. Chemical composition (mass %) and numbers of atoms of doped LSO crystals

| No. | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| La2O3 | 79.10 | 79.21 | 80.13 | 80.31 | 81.23 | 80.21 | 80.50 | 75.72 | 79.73 |
| K2O | 2.21 | 2.19 | 2.10 | 2.25 | 2.34 | 2.34 | 2.08 | 2.13 | 2.09 |
| SiO2 | 19.01 | 19.30 | 19.20 | 19.84 | 19.24 | 18.72 | 19.49 | 19.72 | 19.51 |
| F | 0.21 | 0.27 | 0.24 | 0.24 | 0.22 | 0.24 | 0.27 | 0.27 | 0.28 |

Total 100.53 100.97 101.67 102.64 103.03 101.25 102.39 96.81 101.74

|   | N<sub>La</sub> | N<sub>K</sub> | N<sub>Si</sub> | N<sub>O</sub> | N<sub>F</sub> |
|---|----------------|-------------|-------------|-------------|-------------|
| 1 | 9.081          | 0.879       | 5.918       | 25.792      | 0.208       |
| 2 | 9.018          | 0.862       | 5.956       | 25.742      | 0.258       |
| 3 | 9.101          | 0.824       | 5.911       | 25.770      | 0.230       |
| 4 | 8.964          | 0.867       | 6.003       | 25.770      | 0.230       |
| 5 | 9.137          | 0.910       | 5.867       | 25.788      | 0.212       |
| 6 | 9.212          | 0.827       | 5.827       | 25.770      | 0.230       |
| 7 | 9.050          | 0.830       | 5.942       | 25.770      | 0.230       |
| 8 | 8.954          | 0.854       | 5.924       | 25.747      | 0.253       |
| 9 | 8.998          | 0.872       | 5.400       | 25.718      | 0.282       |

### 3.3 Crystal structure of doped LSO

We selected one of the single crystals of doped LSO, the crystallinity degree of which was appropriate for crystal structure determination by XRD. With this particular crystal grain, the crystal structure as well as the chemical composition were satisfactorily refined under the chemical constraints imposed by the general formula aforementioned. The summary of data collection and refinement parameters are summarized in Table 2. The initial structural parameters were taken from those determined by Okudera et al.27) for La<sub>0.33</sub>Si<sub>2</sub>O<sub>5</sub> (space group P6<sub>3</sub>/m, Z = 1). In the unit cell, there are two La sites of Wyckoff positions 4f (denoted by La1) and 6h (La2), one Si site of 6h, and four O sites of 6h (O1 and O2), 12i (O3) and 2a (O4, channel oxide-ion site). In the initial stage of refinement, we independently refined, without any constraints, the site occupancies (g) of La1, La2, and Si. The g(La2)-value readily exceeded unity, hence we imposed constraints imposed by the general formula aforementioned. The summary of data collection and refinement parameters are summarized in Table 2. The initial structural parameters were taken from those determined by Okudera et al.27) for La<sub>0.33</sub>Si<sub>2</sub>O<sub>5</sub> (space group P6<sub>3</sub>/m, Z = 1). In the unit cell, there are two La sites of Wyckoff positions 4f (denoted by La1) and 6h (La2), one Si site of 6h, and four O sites of 6h (O1 and O2), 12i (O3) and 2a (O4, channel oxide-ion site). In the initial stage of refinement, we independently refined, without any constraints, the site occupancies (g) of La1, La2, and Si. The g(La2)-value readily exceeded unity, hence we imposed constraints imposed by the general formula aforementioned. The summary of data collection and refinement parameters are summarized in Table 2. The initial structural parameters were taken from those determined by Okudera et al.27) for La<sub>0.33</sub>Si<sub>2</sub>O<sub>5</sub> (space group P6<sub>3</sub>/m, Z = 1). In the unit cell, there are two La sites of Wyckoff positions 4f (denoted by La1) and 6h (La2), one Si site of 6h, and four O sites of 6h (O1 and O2), 12i (O3) and 2a (O4, channel oxide-ion site). In the initial stage of refinement, we independently refined, without any constraints, the site occupancies (g) of La1, La2, and Si. The g(La2)-value readily exceeded unity, hence we imposed constraints imposed by the general formula aforementioned. The summary of data collection and refinement parameters are summarized in Table 2. The initial structural parameters were taken from those determined by Okudera et al.27) for La<sub>0.33</sub>Si<sub>2</sub>O<sub>5</sub> (space group P6<sub>3</sub>/m, Z = 1). In the unit cell, there are two La sites of Wyckoff positions 4f (denoted by La1) and 6h (La2), one Si site of 6h, and four O sites of 6h (O1 and O2), 12i (O3) and 2a (O4, channel oxide-ion site). In the initial stage of refinement, we independently refined, without any constraints, the site occupancies (g) of La1, La2, and Si. The g(La2)-value readily exceeded unity, hence we imposed constraints imposed by the general formula aforementioned. The summary of data collection and refinement parameters are summarized in Table 2. The initial structural parameters were taken from those determined by Okudera et al.27) for La<sub>0.33</sub>Si<sub>2</sub>O<sub>5</sub> (space group P6<sub>3</sub>/m, Z = 1). In the unit cell, there are two La sites of Wyckoff positions 4f (denoted by La1) and 6h (La2), one Si site of 6h, and four O sites of 6h (O1 and O2), 12i (O3) and 2a (O4, channel oxide-ion site). In the initial stage of refinement, we independently refined, without any constraints, the site occupancies (g) of La1, La2, and Si. The g(La2)-value readily exceeded unity, hence we imposed
principal MSD values was ca. 6.92, which should be, in general, less than 4. Furthermore, the difference Fourier maps showed significant residual electron density peaks nearby the O3 site. Thus, we split the O3 site into two (O3A and O3B) under the linear constraints on occupancies; g(O3A) + g(O3B) = 1. At this stage of the refinement process for the split-atom model, the reliability (R) indices were $R = 0.0234$ and $wR = 0.0254$.

