Solid-state conversion of single crystals from polycrystalline materials has the advantages of cost-effectiveness, chemical homogeneity, and versatility over the conventional melt growth and solution growth methods, particularly for systems with high melting points, incongruent melting, high reactivity (volatility), and phase transformations at high temperature. Nevertheless, for commercial production, this technique has only been successful in a few limited systems, in particular ferroelectric systems. This is mostly because of the difficulty in controlling the microstructure, particularly suppressing grain growth in the polycrystal during its conversion. This article describes the principle and the current status of the solid-state conversion of single crystals. We first introduce the recently developed principle of microstructural evolution to explain the basis of the microstructure control in polycrystals for solid-state conversion. We then report recent technical developments in fabricating single crystals by the solid-state single crystal growth (SSCG) method and their physical properties. The SSCG method is expected to be studied and utilized more widely in fabricating single crystals with complex compositions as a strong alternative to the melt growth and solution growth methods.

I. Introduction

The fabrication and the use of ceramic single crystals are one of the prime interests in ceramic academia as well as in the ceramic industry. Single crystals are needed to characterize the intrinsic physical properties of materials. As physical properties can vary considerably with the crystallographic orientation of the crystal, the properties can also be maximized when single crystals with specific orientations are used. Various applications of single crystals include substrates of electronic components, optical crystals, piezoelectric components, laser components, and thermoelectric components. For systems where the fabrication of single crystals is difficult, fabrication of textured ceramics has served as an alternative to utilize the improved physical properties of materials. For the fabrication of textured ceramics, oriented seeds (templates) are commonly used. The growth of an individual seed before its impingement with the neighboring seeds is the same as the growth of a seed crystal embedded in a compact for the solid-state conversion of single crystals.

Conventionally, single crystals have been fabricated from a liquid or a vapor. The fabrication technique of single crystals from a liquid can be categorized into two types: growth from a melt of the material and growth from a solution with a solvent or a flux. The melt growth method, typified by the Czochralski and the Bridgman methods, has been developed and is widely used in the fabrication of ceramic single crystals. The main advantage of the melt growth method is high productivity of large single crystals. However, this method is either difficult or ineffective for growing crystals with high melting points, high reactivity, and high volatility. In particular, it is difficult to guarantee chemical homogeneity of the product for materials with complex compositions or incongruent melting points. The requirement of costly equipment is another disadvantage of the melt growth method. Compared with growth from a melt, the growth of single crystals from a supersaturated solution (the solution growth method), either aqueous or flux, is a relatively simple process and does not require sophisticated equipment. As the processing temperature can be lowered considerably from the melting point of the material, the solution growth method, in particular using a flux, can be useful for materials with high volatility or phase transformation at high temperature. With this method, however, fabricating large single crystals is difficult and mass production is practically impossible. In addition, chemical purity and homogeneity are often not achieved.

Growth of single crystals from a vapor has also been developed as an extension of single crystalline thin film growth on a substrate. The material transport for the growth can be accomplished chemically (chemical vapor transport) or physically (physical vapor transport). For some limited
systems, in particular II-VI compounds, and SiC, the vapor growth method has been successful in fabricating high-quality large single crystals with low defect concentrations. Narrow applicability and high production cost of this method, however, limit it to only some specific systems.

The solid-state conversion of single crystals from polycrystals has long been attempted because of the simplicity of the technique and its cost-effectiveness. The solid-state single crystal growth (SSCG) method utilizes the phenomenon of abnormal grain growth in polycrystals. As a result, the method does not require expensive equipment and adopts the conventional ceramic processing technique. Theoretically, one large grain or a seed crystal scavenges all other grains in a polycrystal, the polycrystal becomes a single crystal. For the solid-state conversion of single crystals, grain growth in the polycrystal must be suppressed (or minimized), whereas the growth of a seed crystal must occur with no impingement of the matrix grains against its growth. Microstructure control in the polycrystal is therefore crucial. The main reason why this technique has been successful only for some limited systems is the difficulty of achieving control over the microstructure of the polycrystal that is intended to be converted into a single crystal. This technique commonly utilizes a sintered polycrystal, another issue that has to be addressed is the elimination of pores in the polycrystal. When pores are present in the polycrystal, they become entrapped within the growing single crystal and the quality of the produced single crystal is deteriorated.

When the SSCG method is successful in fabricating single crystals, it has notable advantages over the conventional melt growth and solution growth methods. This method does not require expensive components or equipment, but rather only simple furnaces. The production cost is much lower than that of the conventional methods. The uniformity and versatility of the chemical composition of the produced single crystals are also major advantages over other methods. The SSCG method also enables net-shape production. Above all, it is particularly suitable for producing single crystals with incongruent melting points, wide solubility ranges, highly volatile components or destructive phase transformations upon cooling, such as BaTiO$_3$, Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ (PZT), (1-x) Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$-xPbTiO$_3$ (PMN-PT), (1-x)Pb(Zr$_{1/3}$Nd$_{2/3}$)$_2$O$_3$-xPbTiO$_3$ (PZN-PT), (K$_{1/2}$Na$_{1/2}$)$_2$TiO$_3$ (KNN), and (1-x)(Na$_{1/2}$Bi$_{1/2}$)$_2$TiO$_3$-xBaTiO$_3$ (NBT-BT), and Nd-doped Y$_3$Al$_5$O$_{12}$ (Nd:YAG).

Because of its advantages and uniqueness as described above, the solid-state conversion of single crystals has been attempted in a number of systems. However, it has been successful only for some limited systems in achieving sizes for practical use because of the difficulty in controlling the microstructure of the polycrystal. The systems that have been successfully thus far in fabricating single crystals with sizes that are commercially usable by the SSCG method include BaTiO$_3$, some lead-containing piezoelectric materials such as PMN-PT, and PMN-PT, and some lead-free piezoelectric materials such as NBT-BT and NBT-BT-KNN.

As the solid-state conversion of single crystals has proved a difficult task, an alternative technique, the solid-state conversion of textured ceramics, has been developed and utilized to produce bulk materials with better physical properties than those of ceramics. This technique has also been used in some cases for improvement of mechanical properties. Although mechanical texturing of grains by hot forging was reported to be successful, textured ceramics are commonly fabricated by sintering powder compacts that contain well aligned templates (seed crystals) with shape anisotropy. The template grain growth method has advantages over the hot forging method in terms of cost and quality of the product. The alignment of templates is commonly achieved by tape casting of templates containing powder or slurry, sometimes under an external force field, for example, a magnetic field. The templates can be made of the same material as that of the matrix or a different material (reactive templates). The former case is called templated grain growth (TGG) and the latter case reactive templated grain growth (RTGG). For RTGG, the control of the chemistry of the compact is essential. During sintering of a template containing powder compact, matrix grains as well as the templates can grow. To fabricate well-textured ceramics, the growth of the aligned templates has to be promoted while growth of the matrix grains has to be suppressed. The ideal case would be the elimination of all the matrix grains by the growth of well aligned templates, as in the case of the solid-state conversion of single crystals. In this respect, microstructure control in the matrix is essential to produce good-textured ceramics. As the growth of each template is the same as that of the solid-state conversion of a single crystal, the principle of microstructure control, which is described in the following section, must also be applied to the fabrication of textured ceramics.

