

Multipod Crystals of Perovskite SrTiO₃Takeshi Toshima,^{*,‡} Hiroyuki Ishikawa,[†] Satoshi Tanda,[‡] and Tomohiro Akiyama[†]

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ABSTRACT: We use our designed self-propagating high-temperature synthesis (SHS) method for the synthesis of the multipod crystals of cubic perovskite strontium titanate (SrTiO₃), which has a scale of about 5 μm in length and 200 nm in the cross section of legs. Electron microscopy and diffraction measurements show that the formation mechanism of these multipod crystals is not the same as previous reports of hexapod and tetrapod crystals but fairly similar to snow crystals, in which multi-needle-like crystals lie a on two-dimensional plate and two needle-like crystals grow perpendicular to them. These SrTiO₃ multipod shaped crystals should provide promising materials for fundamental investigations on nanomicro-scale shape dependent unique properties such as piezoelectricity, opt-electricity, catalyticity, superconductivity, and so on. As the first success of synthesis of multipod-shaped perovskite crystals, our method shows a possibility that any materials would form the multipod shapes.

Introduction. Manipulating the shapes of nanomicro crystals remains an important goal of modern materials science. When building nontrivial shapes, self-organization offers the potential for applications to three-dimensional networks,¹ and optical² and mechanical³ devices. These nontrivial shapes are often obtained as simple structures constructed with one- or two-element systems.⁴ For example, the synthesis of ZnO tetrapod⁵ crystals has been successfully controlled, and they are used as functional materials owing to their nontrivial shapes. Systematic manipulation of multipod shapes, such as tetrapod⁶ and hexapod⁷ crystals, has enough potential for the above capabilities. We sought to prove that more functional materials, composed three or more elements, would form the multipod shapes.

The ternary transition metal oxide systems, including SrTiO₃ and high T_c superconductors, with a perovskite structure, are noteworthy for their exceptional dielectric, piezoelectric, electrostrictive, electro-optic, superconducting, and catalytic properties with electro-mechanical devices, capacitors, actuators, transducers, high-k dielectrics, field-effect transistors, and so on. Since the perovskite systems have complex crystal structures, they need a longer formation time during the crystallization than that of one or two element systems. So, the crystals would tend to become usual growth forms with the crystal habits due to being synthesized under nearly *equilibrium conditions*.⁸ However, multipod-shaped crystals are only synthesized under *nonequilibrium conditions*.^{5–7,9,10} Therefore, perovskite systems with multipod shapes have never been realized.

Strontium titanate (SrTiO₃) is an inorganic conductor with a perovskite structure (space group: *Pm3m*, cubic structure with *a* = 3.905 Å) and is employed for research related to photoluminescence,¹¹ catalyst,¹² and substrates.¹³ SrTiO₃ has normally been synthesized under nearly equilibrium conditions (in the solid or liquid phase), because of not only the complex crystal structure but also the high boiling point of the starting material (Ti, 3560 K); it is difficult to realize a vapor phase (nonequilibrium) crystallization. If vapor phase crystallization were realized, then difficulty of the vaporization would be highly advantageous as a responsiveness parameter in the crystallization.

In order to resolve the preceding problems, here we report our designed self-propagating high-temperature synthesis (SHS) method

for multipod crystals of SrTiO₃. We control the growth forms of SrTiO₃ crystal by choosing the shape of the starting material. Choosing the starting materials with a larger surface area enhances the rate of the chemical reaction and indicates the rapid heating and quenching crystal growing conditions needed to synthesize the multipod shapes. We also propose their formation mechanism by comparing those of other multipod crystals. Our results are close to previous reports of hexapod crystals, but the formation mechanism is close to that of the snowflake crystal.