We subsequently considered the occupation of K ions at La1 and/or La2 sites, and that of F ions at O4 site. In the light of the crystal structure of fluorapatite, it is quite conceivable that the F ions preferentially occupy the channel oxide-ion site of O4. The refinement led to the K/ (La + K)-value at La2 site to be negative, suggesting that the relevant site is free from K ions. Hence, we continued the refinement based on the structural model in which the K ions exclusively occupy the La1 site. The refinement resulted in the site compositions of 77.8% La, 21.2% K, and 1.0% cation-vacancy for La1, and 100% La for La2. The difference Fourier maps showed negligible residual density distributions, with the satisfactory R indices of $R = 0.0233$ and $wR = 0.0251$. The structural parameters and ADPs are summarized in Table 3, in which the La1, La2, and O4 sites were relabeled as, respectively, (La,K), La, and (O,F) sites. The g(Si)-value converged to 0.9826(8), corresponding to the silicon site being deficient by ca. 1.7%. The chemical formula was eventually determined to be $[La_{9.11}K_{0.85}]_{29.96}[Si_{15.96}\square_{0.10}]_{26}[O_{25.77}F_{0.23}]_{226}$ ($x = 0.10$).

### 3.4 Structure description

Figure 4 shows the structural model, which shows appreciable positional disordering of O3 atoms that are bonded to Si atoms. Selected interatomic distances, together with their standard deviations, are listed in Table S1. The mean Si–O bond length (0.1629 nm) is in good agreement with those expected from the bond

---

**Table 2. Summary of data collection and refinement parameters for La$_{9.11}$K$_{0.85}$Si$_{15.96}$O$_{25.77}$F$_{0.23}$**

| Chemical formula | Space group | $a$/nm | $c$/nm | $V$/nm$^3$ | $Z$ | Formula weight | Radiation type | Temperature/K | $\theta_{	ext{max}}$/degree | No. of measured reflections | No. of unique reflections | No. of observed reflections |
|------------------|-------------|--------|--------|-----------|-----|-----------------|-----------------|---------------|--------------------------|--------------------------|--------------------------|--------------------------|
| $La_{9.11}\text{K}_{0.85}\text{Si}_{15.96}\text{O}_{25.77}\text{F}_{0.23}$ | P6$_3$/m (No. 176) | 0.97078(2) | 0.72393(1) | 0.59085(3) | 1 | 1881.2 | MoKα | 298 | 5.2871 | 17159 | 3348 | 2369 |

