Fabrication of <001>-oriented apatite ceramics using a non-topochemical reactive α-tristontium phosphate template

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ABSTRACT

Textured ceramics are generally fabricated by reactive-templated grain growth using a template material with a suitable anisotropy and topochemical relationship to the target ceramics. We have previously synthesized hexagonal plate-like α-tristontium phosphate (α-Sr3(PO4)2; α-TSP) single crystals with no topochemical relationship to the apatite system. In the present study, we focused on using the facets of α-TSP particles as nucleation sites for textured apatite, and fabricated <001>-oriented strontium fluoroapatite (Sr10(PO4)6F2; SrFAp) through a reaction between aligned α-TSP platelets and SrF2. The SrFAp phase was formed with a preferred c-axis orientation at 900°C. Sintering in an F-containing atmosphere led, moreover, to fabrication of textured SrFAp ceramics with a high ratio of conversion into apatite. In this way, textured polycrystalline ceramics with no topochemical relationship to the template material can be fabricated through reactive-templated grain growth using the facets of the template particles as nucleation sites.

1. Introduction

Materials with an apatite structure have attracted considerable attention as biomaterials, ion-conducting materials, and optical materials. For improved chemical or physical anisotropy, textured ceramics with a crystallographic orientation aligned in one direction are desirable [1–3]. Apatite-type polycrystalline ceramics with the preferred c-axis orientation have previously been fabricated by magnetic field alignment [4,5].

Alignment of plate-like particles by means of shear stresses followed by sintering and grain growth is a simple fabrication method for highly oriented polycrystalline ceramics referred to as templated grain growth (TGG) or reactive-templated grain growth (RTGG) [6,7]. TGG requires plate-like particles of the target compound, while RTGG requires plate-like precursor particles with a topochemical relationship to the target compound. In RTGG, a reactive template is converted into the target compound by inheriting the crystallographic orientation of the reactive template through an in-situ reaction with complementary reactants. Hydroxyapatite (Ca10(PO4)6(OH)2; HAp) has a hexagonal crystal structure with a P63/m space group and grows preferentially along the c-axis. Thus, HAp with a fiber-like morphology can generally be synthesized in the liquid phase [8,9]. Zhuang et al. [10] synthesized plate-shaped apatite with the preferred orientation along the a(b)-axis at the air-liquid interface of the solution. However, there are still some problems concerning the yield of the synthesized product. In addition, no reactive templates have been reported to have a topochemical relationship with the apatite structure that is suitable for RTGG processing.

In this paper, we focus on the preparation of textured strontium fluoroapatite (Sr10(PO4)6F2; SrFAp), which has collected attentions as a crystal host for functional rare earth ions [5,11]. This involved use of hexagonal plate-like alpha-strontium phosphate (α-Sr3(PO4)2; α-TSP) single-crystal particles synthesized by hydrothermal treatment [12] as reactive templates. Figure 1 shows the crystal structure of α-TSP and strontium fluoroapatite (Sr10(PO4)6F2; SrFAp) as a typical apatite-type material. There is clearly no topochemical relationship between the two materials due to the difference in the tetrahedral arrangement of the PO4 groups.

Our aim in this study was to fabricate apatite bulk ceramics with the preferred c-axis orientation through reactive diffusion of complementary reactants using the facets of α-TSP as nucleation sites.

2. Experimental

2.1. Synthesis of plate-like α-TSP

Plate-like α-TSP single-crystal particles were synthesized according to our previously reported method [12]. In
brief, α-strontium hydrogen phosphate (α-SrHPO₄) precursor particles were produced by a homogeneous precipitation method. An aqueous solution was prepared by mixing 0.0167 mol⋅dm⁻³ strontium acetate 0.5 hydrate (Sr(CH₃COO)₂·0.5H₂O, Wako Pure Chemical Industries, Ltd., Japan), 0.0100 mol⋅dm⁻³ diammonium hydrogen phosphate ((NH₄)₂HPO₄, Wako Pure Chemical Industries, Ltd., Japan), 0.0500 mol⋅dm⁻³ urea ((NH₂)₂CO, Wako Pure Chemical Industries, Ltd., Japan), and 0.0480 mol⋅dm⁻³ nitric acid (HNO₃, Wako Pure Chemical Industries, Ltd., Japan). This starting solution was heated at 80°C for 24 h in an oil bath. The precipitated α-SrHPO₄ precursor particles and the solution were then separated and preserved.