Experimental Section. We synthesized the SrTiO₃ crystals using our designed SHS method, which is a very simple thermodynamic nonequilibrium process for material synthesis. The experimental procedure is as follows: the one end of starting mixtures (titanium powder, sodium perchlorate (NaClO₄), and strontium carbonate (SrCO₃)) is ignited by the external heating in an argon atmosphere at room temperature. Then its heat energy causes a combustion wave to propagate rapidly through the mixture. Its production rate is 5.0 g/s and the desired product is formed according to the following chemical reaction:



This is an exothermic reaction. After the chemical reaction, the product is rinsed in water to remove the sodium chloride.

The key to our success of the controllable crystal growing condition in vapor phase synthesis is the choosing of irregularly shaped titanium powder (the diameter of the particle is less than 45 μm and has a nonsmooth surface). Powder consisting of small particles with irregular shapes has a larger surface area than the same weight of powder with a spherical (smooth) surface. Choosing the starting materials with a larger surface area leads to two types of enhancements in the chemical reaction, which are a higher temperature (The adiabatic temperature of the equation is 3860 K in maximum, which exceeds the boiling point of the other materials in the chemical reaction) and faster propagation of front line of the chemical reaction (similar to a blast wave). Additionally, such a self-propagating chemical reaction rapidly heats and quenches the system. This conduction is the advantage for realization of multipod-shaped crystals.

Results and Discussion. Figure 1, panels A and B show scanning electron microscopy (SEM) images of SrTiO₃ single crystals with cubic and octahedral shapes, respectively. In our method, these crystals are obtained by using spherical shaped powder. There are no appreciable differences between our method

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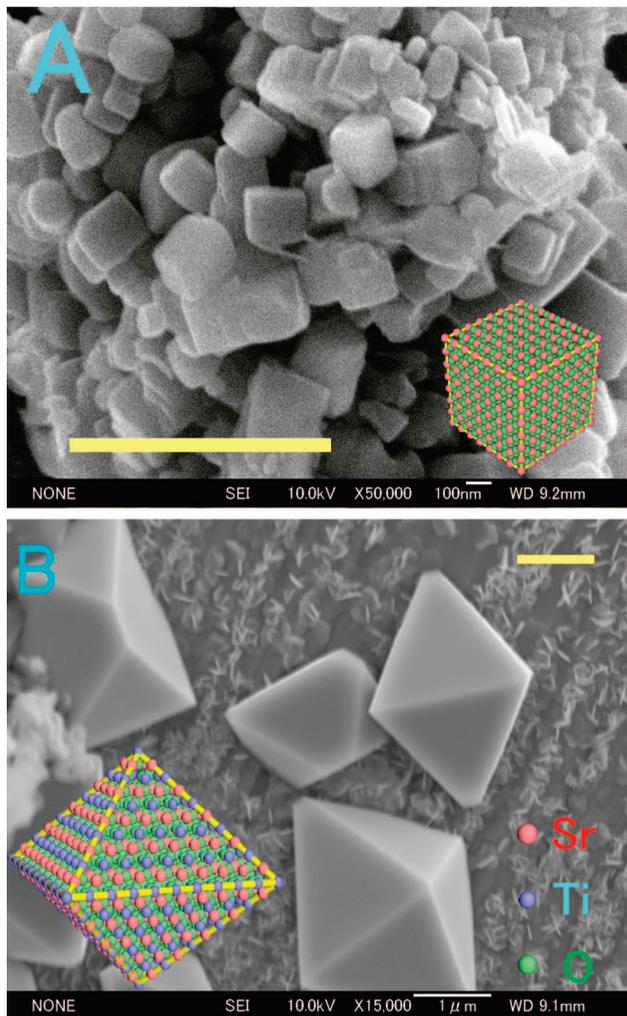


Figure 1. SEM images of SrTiO₃ crystals with (A) cubic shape and (B) octahedral shape. Red spheres are Sr atoms, blue spheres are Ti, and green spheres are O. Scale bar is 1 μm.

and previous reports. These structural geometries are explained by the crystal morphology.