This article describes the principle and the current status of the solid-state conversion of single crystals. As the control of grain growth in polycrystals is critical for the success of the process, we first briefly describe and discuss grain growth models and mechanisms. We then introduce the recently developed principle of microstructural evolution to describe the basis of the solid-state conversion of single crystals. Finally, we summarize recent technical developments in fabricating single crystals, in particular single crystal with sizes that are commercially usable, by the SSCG method and the physical properties of the fabricated single crystals in comparison with those of polycrystals and textured ceramics.

II. Microstructure Evolution in Polycrystals: Model and Principle

(1) Grain Growth Behavior and Conventional Grain Growth Models

As mentioned in the introduction, the critical issue in the solid-state conversion of single crystals (or textured ceramics) is control of the microstructure of the polycrystal that will be converted into a single crystal (or a textured polycrystal). In real systems, various microstructures are observed during annealing of polycrystals as a result of grain growth. Grain growth can be categorized into two types: normal and non-normal. Normal grain growth (NGG), which is an ideal but exceptional case, is characterized by a time-invariant unimodal distribution of grain sizes with respect to the average sized grain. Therefore, the microstructure development is self-similar with respect to the annealing time. In this respect, NGG may be called stationary grain growth in light of the variation in the relative grain size distribution with annealing time. The parabolic (or square) kinetic law of NGG is well documented in the literature. On the other hand, non-NGG is characterized by a time-variant distribution of relative grain sizes, that is, a nonstationary relative grain size distribution. Abnormal grain growth is an extreme type of nonstationary grain growth, which exhibits a bimodal grain size distribution with exceptionally large grains imbedded in fine matrix grains.

Normal grain growth is a result of the linear dependence of boundary migration with respect to the driving force $a_{k}$:

$$v_b = M_b F_b$$

where $v_b$ is the boundary velocity, $M_b$ is the boundary mobility, which is assumed to be a constant, and $F_b$ is the driving force for boundary migration. Figure 1 schematically depicts the free energy state of an atom across a boundary. When there is an energy barrier $\Delta g^*$ (activation energy for diffusion) and an energy difference of an atom, $\Delta g$ (the driving force), between the two states (on grain I and grain II), a net
atomic flux between them results in migration of the boundary. For a system where the energy difference between the two adjacent grains comes from a nonzero curvature of the boundary, that is, curvature-driven boundary migration occurs, the driving force is expressed as the capillary energy and the mobility as an exponential function of the activation energy. Such a diffusion-controlled boundary migration assumes that the energy state of an atom is position-dependent, $g_I$ on grain I and $g_{II}$ on grain II.

In real systems, however, almost all grain growth behavior deviates from normal behavior. To explain the deviation from normal behavior, abnormal behavior in particular, several mechanisms and models have been proposed, including the second phase particle (or pore) drag mechanism,$^{49-51}$ the solute drag mechanism,$^{52-54}$ the liquid film enhancement mechanism,$^{55-57}$ which is highlighted as the introduction of several complexions (types) of the boundary,$^{57,58}$ and the boundary energy and mobility anisotropy mechanism.$^{59-62}$ All these conventional mechanisms, however, assume that the boundary migration is governed solely by the diffusion of atoms across the boundary.

The drag of second phase particles (or pores) appears as a reduction of the driving force, $\Delta g$ in Fig. 1. According to the particle drag mechanism, abnormal grain growth occurs when the pinning force of second phase particles is reduced locally with their coarsening or dissolution.$^{50,51}$ This explanation, however, cannot be applied to single-phase systems. Even for two-phase systems, AGG has been observed only in some specific systems. In some instances AGG occurs in highly porous materials with uniform distribution of pores,$^{63-65}$ where the pore drag must be considerably high. These experimental observations indicate that local separation of the boundary from second phase particles (or pores) is not the fundamental cause of AGG.

The drag of impurities at the boundary also appears as a reduction of the driving force, $\Delta g$. According to the analysis of impurity drag,$^{66,67}$ the boundary velocity is not linearly proportional to the driving force. Some modeling studies of microstructural evolution for systems with impurities reported a deviation from the normal behavior$^{53}$ and the formation of abnormal grains.$^{54}$ This mechanism, however, does not provide an explanation as to why AGG occurs only in some specific systems and not in other solute-segregated systems. In addition, this mechanism cannot predict the stagnation of grain growth (stagnant grain growth: SGG), a recently observed growth mode in systems that exhibit AGG under specific ranges of temperature$^{68}$ and oxygen partial pressure.$^{65,69}$ Comprehensively different grain growth behavior in samples with similar solute segregation, normal and stagnant (or abnormal),$^{65,69}$ and the variation in grain growth behavior with respect to the solute concentration$^{69}$ can also not be explained by the solute drag mechanism.

The idea of the enhancement of boundary mobility, that is, a reduction of $\Delta g^{*}$ in Fig. 1, with liquid film formation at the boundary (liquid film enhancement mechanism) was also introduced to explain AGG$^{55-57}$ and was highlighted as the introduction of several complexions of grain boundaries. A considerable enhancement of the mobility of the boundary with a specific complexion over those of the boundaries with other complexions$^{57,58}$ was suggested based on TEM observations of the boundaries of grains with different sizes. The presence of a thin liquid film in front of large abnormal grains was interpreted as film enhanced migration of the boundary and the cause of AGG. This interpretation, however, raises the question of “cause and effect”. The presence of the film may be a result of AGG with the accumulation of solutes at the boundaries of abnormal grains rather than the cause of AGG. In fact, the migration kinetics appears to decrease with solute segregation and film formation in a Ti-excess BaTiO$_3$ system.$^{71,72}$ In addition, the explanation based on the boundary complexion is not applicable to AGG in single-phase systems and also in solid-liquid two-phase systems with a considerable fraction of liquid.

The mechanism of the anisotropies in boundary mobility ($\Delta g^{*}$) and boundary energy ($\Delta g$) assumes that boundaries of some specific grains maintain much higher mobility or energy than other boundaries during their migration. Although some simulations predicted AGG$^{59-62}$ the basic assumption is not well justified for real systems. Little experimental evidence for this mechanism is available.

All the conventional mechanisms mentioned above fail to adequately explain AGG observed in many different systems. Neither do they provide general directions of microstructure control with respect to processing parameters.