The separated 0.5 g of α-SrHPO₄ precursor particles were ball-milled using a planetary mill (Pulverisette 6, Frisch, Germany) for 60 min at a rotation rate of 300 rpm in a ZrO₂ pot with 179.8 g of 2-mm-diameter ZrO₂ beads and 40 cm³ of distilled water.

In order to produce the α-TSP particles, a hydrothermal treatment (TEM-DS hydrothermal device, Taiatsu Glass Industries, Ltd., Japan) of both the ball-milled α-SrHPO₄ particles and the preserved solution from the homogeneous precipitation system, was conducted at 150°C for 3 h.

2.2. RTGG processing of SrFAp by reaction of the α-TSP template and strontium fluoride

Figure 2 illustrates the experimental flow for <001>-oriented SrFAp ceramics produced by the RTGG process, together with an SEM image of α-TSP particles as templates. In this study, we fabricated two kinds of SrFAp ceramics: i) “stacked specimens” produced by thermal-pressing green sheets, and ii) “rolled specimens” produced by roll-pressing the above stacked specimens as shown in Figure 2.

First, plate-like α-TSP particles (17.5 g) and strontium fluoride (SrF₂, Sigma-Aldrich, St. Louis, USA) particles (1.4741 g) were mixed in an agate mortar in a stoichiometric ratio. The solvent was then prepared by mixing ethanol and toluene. Slurries for tape casting were prepared by mixing the starting materials, solvent, binder (polyvinyl butyl), and plasticizer (dibutyl phthalate). Green sheets were produced by tape casting using a doctor’s blade. The sheets were cut, laminated, and pressed at 80°C and 20 kgf⋅cm⁻² to form green compacts. These were cut into smaller pieces (10 × 10 mm) that are referred to hereafter as “stacked specimens”. The stacked specimens were heated in air at 500°C for 1 h in an electric furnace (TFF300 No. F611, Tokyo Technological Labo Co., Ltd., Japan) to remove organic ingredients, heated in air at 1000°C for 10 h, and finally sintered at 1500°C for 2 h in an electric furnace (SC-3035F-SP, Motoyama Corporation, Japan).

Roll-pressed compacts were simultaneously produced. The green compacts were roll-pressed until their thickness was almost halved; these specimens are referred to hereafter as “rolled specimens”. The organic ingredients in the rolled specimens were baked out under the same conditions as those in the stacked specimens. The rolled specimens were heated at 1000°C for 10 h, and then sintered at 1500°C for 2 h in air using the SC-3035F-SP furnace.

Further heat treatment was conducted under a controlled F-containing atmosphere to improve the
conversion ratio from α-TSP to SrFAp. Both the stacked and rolled specimens were heated under flowing air (300 cm³/min) in a tubular furnace (KTF433N, Koyo Thermo Systems Co., Ltd., Japan). The specimens were then heated at 1000°C for 10 h and sintered at 1500°C for 2 h under an F-containing atmosphere in an electric furnace (FC-410, Toyo Seisakusho Co., Ltd., Japan). The F-atmosphere was produced by the powder bed method. An appropriate amount of SrF₂ powder was sprinkled around the specimens, and the system was closed by covering the alumina boat.