Figure 2, panels A and B, respectively, are SrTiO₃ hexapod and decapod crystals synthesized by using irregular shaped powder. The angle between neighboring legs is approximately 90° in Figure 2A. As seen in the inset of Figure 2B, eight legs lie on a plate (b–c plate), and two legs are perpendicular to them (along the a axis). These results are clearly different from previous reports,⁹ in which multi-needle crystals are connected at one end, their lengths are not the same and the configuration rule of legs is not in force. It is difficult to believe that our results are coincidental.

Figure 3, panels A and B, respectively, are X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS) analysis of SrTiO₃ crystals. From the analysis of (A), the production is almost SrTiO₃ crystals. Other productions (Sr₂TiO₄, Sr₃Ti₂O₇, TiO₂, and SrCO₃) are very few. The ratio of atoms is shown in the inset of Figure 3B. The quantitative analysis of the production is about Sr/Ti = 51.15:48.85.

The discovery of multipod crystals poses the problem of determining their formation mechanism. Our multipod crystals are similar in appearance to previously reported materials of hexapod⁷ crystals, tetrapod^{5,6} crystals and snowflake¹⁰ crystals, where the mechanisms are clearly different in each case. Which formation mechanism is closest to our results?

The geometry of hexapod crystals is most similar to that of our multipod crystals. Their sizes are comparable to our results. However, the time scale of the chemical reaction is far from our

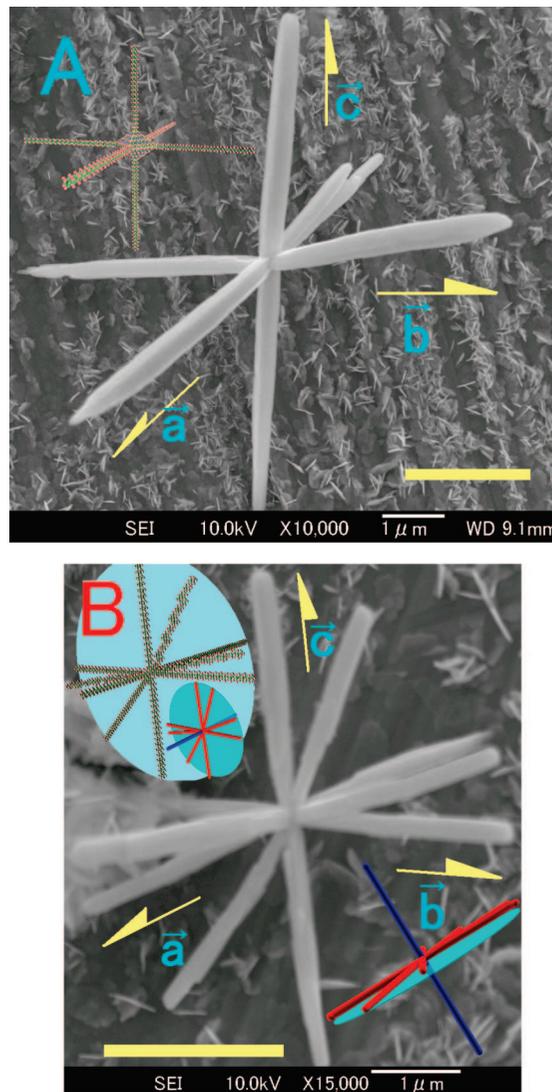


Figure 2. SEM images of SrTiO₃ crystals with (A) hexapod (6-pods) shape and (B) decapod (10-pods) shape. Insets are models of configuration of the SrTiO₃ legs. All of the red-colored legs in panel b lie on the cyan-colored disk (b–c plate). Scale bar is 2 μm.

results. Our multipod crystals are obtained in few seconds, but other approaches require several hours. Additionally, we find that the core and leg cross-sections are a similar size, whereas the core cross-sections of previously reported crystals were smaller than that of the legs.⁷