To convert a polycrystal to a single crystal, grain growth, in particular AGG, in the polycrystal has to be suppressed, preferably made stagnant, while a seed crystal has to scavenge all the grains in the polycrystal. It is, therefore, necessary to control the grain growth in the polycrystal. Apart from the conventional mechanisms of AGG, all of which are based on the diffusion control of boundary migration, a structure-dependent migration mechanism of grain boundary, the so-called mixed control mechanism, was proposed recently.$^{48,73,74}$ On the basis of experimental observations of grain growth$^{64,65,69,71}$ as well as single crystal growth behavior.$^{73,75}$ This mechanism can explain the occurrence of various types of grain growth behavior in polycrystals and provides the groundwork for the discovery of the general principle of microstructural evolution.$^{48,74,76}$

(2) Mixed Control Mechanism of Boundary Migration and the Principle of Microstructural Evolution

Many investigations on grain growth$^{63-65,68-70,77,78}$ have shown that grain growth behavior is largely governed by the grain-boundary structure, either rough (atomically disordered) or faceted (atomically ordered). Non-NGG, in particular abnormal grain growth, occurs only in faceted systems. A recent investigation$^{73}$ showed that the migration kinetics of faceted boundaries is nonlinear with respect to the driving force, as shown in Fig. 2, demonstrating again the presence of a critical driving force for appreciable migration of a faceted boundary. The migration rate is negligible for a driving force smaller than a critical value, whereas the migration rate is quite linearly proportional to the driving force above a critical value. (The deviation from the linearity was attributed to an increased accumulation of solutes with migration.$^{73}$) This result suggests that the migration mechanism of a faceted boundary varies with the driving
force. High-resolution TEM micrographs\textsuperscript{88–91} showed that a faceted boundary migrates via step formation and growth, the so-called step growth mechanism, implying that the presence of atomic steps is essential for the migration of faceted boundaries. This process is similar to that of two-dimensional nucleation and growth for the growth of a faceted single crystal from a solution or a vapor.\textsuperscript{76,92} Phenomenologically, boundary migration is a result of the serial processes of the jump of atoms from a grain to an adjacent grain (diffusion across the boundary) and their attachment (interface reaction) on the adjacent grain. Therefore, the migration should be governed by a slow process, either diffusion or interface reaction.\textsuperscript{48,74,76} Note that all the conventional mechanisms assume that migration is governed only by diffusion. However, if the attachment of an atom increases its free energy state to a level higher than its original state, the atom tends to detach and jump back to the original grain. Figure 3(a) depicts this situation through a free energy diagram. The migration of the boundary is then governed by a stable attachment, which means the interface reaction, similar to the case of the two-dimensional nucleation on a single crystal. If the energy increase with the attachment of an atom on a flat surface is smaller than the driving force, as schematically shown in Fig. 3(b), the attached atom must be stable and do not return to the original grain. In this case, the diffusion of atoms governs the overall kinetics.

Therefore, the migration of a faceted boundary is governed either by the interface reaction or the diffusion of atoms (mixed control of the boundary migration) for a driving force smaller or larger than a critical value, respectively. The transition between the interface reaction control and the diffusion control is related to the critical driving force for appreciable migration.\textsuperscript{9} Physically, the critical driving force would be governed by the energy increase of an atom with its attachment on the growing grain. Because of the high dependence of the step free energy on the crystallographic plane, however, the migration kinetics can vary substantially depending on the crystallographic orientation of the migrating facet, as shown in Fig. 2. At a given temperature, the diffusion kinetics of atoms across the boundary is governed by the activation energy, $\Delta g^*$, for jumping across the boundary and the driving force, $\Delta g$. From boundary to boundary, $\Delta g$ can vary because $\gamma_b$ is not a constant. For perovskites, $\gamma_b$ is reported to vary within a range of a few times for different orientations.\textsuperscript{96–97} $\Delta g^*$ is also thought to vary from boundary to boundary. The considerable difference in migration kinetics between (100) and (210) boundaries in Fig. 2 must be due to the difference in $\Delta g^*$ as well as $\Delta g$.

In many systems, the grain boundaries are not fully faceted but rather only partially faceted. For such systems, the migration kinetics of a boundary is expected to be governed by its facet migration because the migration rate of a facet is governed either by a slower interface reaction or diffusion for a driving force smaller or larger than a critical value, respectively, as can be seen in Fig. 2. In solid/liquid two-phase systems, theoretical\textsuperscript{98} and experimental\textsuperscript{99} studies suggested that the growth of partially faceted grains is governed by the migration of facets.

If we accept the mean field concept for boundary migration, the driving force (per unit volume) for the migration of a boundary is expressed as

$$\Delta g = 4\left(1/G - 1/G\right)\gamma_b$$

where $G$ is the average size of grains, $G$ is the size of the grain concerned, and $\gamma_b$ is the boundary energy. As an individual grain has its own driving force depending on its size relative to the average size, the driving force for growth of grains in a polycrystal has a range with the maximum value for the largest grain, as schematically shown in Fig. 4. Grain growth behavior must then be governed by the value of $\Delta g_{\text{max}}$ relative to $\Delta g_b$ (Fig. 4). The principle of microstructural evolution was deduced for solid/liquid two-phase systems as the coupling effect of $\Delta g_{\text{max}}$ and $\Delta g_b$.\textsuperscript{76,95} The coupling effect principle has proved valid for explaining different types of microstructural evolution observed in many two-phase systems.\textsuperscript{64,79,99–116} For single-phase systems, experimental results of different systems and under different conditions\textsuperscript{65–68,70,77–81,87} also support the applicability of the same principle, indicating the generality of the principle of microstructural evolution in polycrystals. The microstructural evolution principle\textsuperscript{65} predicts various types of grain growth behavior as follows:

1. Normal grain growth (NGG) for $\Delta g_b = 0$  
2. Pseudo-normal grain growth (PNGG) for $0 < \Delta g_b < \Delta g_{\text{max}}$  
3. Abnormal grain growth (AGG) for $0 < \Delta g_b \sim \Delta g_{\text{max}}$  
4. Stagnant grain growth (SGG) for $\Delta g_{\text{max}} \ll \Delta g_b$

Except for the normal type, the type of grain growth is time variant, that is, nonstationary, because $\Delta g_{\text{max}}$ varies (in general, decreases) during annealing as a result of grain growth. Even under a condition $\Delta g_{\text{max}} < \Delta g_b$, however, where practically stagnant behavior is exhibited, very slow grain growth takes place because the boundary migration is not nil, although it is insignificant. For the regime of interface reaction control, the boundary migration rate is nonlinear with respect to the driving force. Our previous calculations for solid–liquid two-phase systems\textsuperscript{95,110} showed that, as the annealing time increases, $\Delta g_{\text{max}}$ can increase as a result of faster growth of the largest grain than any other grains and can exceed $\Delta g_b$. The largest grain will then grow rapidly and become an abnormal grain, exhibiting incubated abnormal grain growth behavior. The incubated AGG observed in a two-phase system as well as in a single-phase system is, in turn, experimental support for the nonlinear migration of faceted interfaces in the interface reaction controlled regime.