2.3. Characterization of green sheets and sintered specimens

The crystalline phases and surface textures of the green sheets and sintered specimens were determined by X-ray diffraction (XRD; Ultima IV, Rigaku Co., Japan) using Cu-Kα radiation at 40 kV and 40 mA. Room-temperature XRD measurements were conducted for the sintered specimens in the following two stages to compare the phases and surface textures with those of the bulk product, first on the as-sintered surface (Surface hereafter), and then on the same specimen after removal of the surface layer of ~100 μm (Bulk hereafter). The rate of conversion into SrFAp was calculated based on the highest peaks of SrFAp and α-TSP. The degree of orientation of these specimens was evaluated based on the Lotgering factor, f [13]. f here is widely used for qualitative analysis of the preferred orientation of polycrystals. f is calculated using both the intensities of the XRD peaks of the present specimens and those of a randomly oriented specimen. f = 0 indicates that the specimen has a random orientation, and f = 1 appears when the specimen is of the fully preferred orientation or a single crystal. The rate of conversion into SrFAp was calculated based on the highest peaks of SrFAp and α-TSP.

Phase changes and texture development during heat treatment were examined by high-temperature XRD (HTXRD; RINT-TTR II, Rigaku Co., Japan) using Cu-Kα radiation at 50 kV and 300 mA. XRD measurement was carried out with the Bragg-Brentano geometry, and the obtained patterns were analyzed using RIETAN-FP [14]. The conversion ratio for the sintered specimens was estimated based on the scale factor. The scale factor is a fitting parameter for diffraction intensity in Rietveld analysis and is assigned to all crystalline phases in the case of multiphase fitting. The stronger the XRD peaks, the higher the scale factor. A change in the scale factor means a change in the amount of the phase in the specimen. Therefore, we used the scale factor as an indicator of the progress in the chemical reaction. The r-value of the March-Dollase function is a statistics-based index for orientation [15]. r is a parameter used to refine fitting of the XRD pattern for a textured specimen in Rietveld analysis. In the March-Dollase function, the degree of alignment with the preferred-orientation axis of each grain is evaluated using the all Bragg reflections. Hence, this metrics can be used to evaluate the contribution of grains that are weakly aligned with a preferred-orientation vector. In the case of plate-like specimens, when an XRD pattern obtained by Bragg-Brentano geometry is used, r decreases to below 1 depending on the degree of alignment. In this study, r was adopted as a statistically meaningful index to track texture development during heat treatment.
3. Results and discussion

The XRD pattern of a green sheet surface is shown in Figure 3. Intense peaks were seen to be associated with the (00l) planes, indicating that the plate-like α-TSP particles have a strong (001) texture. The present α-TSP particles can be expected to be a useful template substance for textured ceramics.

Figure 4 shows XRD patterns of surface and bulk specimens sintered in air at 1000°C for 10 h. The surface and bulk specimens correspond to the exterior and interior of the resulting ceramics, respectively. The surface specimen corresponds to the as-sintered surface measured for XRD, while the bulk specimen was prepared by removing the surface layer using #500 and #1000 silicon-carbide waterproof sandpapers. The XRD patterns showed that SrFAp and α-TSP were present in all of the specimens. The formation of SrFAp must be due to an in-situ reaction between α-TSP and SrF₂ that occurred during sintering. We also observed enhanced (002) and (004) peaks related to SrFAp. The degree of orientation of SrFAp derived from the rolled specimens (Figure 4(c, d)) was higher than that from the stacked ones (Figure 4(a, b)). On the other hand, the degrees of orientation in the surface specimens (Figure 4(b, d)) were higher than those in the bulk specimens (Figure 4(b, d)). This result suggests that the outermost surface of the SrFAp had the texture with the strongest orientation to the c-axis. α-TSP peaks were also observed, however, indicating the presence of abundant unreacted α-TSP.

Table 1 presents a summary of the degrees of the c-axis orientation and conversion rate into SrFAp. Here, the degree of the c-axis orientation is shown by the Lotgering factor (f); and we determined that an f value of 0.3 and higher represents a “<001>-oriented apatite”. The f values vary from zero to unity; f = 0 corresponds to a random orientation, and f = 1 to a perfect orientation. Furushima et al. have reported that the orientation angle of grains in the plate-oriented Bi₄Ti₃O₁₂ ceramics was 45° in the case of f = 0.3 [16]. In addition, according to a report by Yan et al. [17], the authors determined that f = 0.3 has a moderate orientation in the case of Cr₂AlC bulk ceramics. Based on these two findings, we considered f = 0.3 or higher as reference values standing for oriented polycrystals in this study. Among the examined specimens, we concluded that the “rolled specimens” represented the best fabrication process from the viewpoint of c-axis orientation and SrFAp formation.