$\mu$/mm$^{-1}$ = 1.664 |
valence sum (0.162 nm) and the sum of ionic radii of $\text{Si}^{4+}$ and $\text{O}^{2-}$ (0.164 nm).\textsuperscript{31–33} The (La,K) and La sites are, respectively, nine-fold and seven-fold coordinated. The mean bond lengths of the polyhedra are 0.266 nm for [(La,K)O$_6$] and 0.253 nm for [La(O,F)$_7$], which are comparable to those of, respectively, [LaO$_6$] (the mean = 0.262 nm) and [LaO$_7$] (the mean = 0.254 nm) in La$_{0.33}$Si$_6$O$_{26}$.$\textsuperscript{27}$ In accordance with previous studies (\textsuperscript{6,7,27}) the ADP ellipsoid of (O,F) site, corresponding to O4 site of La$_{0.33}$Si$_6$O$_{26}$, showed a very large component along the c-axis, although the magnitude was comparable with those reported so far. The ratio of the largest/smallest principal ADP components of the (La,K), La, Si, O1, O2, O3A and O3B sites were necessarily less than 3.68, indicating that the refinement was entirely successful to obtain the reasonable structural model.

We also evaluated the relevant bond lengths by the charge distribution method.\textsuperscript{34,35} In this method, the ratio of the formal oxidation number (q) to the computed charge (Q) of cation ($q/Q$) indicates the correctness of the structure determination. In the present K$_2$O- and F-doped LSO, the relevant ratios ranged from 0.99 of Si site to 1.02 of (La,K) site (Table S2). Since all of these ratios are close to unity, we concluded that the final structural model is satisfactory.

4. Conclusions

We have for the first time successfully prepared the thin tabular single crystals of doped LSO. Based on the linear correlations among the numbers of La, Si, and F atoms, the general formula was established as [La$_{8.964+1.426x}$K$_{0.035−0.055x}$Si$_{5.90−1.391x}$F$_{0.258−0.243x}$O$_{25.77−0.23}$(0 ≤ x ≤ 0.134)], where x represents the amount of silicon deficiency denoted by $\square$. Based on the XRD data of one of the single-crystal grains, we refined the crystal structure and determined the chemical formula to be [La$_{9.33}$O$_{26}$]$_{100}$[Si$_{5.90}$$\square$_{0.10}]$_{50}$[O$_{25.77}$F$_{0.23}$]$_{26}$ (x = 0.10), The K and F ions preferentially occupied, respectively, the La and O (channel oxide-ion) sites, with the silicon site being deficient by ca. 1.7%. The tabular crystals of doped LSO showed relatively high aspect ratios with well-developed [001] faces, hence they must be potentially applicable to the template particles of TGG method for the preparation of c-axis-oriented polycrystals. Although, the principal reason for the morphological variation of doped LSO is still unclear, the thin tabular morphology could be closely related to the relatively low growth temperature as well as the presence of fluorine in the flux solution.

Acknowledgement This research was supported by a Grant-in-Aid for Scientific Research (No. 16H02396) from the Japan Society for the Promotion of Science.

Appendix A. Supporting information Supplementary data associated with this article can be found in the online version.