For the solid-state conversion of single crystals, grain growth in the matrix has to be suppressed and, preferably,
As the temperature increases, the driving force for the growth of a seed crystal, \( \Delta g_{\text{seed}} \), must be larger than \( \Delta g_c \). It is, therefore, necessary to adjust \( \Delta g_{\text{max}} \) and \( \Delta g_c \). The maximum driving force is governed by the average grain size and the grain size distribution. Therefore, the initial powder determines \( \Delta g_{\text{max}} \) at the beginning of the sintering of a powder compact. The critical driving force \( \Delta g_c \) varies with temperature, doping and atmosphere, including oxygen partial pressure in particular. As the temperature increases, \( \Delta g_c \) decreases because of a reduction in the step free energy. Regarding the effects of dopant species and oxygen partial pressure, there are no general rules. Depending on the dopant species and its concentration, \( \Delta g_c \) can either increase or decrease. Some recent investigations for perovskite systems, however, have shown a strong correlation between the boundary structure, which reflects the boundary step free energy and \( \Delta g_c \), and the total vacancy concentration. As the total vacancy concentration was increased by any means, doping or oxygen partial pressure change, the boundary structure tended to become defaceted and hence \( \Delta g_c \) decreased. This result is similar to boundary roughening with increasing temperature as a result of an increased thermal vacancy concentration.

Examples of microstructure control with a changing \( \Delta g_c \) can be found in previous experiments with BaTiO$_3$ and Ni. In TiO$_2$-excess BaTiO$_3$, grain-boundary roughening occurs with decreasing oxygen partial pressure, \( P_{O_2} \). For powder compacts of the same starting powder, various types of grain growth behavior appeared with a decreasing \( P_{O_2} \), as shown in Fig. 5. At \( P_{O_2} = 0.2 \) atm, all the boundaries were faceted, and \{111\} twins formed and twin-assisted abnormal grain growth occurred, indicating \( \Delta g_{c,0.2} > \Delta g_{\text{max}} > \Delta g_{c,(111)} \). At \( P_{O_2} = 2 \times 10^{-17} \) atm, where \( \approx \)90\% of the boundaries were faceted, \{111\} twins did not form and grain growth behavior became stagnant (\( \Delta g_{c,2\times10^{-17}} > \Delta g_{\text{max}} \)). At \( P_{O_2} = 8 \times 10^{-18} \) atm, a different type of AGG from that at \( P_{O_2} = 0.2 \) atm took place in the absence of \{111\} twins (\( \Delta g_{\text{max}} \approx \Delta g_{c,8\times10^{-18}} \)). The shape of abnormal grains is equiaxed and macroscopically rounded. However, approximately 80\% of the boundaries were flat and faceted at a nanometer scale. At \( P_{O_2} = 4 \times 10^{-19} \) atm, where faceted boundaries accounted for only \( \approx \)15\%, the grain growth behavior was quite normal (\( \Delta g_{\text{max}} \gg \Delta g_{c,4\times10^{-19}} \)). A similar microstructural variation from SGG to AGG and NGG (or pseudo-normal GG) with increasing temperature was also observed in ultrafine Ni, a metal system. With an increase in temperature, that is, with a decrease in \( \Delta g_c \), a repetitive (primary and secondary) growth behavior from SGG to AGG and finally to NGG appeared as a result of the variation in both \( \Delta g_c \) and \( \Delta g_{\text{max}} \).

### III. Single Crystal Fabrication and Properties: Current Developments

If a polycrystal exhibits SGG behavior, as in the case of Fig. 5(b), the polycrystal can be converted into a single crystal with the growth of a seed crystal. In the practice of solid-state conversion, a seed crystal can be placed on top of a sintered polycrystal or embedded within a powder compact, as schematically shown in Fig. 6. A seed crystal can also be nucleated in the matrix by applying a temperature gradient or adding a dopant. A temperature gradient or doping can be beneficial for solid-state conversion. Figure 7 shows the growth of BaTiO$_3$ single crystals under a temperature gradient (a) and in the presence of an SiO$_2$ dopant between a seed and the polycrystal (b). Surface defects, such as twins and dislocations, on a seed crystal can also enhance the crystal growth.

Figure 8 shows a BaTiO$_3$ single crystal fabricated by the SSCG method. The crystal is translucent as a result of the practical absence of entrapped pores. Chemical homogeneity and versatility are unique advantages of the solid-state conversion of single crystal over the conventional melt growth or solution growth methods. Figure 9 shows an example of a growing BaTiO$_3$ single crystal with three layers of three different dopants, Mn, Cr, and Ce. As this example shows, single crystals with multiple modulated compositions can be prepared by the SSCG method. Net-shape fabrication of single crystals from preforms is another unique advantage of the SSCG method. Fabrication of sapphire tubes by the SSCG method is an early example. Single crystal composites and tube- or ring-shaped single crystals, which are shown in Fig. 10, are other examples. The currently obtain-
able sizes of single crystals by the SSCG method are various depending on the system. This section briefly describes the state-of-the-art of single crystals fabricated by the SSCG method, including in particular their development and commercial availability. The physical properties of the fabricated single crystals are compared with those of polycrystalline and textured ceramics.

(1) Mn–Zn Ferrite
Mn–Zn ferrite is widely used for magnetic components, such as transformers, choke coils, noise filters, and reading heads, because of its high magnetic permeability and low core losses.120,121 The technique that was initially attempted for
fabricating ferrite single crystals was the Bridgman method. Due to the high vapor pressure of ZnO and impurity involvement at the processing temperature, it was difficult to fabricate large single crystals with controlled and uniform chemical composition. In efforts to overcome these technical issues of chemistry control, solid-state growth of single crystals was attempted in the 1980s. Using seed crystals, Matsuzawa and Mase were able to convert poly-crystals into single crystals of ~5.5 mm thickness while suppressing AGG in the polycrystal. Later, Hirota et al. reported the fabrication of B-doped Mn–Zn ferrite single crystals of ~9 mm size in an N₂–O₂ mixture atmosphere. They studied the effects of different additives on crystal growth. As the chemical inhomogeneity problem of Mn–Zn ferrite in the melt growth method was alleviated with the development of a modified Bridgman method, the SSCG method is, however, no longer widely used for the fabrication of ferrite single crystals.

(2) Al₂O₃
Translucent polycrystalline alumina (PCA) has been widely used as a light-transmitting material at high temperature and in corrosive environments, including its use as a material for the arc chamber (plasma envelope) of high-pressure sodium vapor lamps. However, PCA has a low in-line transmittance because of the scattering of light at grain boundaries, pores, second phase inclusions, and the surface. Among these factors, grain boundaries and pores are the prime factors that affect the light scattering of PCA. Moreover, the sodium in the arc chamber reacts with alumina at grain boundaries to form sodium aluminate, which shortens the lifetime of the lamp. This situation highlighted the need for a means of fabricating a single crystalline alumina (sapphire) tube.