Tetrapod crystals also have a similar geometry. Their growing condition is also reached in the vapor phase of the starting materials. Additionally, the nondendritic shape is similar to our results, and the relationship between the sizes of the core and legs is closer than that of previously reported hexapod crystals. Tetrapod crystals can have such a nontrivial geometry because they are polycrystals. Four needle-like single crystals are joined at the center of a tetrapod crystal owing to stacking faults with the wurtzite and zinc blende structures.^{5,6} However, SrTiO₃ crystal has a simple cubic structure. Therefore, there are no stacking faults such as those found with tetrapod crystals. Figure 4A,B, respectively, are a transmission electron microscopy (TEM) image and transmission electron diffraction (TED) pattern of a SrTiO₃ single crystal with a cubic body and a leg obtained from the same batch of multipod crystals. The leg grows in the [110] direction and forms an angle of 135° with the two sides of the cubic body. The TED patterns are exactly the same for the cubic body and the end of leg. An analysis of the TEM image and TED pattern shows that the cubic body and the leg are seamless (a single-phase crystal).

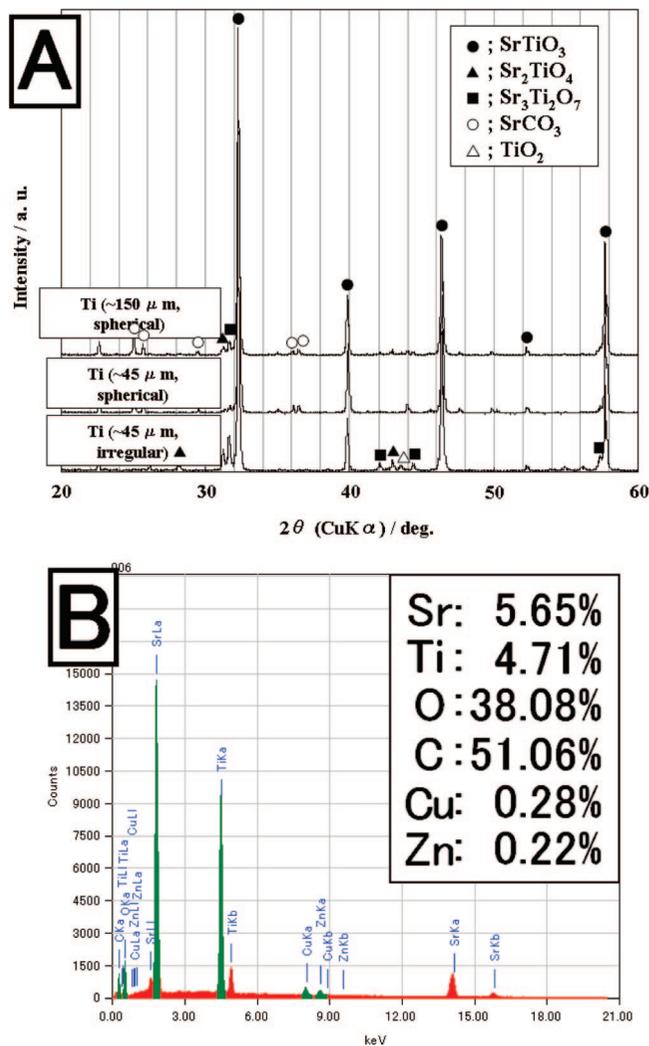


Figure 3. (A) X-ray diffraction (XRD) analysis of SrTiO₃ crystals. Upper: Using Ti powder with spherical shapes and large radius (~150 μm). Middle: Spherical shapes and small radius (~45 μm). Lower: Irregular shapes and small radius (~45 μm). (B) Energy dispersive X-ray spectroscopy (EDS) analysis of SrTiO₃ crystals obtained by using the irregular shaped powder. The peak of carbon is due to substrate (we use the graphite as the substrate in this analysis). The peaks of copper and zinc are noises due to the experimental system.