To clarify the phase transition from α-TSP to SrFAp, we performed HTXRD measurement. The scale factors for the α-TSP, SrFAp, and SrF₂ phases were calculated from the peak intensities in the HTXRD patterns. The results are presented in Figure 5(a). The α-TSP-to-SrFAp conversion reaction was promoted at above 800°C. SrFAp must be formed by a reaction between α-TSP and SrF₂. Actually, we performed the experiments on the basis of stoichiometric composition of SrFAp as a nominal composition. At above 1000°C, however, only a minor change was detected in the amount of the SrFAp phase formed, and unreacted α-TSP was still present. These results indicate that the conversion reaction was incomplete, presumably because a considerable amount of SrF₂ was vaporized and removed from the specimens by 1000°C heat.

The development of a (001) texture was examined next based on the r-value for the March-Dollase function;
and the results are shown in Figure 5(b). The $r$-value shows the degree of orientation along <001>; and $r = 0$ indicates complete orientation, while $r = 1$ indicates no orientation. The $r$-value of SrFAp ($r = -0.8$) appeared at and above 900°C. Although these results are in good agreement with the formation of SrFAp at 900°C or higher in Figure 5(a), the degree of orientation in the formed SrFAp was quite low. Thus, a significant increase in (001) texture of SrFAp may occur up to 900°C, because little change took place above this temperature. This suggests that the texture development mechanism is different from the conventional mechanism involving preferential growth of coarse particles originating from reactive templates at high temperatures.

In order to discuss the texture development mechanism of SrFAp via RTGG route, we observed the microstructure of the heated specimens. Figure 6 shows SEM images of the internal microstructure of the specimens following HTXRD measurements up to 1300°C as a model of complete reaction. In the over view of the fracture surface parallel to the tape casting direction (Figure 6(a)), unreacted plate-like α-TSP particles were observed.

Table 1. Summary of the degree of c-axis orientation and the rate of conversion into SrFAp.

| Fabrication conditions | Stacked specimens | Rolled specimens |
|------------------------|-------------------|------------------|
|                        | Surface | Bulk | Surface | Bulk |
| c-axis orientation ($f$ value) | 0.52 | 0.12 | 0.35 | 0.42 |
| Conversion rate into SrFAp (%) | 52.1 | 77.7 | 78.2 | 56.7 |

Figure 4. XRD patterns of four kinds of specimens sintered in air at 1000°C for 10 h: (a) Surface of stacked specimen, (b) Bulk of stacked specimen, (c) Surface of rolled specimen, and (d) Bulk of rolled specimen.

Figure 5. Calculation results based on HTXRD measurements for rolled specimens: (a) scale factor for each crystalline phase and (b) temperature dependence of the $r$-value for the March-Dollase function.
Furthermore, plate-like particles with a developed plane size of one to few microns were observed on the unreacted \( \alpha \)-TSP particles (Figure 6(b, c)). SEM images in Figure 6(b) and (c) are corresponding to the grain growth region and nucleation one, respectively. In these particles (Figure 6(b, c)), fluorine (F) was detected by energy dispersive X-ray spectrometry (EDX). The results indicate that they may be composed of SrFAp.

Next, we observed the internal microstructure of the specimen heated at 900°C as a model of incomplete reaction. The SEM images are shown in Figure 7, together with model of the reaction mechanism. In the view from the surface parallel to the direction of tape casting Figure 7(a, b), fine (submicron) particles were seen on the surface of porous \( \alpha \)-TSP particles. These fine particles contained fluorine. In the view from the cross section of the specimens, we observed both dense and porous particles. These images suggest that the progress of the reaction is different from that of individual particles, and that the conversion of \( \alpha \)-TSP into SrFAp is faster than apatite nucleation. Thus, as illustrated in Figure 7(d), it is assumed that in the present system of \( \alpha \)-TSP and \( \text{SrF}_2 \), the formation of randomly-oriented SrFAp on the facets of \( \alpha \)-TSP occurred first, followed by preferential growth along the c-axis. We consider that self-oriented SrFAp had already nucleated on the surface of the plate-like \( \alpha \)-TSP at this temperature (900°C), and that this preferred orientation was maintained even during grain growth (over 900°C).