A modified Czochralski method and the floating zone method were first adopted to produce sapphire arc tubes. Although sapphire arc tubes could be fabricated by the modified Czochralski method without additional machining steps, their production cost was high and productivity was low. In the case of the floating zone method, it was difficult to grow net-shaped tubes. To address the need for improved productivity and reduced production cost, the solid-state conversion of sapphire arc tubes was attempted in the 1990s. The attempts were partly successful as the produced tubes were not single crystal. The total transmittance of the sapphire tube produced by solid-state conversion was 98.2%, which was slightly higher than that (96%) of PCA, and its in-line transmittance of 35% was four times higher than that of PCA and comparable with that (50%) of melt grown sapphire tubes. With the improvement of melt growth techniques, however, sapphire tubes are now usually produced by a melt growth method, such as the edge-defined film feed growth method.

(3) BaTiO₃ and Ba(Zr,Ti)O₃
BaTiO₃ is a widely used ferroelectric material for electronic parts, such as multilayer ceramic capacitors, PTC-thermistors, and piezoelectric components. It is, however, practically impossible to grow large BaTiO₃ single crystals from a melt because of a phase transformation between hexagonal and tetragonal, which takes place at 1430°C. BaTiO₃ single crystals have conventionally been produced by...
the solution method with a flux,\textsuperscript{133–137} including in particular the top-seeded solution growth (TSSG) method.\textsuperscript{135–137} As the production of BaTiO\textsubscript{3} single crystals by the solution method is costly, however, the solid-state conversion of BaTiO\textsubscript{3} single crystals has been attempted several times. Yamamoto and Sakuma\textsuperscript{10} were able to grow BaTiO\textsubscript{3} single crystals with a 3 mm × 3 mm × 0.5 mm size by utilizing the abnormal grain growth behavior of BaTiO\textsubscript{3}. The fabricated single crystal was translucent because of the presence of some island crystals and entrapped pores within it. Later, Yoo \textit{et al.}\textsuperscript{12} succeeded in growing cm-sized BaTiO\textsubscript{3} single crystals by regulating the number of abnormal grains in a polycrystal through a controlled doping of SiO\textsubscript{2} at the surface of the polycrystal. Lee \textit{et al.}\textsuperscript{25} were able to grow cm-sized single crystals by utilizing the phenomenon of secondary abnormal grain growth in BaTiO\textsubscript{3} at a temperature above the eutectic point. During the secondary abnormal grain growth, only a small number of grains grew abnormally and a secondary abnormal grain became a single crystal with size larger than 1 cm × 1 cm. Later, Kang and his coworkers\textsuperscript{8,69} found that the growth of μm-sized polycrystalline BaTiO\textsubscript{3} grains can be suppressed for over a hundred hours by presintering in H\textsubscript{2} and sintering in air. Utilizing this grain growth behavior, Choi \textit{et al.}\textsuperscript{18} showed that BaTiO\textsubscript{3} single crystals can easily be grown with a seed. Using this technique, several cm-sized BaTiO\textsubscript{3} single crystals with less than 1% porosity are now commercially fabricated.\textsuperscript{39}

The Ba(Zr\textsubscript{x},Ti\textsubscript{1−x})O\textsubscript{3} (BZT) system has received much attention from electroceramists because of its high electric-field-induced strain and high piezoelectric properties in both ceramics and single crystals.\textsuperscript{8,24,139,140} The addition of Zr to BaTiO\textsubscript{3} decreases the Curie temperature of BaTiO\textsubscript{3}, but increases the tetragonal–orthorhombic transition temperature and the orthorhombic–rhombohedral transition temperature.\textsuperscript{141,142} With control of the Zr concentration, it is possible to stabilize either a rhombohedral or an orthorhombic phase at room temperature.\textsuperscript{142} As precise control of the Zr concentration is critical to the piezoelectric properties of BZT,\textsuperscript{140} the melt or solution growth method does not seem to be suitable for the growth of BZT single crystals. No report is available for the growth of BZT single crystals by these methods. Millimeter-sized BZT single crystals, however, were grown by the templated grain growth method.\textsuperscript{24} A high strain (~0.5% at 50 kV/cm) and a high piezoelectric strain coefficient (~355 pC/N), but a large hysteresis in strain, were reported for single crystals fabricated by the TGG method. Taking advantage of the phenomenon of grain growth suppression of BaTiO\textsubscript{3} in air after presintering in H\textsubscript{2},\textsuperscript{64,69} Lee\textsuperscript{8} was able to fabricate net-shaped BZT single crystals of different shapes, for example, the ring-shaped single crystal in Fig. 10(a).

Table I lists the dielectric and piezoelectric properties of BaTiO\textsubscript{3} and BZT ceramics and single crystals. In BaTiO\textsubscript{3}, the dielectric constant of [001] oriented single crystals is much higher than that of ceramics, whereas the piezoelectric constant, \textit{d}_{33}, of the single crystals is inferior to that of ceramics.\textsuperscript{39,141,143,144} Compared with BaTiO\textsubscript{3} single crystals grown by the solution method, BaTiO\textsubscript{3} single crystals grown by the SSGC method exhibit a somewhat lower dielectric constant, but a much higher piezoelectric constant and electro-mechanical coupling factors.\textsuperscript{39,141,143,144} These results indicate that the quality of SSGC single crystals is, at least, on par with that of TSSG single crystals. In BZT, small single crystals grown by templated grain growth did not show significant advantages over ceramics in terms of dielectric and piezoelectric properties.\textsuperscript{24} However, the properties of single crystals that were recently commercially produced are several times higher than those of ceramics. This indicates that the dielectric and piezoelectric properties of BZT can be considerably enhanced when single crystals are properly fabricated.\textsuperscript{8,39}

(4) Pb-Containing Piezoelectric Materials

Because of their high piezoelectric properties, lead-containing perovskites have been intensively studied and utilized as materials for piezoelectric components.\textsuperscript{145,146} Typical examples are solid solutions of Pb(Mn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN) or Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PZN) with PbTiO\textsubscript{3} (PT). It was also reported that single crystals of solid solutions of PMN–PT and PZN–PT exhibit ferroelectric properties that are superior to those of ceramics of the same composition near the morphotropic phase boundary (MPB).\textsuperscript{145,147} The techniques that have commonly been studied and used for fabricating PMN–PT single crystals are the Bridgman method\textsuperscript{43,152} and the flux method.\textsuperscript{153,154} Although simple and economical, the flux method does not readily produce good quality crystals with high productivity. Commercial production of PMN–PT single crystals by the Bridgman method has been successful with good reproducibility. However, the production cost is high and a compositional gradient is usually present in the produced crystals.