Snowflake crystal growth, which is a well-known example of vapor phase growth as expressed in the Nakaya-diagram, corresponds to the growth of snowflake crystal shapes that depend on temperature and vapor saturation. Our synthesis is the supersaturated state; the vapor density is not uniform around the crystal nucleus. The edges of the crystal nucleus experience a higher vapor density and grow more rapidly than at other positions.¹⁴ This is known as the Berg effect. If legs grow at the six edges of a crystal nucleus with an octahedral shape, a hexapod crystal will be obtained (inset of Figure 2A). This condition is exactly the same as that of snowflake crystal growth except for the accompanying chemical reaction. The decapod crystal in Figure 2B has eight legs (red) on a two-dimensional plate and two legs (blue) perpendicular to the plate, as seen in the inset. The snowflake crystals exhibit two-dimensional tabular and columnar growth, and the columnar legs are also perpendicular to the tabular legs. And the two-dimensional tabular crystal growth takes on an infinite variety of form. This configuration accounts for our crystal growth mechanism in the same way as that of snowflake crystals.

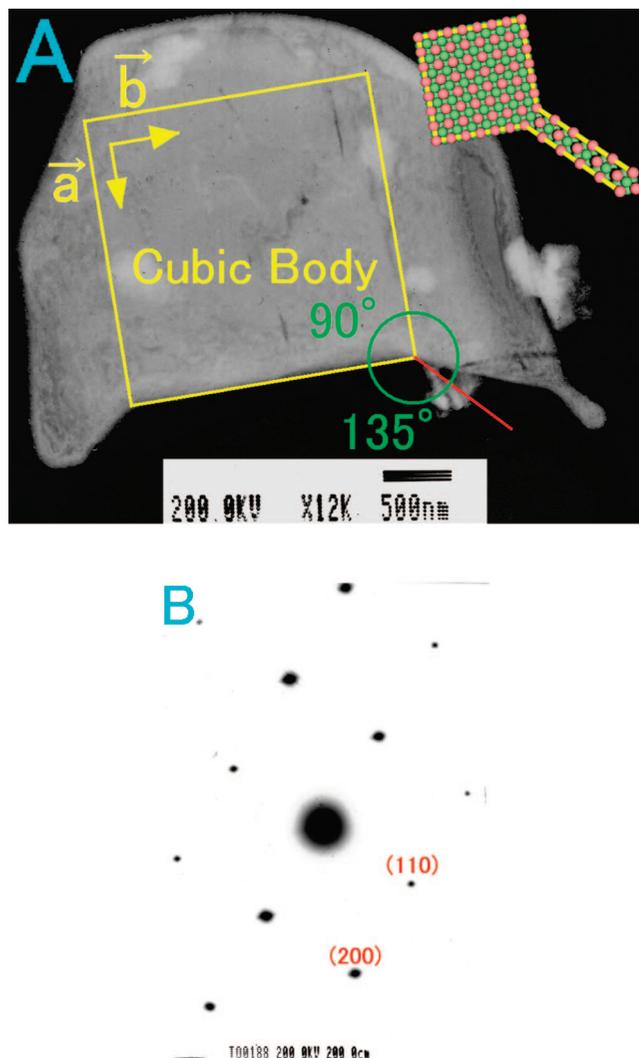


Figure 4. SrTiO₃ single crystal (cubic body with a leg). (A) TEM image. Inset is a sketch of this crystal. (B) TED pattern of SrTiO₃ single crystal. The TED analysis shows that the leg grows [110] direction.

Conclusion. In summary, single-crystalline SrTiO₃ multipod crystals have been synthesized by the SHS method. Choosing the shapes of starting materials changes the efficiency of the chemical reaction and indicates the controllable vapor phase crystal growth condition. Specifically, this is the first report of multipod crystals with perovskite structure (three elements system). We compared their formation mechanism with those of other crystals with a star-like geometry. Our crystals have a similar shape to hexapod and tetrapod crystals, but the formation mechanism is the same as that of snowflake crystals. Multipod perovskite crystals will find applications in various fields, for example, with SrTiO₃, which is a good catalyst owing to its large specific surface, in three-dimensional devices such as cellular phone antennas owing to their fixed high dielectric constant, and the success of the multipod shaped perovskite crystal shows the possibility of three-dimensional high-T_c superconductor networks.

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