References

1) S. Nakayama, T. Kageyama, H. Aono and Y. Sadaoka, J. Mater. Chem., 5, 1801–1805 (1995).
2) S. Nakayama, M. Sakamoto, M. Higuchi, K. Kodaira, M. Sato, S. Kakita, T. Suzuki and K. Itoh, J. Eur. Ceram. Soc., 19, 507–510 (1999).
3) S. Nakayama and M. Highuchi, J. Mater. Sci. Lett., 20, 913–915 (2001).
4) K. Fukuda, T. Asaka, M. Okino, A. Berghout, E. Béchade, O. Masson, I. Julien and P. Thomas, Solid State Ionics, 217, 40–45 (2012).
5) K. Fukuda, T. Asaka, R. Hamaguchi, T. Suzuki, H. Oka, A. Berghout, E. Béchade, O. Masson, I. Julien, E. Champion and P. Thomas, Chem. Mater., 23, 5474–5483 (2011).
6) K. Fukuda, T. Asaka, M. Oyabu, D. Urushihara, A. Berghout, E. Béchade, O. Masson, I. Julien and P. Thomas, Chem. Mater., 24, 4623–4631 (2012).
7) K. Fukuda, T. Asaka, S. Hara, M. Oyabu, A. Berghout, E. Béchade, O. Masson, I. Julien and P. Thomas, Chem. Mater., 25, 2154–2162 (2013).
8) K. Fukuda, M. Okabe and T. Asaka, J. Am. Ceram. Soc., 99, 2816–2822 (2016).
9) K. Fujii, M. Yashima, K. Hibino, M. Shiraïwa, K. Fukuda, S. Nakayama, N. Ishizawa, T. Hanashima and T. Ohhara, J. Mater. Chem. A, 6, 10835–10846 (2018).
10) J. Rakovan, Rev. Mineral. Geochem., 48, 51–86 (2002).
11) T. Sakakura, M. Kamoshita, H. I grandi, J. Wang and N. Ishizawa, Acta Crystallogr. E, 66, 168 (2010).
12) B. M. Wanklyn, F. R. Wondre, G. B. Ansell and W. Ishizawa, Acta Crystallogr. E, 66, 113 (2010).
13) J. Ito, F. Werner and F. Kubel, J. Mater. Lett., 59, 3660–3665 (2005).
14) M. Setoguchi, J. Cryst. Growth, 99, 879–884 (1990).
15) J. Ito, Am. Mineral., 53, 890–907 (1968).
16) U. Nakaya, Snow Crystals—Natural and Artificial, Harvard University, Cambridge, Mass. (1954).
17) J. B. Murowchick and H. L. Barnes, Am. Mineral., 72, 1241–1250 (1987).
18) Y. Deursch and S. Sarig, J. Cryst. Growth, 42, 234–237 (1977).
19) J. A. Horn, S. C. Zhang, U. Selvaraj, G. L. Messing and S. Trolier-McKinstry, J. Am. Ceram. Soc., 82, 921–926
(1999).
20) C. Duran, S. Trolier-McKinstry and G. L. Messing, J. Am. Ceram. Soc., 83, 2203–2213 (2000).
21) G. L. Messing, S. Trolier-McKinstry, E. M. Sabolsky, C. Duran, S. Kwon, B. Brahmaroutu, P. Park, H. Yilmaz, P. W. Rehrig, K. B. Eitel, E. Suvaci, M. Seabaugh and K. S. Oh, Crit. Rev. Solid State, 29, 45–96 (2010).
22) APEX3 Suite, version 2015.07; Bruker Analytical X-ray System Inc.: Madison, WI (2015).
23) V. Petricek, M. Dusek and L. Palatinus, “JANA2006: The Crystallographic Computing System”, Institute of Physics, Praha, Czech Republic (2006).
24) K. Momma and F. Izumi, J. Appl. Crystallogr., 44, 1272–1276 (2011).
25) G. W. Brindley, Philos. Mag., 36, 347–369 (1945).
26) F. Izumi and K. Momma, Solid State Phenom., 130, 15–20 (2007).
27) H. Okudera, Y. Masubuchi, S. Kikkawa and A. Yoshiasa, Solid State Ionics, 176, 1473–1478 (2005).
28) M. C. Schafer and T. Schleid, Z. Anorg. Allg. Chem., 636, 2069 (2010).
29) K. Fukuda, R. Watanabe, M. Oyabu, R. Hasegawa, T. Asaka and H. Yoshida, Cryst. Growth Des., 16, 4519–4525 (2016).
30) K. Sudarsanan, P. E. Mackie and R. A. Young, Mater. Res. Bull., 7, 1331–1338 (1972).
31) R. D. Shannon, Acta Crystallogr. A, 32, 751–767 (1976).
32) I. D. Brown and D. Altermatt, Acta Crystallogr. B, 41, 244–247 (1985).
33) N. E. Brese and M. O’Keeffe, Acta Crystallogr. B, 47, 192–197 (1991).
34) R. Hoppe, S. Voigt, H. Glaum, J. Kissel, H. P. Müller and K. Bernet, J. Less-Common Met., 156, 105–122 (1989).
35) M. Nespolo, G. Ferraris and H. Ohashi, Acta Crystallogr. B, 55, 902–916 (1999).