To overcome the high production cost and chemical inhomogeneity problem, solid-state conversion of PMN-PT single

\begin{table}[h]
\begin{center}
\caption{Dielectric and Piezoelectric Properties of BaTiO\textsubscript{3} and Ba(Zr\textsubscript{x},Ti\textsubscript{1−x})O\textsubscript{3} Ceramics and Single Crystals}
\begin{tabular}{lcccr}
\hline
 & Dielectric constant & \textit{tan} \textdelta & \textit{T}_\text{c} (°C) & \textit{d}_{33} (pC/N) & \textit{k}_{33} \\
\hline
\textbf{Ceramics} & & & & & \\
BaTiO\textsubscript{3}\textsuperscript{41} & 1900 & <0.01 & 120 & 191 & 0.493 \\
Ba(Zr\textsubscript{0.05},Ti\textsubscript{0.95})O\textsubscript{3}\textsuperscript{140} & 1800 & – & – & 174 & 0.43 \\
Ba(Zr\textsubscript{0.05},Ti\textsubscript{0.92})O\textsubscript{3}\textsuperscript{140} & 1600 & – & – & 236 & 0.57 \\
Ba(Zr\textsubscript{0.03},Ti\textsubscript{0.97})O\textsubscript{3}\textsuperscript{140} & 900 & – & – & 130 & 0.41 \\
\textbf{Single crystals} & & & & & \\
[001] BaTiO\textsubscript{3} (Solution method)\textsuperscript{41} & 2920 (a-axis) & – & 120 & 85.6 & 0.56 \\
 & 3600 (c-axis) & – & 135 & – & – \\
[001] BaTiO\textsubscript{3} (TSSG)\textsuperscript{143} & 150 (c-axis) & – & – & – & – \\
[001] BaTiO\textsubscript{3} (SSCG)\textsuperscript{144} & 2430 (a-axis) & – & 132 & 140 & – \\
 & 770 (c-axis) & – & – & – & – \\
[001] BaTiO\textsubscript{3} (SSCG)\textsuperscript{39} & 2800 (a-axis) & <0.01 & 130 & 150 & 0.62 \\
[001] Ba(Zr\textsubscript{0.05},Ti\textsubscript{0.95})O\textsubscript{3} (Laser floating zone)\textsuperscript{129} & – & – & 500 & – & – \\
[001] Ba(Zr\textsubscript{0.05},Ti\textsubscript{0.95})O\textsubscript{3} (SSCG)\textsuperscript{24} & 770 & – & – & 340 & 0.74 \\
[001] Ba(Zr\textsubscript{0.05},Ti\textsubscript{0.95})O\textsubscript{3} (SSCG)\textsuperscript{8} & 4000 & <0.01 & 80–95 & 1150 & 0.9 \\
\hline
\end{tabular}
\end{center}
\textsuperscript{TTSSG, top-seeded solution growth; SSGC, solid-state single crystal growth; TGG, templated grain growth; \textit{d}_{33}, induced polarization in direction 3 (parallel to a direction in which material is polarized) per unit stress applied in direction 3; \textit{k}_{33}, electromechanical coupling factor for electric field in direction 3 and longitudinal vibrations in direction 3 (bar type).}
\end{table}
crystals has been attempted since the late 1990s. Khan et al.\textsuperscript{13} succeeded in growing PMN–35PT single crystals of ~0.5 mm size in the presence of a small amount of a PbO-based liquid with the addition of PbZrO\(_3\) or PbO. The growth kinetics of PMN–PT single crystals was also studied.\textsuperscript{155} Kim et al.\textsuperscript{13} were also able to grow PMN–PT single crystals with the addition of Li\(_2\)O/PbO and the introduction of dislocations in the substrate. However, the produced single crystals were not large enough for practical use and contained a considerable fraction of pores of several and several tens of microns. Apart from these academic studies, commercial production of lead-containing piezoelectric single crystals by the SSCG method has been attempted and successful.\textsuperscript{8} A company now produces several cm-sized PMN-based single crystals, such as PMN–PT and PMN–PZT with less than 1\% porosity.\textsuperscript{39} The company\textsuperscript{8,39} also demonstrated that single crystals with complex shapes, such as the 2-2 composite shown in Fig. 10(b), can be manufactured with no machining steps.

Table II lists the dielectric and piezoelectric properties of Pb-containing (textured) ceramics and single crystals fabricated by various methods. The piezoelectric properties of [001] textured PMN–PT ceramics are much higher than those of ordinary PMN–PT ceramics.\textsuperscript{156} However, [001] oriented single crystals with similar compositions, regardless of their fabrication method, exhibit even higher piezoelectric properties than those of [001] textured PMN–28PT ceramics.

The properties of single crystals fabricated at the laboratory scale exhibit considerable variations according to the fabrication method. The Bridgman and flux methods appear to give better properties than the SSCG method. Several companies are now producing Pb-containing piezoelectric single crystals by the Bridgman and the SSCG method.\textsuperscript{39,150–152} In contrast to those of lab-scale products, the properties of the commercial products do not exhibit a considerable difference in piezoelectric properties according to the fabrication method, either the melt growth or the solid-state growth method. Considering the cost-effectiveness and simplicity of the process, the SSCG method appears to be more promising for mass production than the Bridgman method. According to recent data provided by a company,\textsuperscript{39} high \(T_c\) relaxor-PZT single crystals are also being produced by the SSCG method.

### (5) NBT-Based Lead-Free Piezoelectric Materials

Solid solutions of (Na\(_{1.2}\)Ba\(_{0.8}\)TiO\(_3\)) (NBT) with BaTiO\(_3\) (BT) and also with (K\(_{1.2}\)Na\(_{0.8}\)Nb\(_2\)O\(_6\)) (KNN) have been developed and studied quite intensively in response to the demand for lead-free piezoelectric materials.\textsuperscript{157–160} Most NBT-based materials, however, exhibit piezoelectric properties that are significantly inferior to those of lead-containing materials. For the maximum use of the piezoelectric properties of NBT–BT materials, fabrication of single crystals has been attempted.\textsuperscript{14,161–165} Ge et al.\textsuperscript{162} fabricated single crystals of NBT–5BT with 35 mm diameter and 10 mm thickness, close to the MPB composition, by the TSSG method. Later, Mn-doped NBT–10BT single crystals with improved piezoelectric and ferroelectric properties were grown by the same method.\textsuperscript{165} Although these investigations reported the fabrication of NBT–BT single crystals by the TSSG method, the problem of chemical inhomogeneity of the single crystals was inevitable due to the incongruent solidification of the compound and the volatilization of low melting point elements, such as Na and Bi, during the solution growth process. To overcome these problems, Moon et al.\textsuperscript{14} adopted the SSCG method and were able to fabricate cm-sized NBT–5BT single crystals using SrTiO\(_3\) seeds. Using the same technique as that of Moon et al., Park et al.\textsuperscript{15} succeeded in fabricating 91(Na\(_{1.2}\)Ba\(_{0.8}\)TiO\(_3\))–6BaTiO\(_3\)–3(K\(_{1.2}\)Na\(_{0.8}\)Nb\(_2\)O\(_6\)) (NBT–6BT–3KNN) single crystals with a more complex composition.