![Figure 6](image1.png)  
**Figure 6.** SEM images of the fracture surface of a specimen heat-treated at 1300°C parallel to the tape-casting direction: (a) overall image of the specimen, (b) the grain growth region, and (c) the nucleation region.

![Figure 7](image2.png)  
**Figure 7.** SEM images of the internal microstructures of specimens heated at 900°C: (a, b) surfaces parallel to the tape-casting direction and (c) a cross-sectional view together with (d) a model of the reaction mechanism.
This directional growth is presumably due to the reactive diffusion mechanism reported by Fukuda et al. for textured La-Si-O (LSO) ceramics \[18\]. Fukuda et al. fabricated apatite-structured bulk LSO ceramics with a preferred c-axis orientation by isothermal heating of diffusion pairs consisting of La$_2$SiO$_5$ and La$_2$Si$_2$O$_7$. During the initial stage of LSO formation in this system, randomly oriented crystallites were formed at the interface between the diffusion pairs. Then LSO crystallites with a c-axis orientation parallel to the diffusion direction grew preferentially along the c-axis. As a result, LSO polycrystals with a preferred orientation were produced at the interface. For apatite-type phosphates also, the control of the reactive diffusion direction could be a key to the fabrication of c-axis-oriented polycrystals.

As mentioned above, it was revealed that the reaction into SrFAp had not been completed without a supply of fluorine. Therefore, in order to improve the ratio of conversion from α-TSP into SrFAp, reactive sintering was carried out in an F-containing atmosphere. Figure 8 shows XRD patterns for the resulting specimen surfaces. The XRD patterns in Figure 8(a, b, c) showed that the crystalline phase in the resulting specimens was of the SrFAp single phase. Of special note were the enhanced (002) and (004) peaks related to SrFAp in Figure 8(a, b), compared with the XRD pattern (Figure 8(c)) from the ICDD database (PDF#00-050-1744). The degree of orientation of SrFAp derived from the rolled specimens (Figure 8(b); \(f\) value: 0.28) was higher than that derived from the stacked ones (Figure 8(a); \(f\) value: 0.31). Upon heating under a closed atmosphere containing SrF$_2$, the ratio of conversion from α-TSP into SrFAp in the two specimens reached almost 100%. This implies that heating in air suppressed the conversion to apatite because of the loss of fluorine from the system. In contrast, a controlled atmosphere enabled the conversion reaction to continue to completion.

We conclude that textured polycrystalline ceramics with no topochemical relationship to the template material can be fabricated via the RTGG route using the facets of the template particles as nucleation sites.

### 4. Conclusion

Plate-like α-TSP single-crystal particles with c-axis orientations were mixed with fine SrF$_2$ powder in a stoichiometric ratio, and the product was formed into green sheets by the doctor blade technique. The sheets were laminated and then subjected to thermal pressing or roll pressing to form green compacts. These were then sintered in air or an F-containing atmosphere to examine the inheritance of the crystal orientation from the template. In general, the RTGG method requires precursor particles with a topochemical relationship to the target material. Even though this was not the case for the α-TSP and SrFAp used here, however, textured SrFAp polycrystalline ceramics were fabricated. The mechanism involved two key steps: i) nucleation of crystallites of the target material on the facets of the template particles,
and ii) preferential growth of these crystallites. By sintering in an F-containing atmosphere and preventing the depletion of the reaction sources, textured polycrystalline ceramics with a high conversion ratio with respect to apatite were fabricated.

Disclosure statement
No potential conflict of interest was reported by the authors.

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