Table III lists the piezoelectric properties of fabricated NBT–BT based lead-free (textured) ceramics and single crystals. In the NBT–BT system, undoped NBT–6(7)BT ceramics\textsuperscript{166–168} exhibit a piezoelectric constant \(d_{33}\) of 125–176 pC/\textmu m, whereas textured NBT–BT ceramics and NBT–BT single crystals exhibit piezoelectric constants up to 322 and 450 pC/\textmu m, respectively. It appears, however, that the piezoelectric properties of textured ceramics\textsuperscript{169,170} are comparable to those of single crystals. With regard to the fabrication method of single crystals, the piezoelectric constant of single crystals grown by the SSCG method appears to be inferior to that of single crystals grown by the flux and the Bridgman methods, possibly because of the presence of many pores in the single crystals.

An NBT-based material with a composition of 92(Na\(_{1.2}\)Ba\(_{0.8}\)TiO\(_3\))–6BaTiO\(_3\)–2(K\(_{1.2}\)Na\(_{0.8}\)Nb\(_2\)O\(_6\)) (NBT–6BT–2KNN)
was recently developed as a piezoelectric material with a giant strain that is higher than that of PZT-based ceramics.\textsuperscript{\textcircled{171}} The developed material exhibited a high converse piezoelectric constant ($S_{\text{max}}/E_{\text{max}} = d_{33}^\text{t}$) of 570 pm/V. For practical application of this material, however, the problem of its large hysteresis in electric-field-induced strain\textsuperscript{\textcircled{171}} must be resolved. Park \textit{et al.}\textsuperscript{\textcircled{17}} showed that the hysteresis problem can be relieved using NBT–6BT–3KNN single crystals fabricated by the SSCG method. A [001] oriented NBT–6BT–3KNN single crystal exhibited a converse piezoelectric constant of 1050 pm/V at 4 kV/mm.\textsuperscript{\textcircled{15}} The electric-field-induced strain characteristics were also noticeably improved, but the NBT–6BT–3KNN single crystals contained many entrapped pores. For the development and commercial use of lead-free piezoelectric single crystals by the SSCG method, including NBT-based crystals in particular, more efforts are needed to reduce electromechanical hysteresis (in terms of the properties) and porosity (in terms of the processing).

(6) Other Materials

Transparent neodymium-doped yttrium aluminum garnet (Nd:YAG) is commonly used as a laser medium for solid-state lasers because of its transparency, good thermal stability, and shock resistance.\textsuperscript{3,172} Chemically homogeneous and transparent Nd:YAG ceramics can be fabricated by hot isostatic pressing\textsuperscript{173} or pressureless sintering with doping.\textsuperscript{174,175} The quality of the material, however, can be maximized by using single crystals. Nd:YAG single crystals have been commercially produced by the Czochralski method.\textsuperscript{176} Although the produced single crystals exhibit better optical properties than ceramics, only a fraction of the grown crystal is used because of chemical nonuniformity of the product.

There is demand for the fabrication of Nd:YAG single crystals by the SSCG method. Ikese \textit{et al.}\textsuperscript{\textcircled{38}} were able to fabricate almost pore-free Nd:YAG single crystals of several mm-size by the SSCG method. The crystals exhibited a laser oscillation efficiency ($\eta$ = 63\%) that is higher than that of ceramics ($\eta$ = 57\%) and comparable with that of Czochralski grown single crystals ($\eta$ = 67\%). The SSCG method, however, has not yet proved successful in fabricating single crystals with sizes that are commercially usable.

Some fluoride and perovskite oxides, such as yttria-stabilized zirconia (YSZ), cerium-gadolinium oxide (CGO), and La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-x}$ ($\text{LSGM}$), have been intensively studied for use as an electrolyte for solid oxide fuel cells (SOFCs) because of their good ionic conductivity at elevated temperatures.\textsuperscript{177} However, poor chemical stability of the materials at high operating temperatures impedes wide-range application.\textsuperscript{177} Apatite-type oxides, such as Si- and Ge-based apatites, can be alternatives to fluoride and perovskite electrolytes for SOFC applications due to their high oxygen ion conductivity.\textsuperscript{177} As the conductivity along a specific axis is much higher than that along other axes, fabrication of single crystals of these materials warrants exploration. Their fabrication by the melt growth method, however, is difficult because of their high melting points. Fabrication of hexagonal apatite-type La$_9$Si$_6$O$_{26}$ single crystals by the SSGC method has been attempted by Nakayama \textit{et al.}\textsuperscript{\textcircled{88}} and was successful. The fabricated single crystal showed a conductivity that is 100 times higher than that of ceramics, but 5–10 times lower than that of melt-grown single crystals, thus illustrating the remarkable benefit of using single crystals in this area. Much more efforts are anticipated in the future for fabricating large apatite-type solid electrolyte single crystals by the SSCG method.

IV. Concluding Remarks and Perspectives

The solid-state conversion of single crystals has advantages over the conventional melt growth and the solution growth methods, in particular for complex systems, in terms of cost-effectiveness, easy control of chemistry, and the chemical uniformity of the product. Net-shape production is another advantage. Despite these ample advantages, studies on the fabrication of single crystals by the SSCG method have only been carried out by a few research groups and commercial application of the technique has been very limited. The limited research and applicability of this technique are due to the difficulty in the control of microstructure, in particular the control of AGG in the polycrystal that has to be converted into a single crystal. The conventional mechanisms of AGG, including the second phase particle (or pore) drag mechanism, solute drag mechanism, liquid film enhancement mechanism, which is highlighted as the introduction of several complexions of boundaries, and the interfacial energy/mobility anisotropy mechanism, were not able to generally explain various types of microstructural evolution in polycrystals. Understanding of the conventional mechanisms has not been sufficient for the technical development of solid-state conversion of single crystals.

In the 1990s, it was suggested that AGG in solid–liquid two-phase systems can be well explained by the migration mechanism and behavior of the faceted solid–liquid interface.\textsuperscript{100,101} Based on this understanding and subsequent experiments, Kang \textit{et al.} developed the mixed control model of grain growth and the principle of microstructural evolution in two-phase systems.\textsuperscript{76,95} The principle is the coupling of the

### Table III. Piezoelectric Properties of (Na$_{1/2}$Ba$_{1/2}$)TiO$_3$-Based Ceramics and Single Crystals

<table>
<thead>
<tr>
<th>Ceramic Type</th>
<th>$T_d$ (°C)</th>
<th>$d_{33}$ (pC/N)</th>
<th>$S_{max}$/$E_{max}$ (pm/V)</th>
<th>Electromechanical coupling factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBT–6BT\textsuperscript{166}</td>
<td>130</td>
<td>125</td>
<td>240</td>
<td>$k_{33}$, 0.55</td>
</tr>
<tr>
<td>NBT–6BT\textsuperscript{168}</td>
<td>100</td>
<td>155</td>
<td>–</td>
<td>$k_p$, 0.36</td>
</tr>
<tr>
<td>NBT–7BT\textsuperscript{167}</td>
<td>105</td>
<td>176</td>
<td>–</td>
<td>$k_p$, 0.23</td>
</tr>
<tr>
<td>NBT–6BT–2KNN\textsuperscript{71}</td>
<td>–</td>
<td>30</td>
<td>570</td>
<td>–</td>
</tr>
<tr>
<td>Textured Ceramics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBT–6BT\textsuperscript{169}</td>
<td>130</td>
<td>240</td>
<td>–</td>
<td>$k_p$, 0.412</td>
</tr>
<tr>
<td>NBT–7BT\textsuperscript{170}</td>
<td>–</td>
<td>322</td>
<td>–</td>
<td>$k_\tau$, 0.665</td>
</tr>
<tr>
<td>Single crystals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[001] NBT–5.5BT (Flux method)\textsuperscript{184}</td>
<td>–</td>
<td>450</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[001] NBT–6BT (Bridgman)\textsuperscript{61}</td>
<td>145</td>
<td>160</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[001] NBT–4BT (TSSG)\textsuperscript{164}</td>
<td>146</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[001] NBT–5BT (TSSG)\textsuperscript{162}</td>
<td>130</td>
<td>280</td>
<td>–</td>
<td>$k_\tau$, 0.5</td>
</tr>
<tr>
<td>[001] Mn-doped NBT–10BT (TSSG)\textsuperscript{165}</td>
<td>110–120</td>
<td>483</td>
<td>–</td>
<td>$k_\tau$, 0.56</td>
</tr>
<tr>
<td>[001] NBT–5BT (SSCG)\textsuperscript{14}</td>
<td>145</td>
<td>207</td>
<td>200</td>
<td>$k_{33}$, 0.5</td>
</tr>
<tr>
<td>[001] NBT–6BT–3KNN (SSCG)\textsuperscript{15}</td>
<td>–</td>
<td>15</td>
<td>1050</td>
<td>–</td>
</tr>
</tbody>
</table>

$k_\tau$, factor for electric field in direction 3 and vibrations in direction 3 (thin disk).
maximum driving force for grain growth in the system and the critical driving force for appreciable growth of grains. For single-phase systems with grain boundaries, many experimental studies suggested that the migration of a faceted boundary is governed by this mixed mechanism, as in the case of a faceted solid/liquid interface. It was thus found that the same mechanism and the same principle as those for single-phase systems are valid for single-phase systems with grain boundaries. The discovery of the microstructural evolution principle has led to systematic studies on the solid-state conversion of single crystals.

Studies on the fabrication and commercial production of ceramic single crystals by the SSCG method, however, have been quite limited. In particular, commercial production by this method is available only for BaTiO$_3$-based materials and lead-based piezoelectric materials. This is mainly because of the difficulty in controlling and suppressing grain growth in the corresponding polycrystals for the long time period of their solid-state conversion. The elimination of pores in polycrystals is another difficulty. The selection and use of good seed crystals can also be a critical factor. For academic as well as industrial motivations, the research and development of single crystals are shifting for materials from simple compounds to complex compounds with new or improved properties. As the composition of the compounds becomes more complicated, it becomes more difficult to use the melt growth or solution growth method for the fabrication of single crystals because of the common problem of chemical inhomogeneity in the fabricated single crystals. The SSCG method can be a strong alternative or a unique technique for the fabrication of those single crystals. It is anticipated that more studies on the SSCG method for a wide range of systems along with further development of this technique will be carried out in the future.

Acknowledgments

This research was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (MSIP) (2011-0017556) and also by the Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2013M3A6B1087882).

References

122K. H. Brosnan, “Processing, Properties, and Application of Textured 0.72Pb(Zr0.53Ti0.47)O3–0.28PbTiO3 Ceramics,” Ph. D. Thesis, Pennsylvania State University, University Park, PA, May 2007.


Suk-Joong L. Kang is a Distinguished Professor in the Department of Materials Science and Engineering at KAIST. He received a B.S. from Seoul National University in 1973, a M.S. from KAIST in 1975, a Dr-Ing from Ecole Centrale de Paris in 1980, and Dr. d’Etat from the University of Paris VI in 1985. Dr. Kang has published more than 260 papers on sintering and microstructural evolution in ceramics and metals. He is the author of the text, *Sintering: Densification, Grain Growth and Microstructure* (2005). He developed the “Pore Filling Theory” of liquid phase sintering. For more than 15 years he has particularly contributed to the understanding of microstructural evolution. He introduced the concept of the mixed control of boundary migration, and deduced the principle of microstructural evolution. Dr. Kang is a fellow of the American Ceramic Society, and a member of the World Academy of Ceramics, the Korean Academy of Science and Technology, and the National Academy of Engineering in Korea, and Editor-in-Chief of the Journal of Asian Ceramic Societies. He is the recipient of academic awards from the Korean Institute of Metals and Materials and the Korean Ceramic Society, the Soosan Award from the American Ceramic Society, the Richard Brook Award (2015) from the European Ceramic Society, the Incheon Prize from the Incheon Memorial Foundation, and the Korea Engineering Award from the President of Korea.

Ji-Hoon Park received a B.S. degree in Materials Science and Engineering (MSE) from Inha University, Incheon, in 2009, and a M.S. degree in MSE from the Korea Advance Institute of Science and Technology (KAIST), Daejeon, in 2011. Since 2009, he has been part of the Materials Interface Laboratory at KAIST while pursuing a Ph. D. degree. His current research interests include the fabrication of lead-free piezoelectric single crystals using the Solid-state Single Crystal Growth method and characterization of piezoelectric properties.

Seok-Young Ko is a Ph. D. student in the Department of Materials Science and Engineering (MSE) at the Korea Advanced Institute of Science and Technology (KAIST). He earned his B.S. and M.S. degrees in MSE from KAIST. His research interests are focused on the sintering of lead-free piezoelectric materials and related phenomena. His current work involves the processing of lead-free piezoelectric ceramics and enhancement of their electrical properties.

Ho-Yong Lee is a Professor in the Department of Materials Science and Engineering at Sungmoon University. He received a B.E. degree in Mineralogy and Petroleum from Seoul National University in 1987. From March 1987 to February 1993 he studied at Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea, and received his M.S. and Ph.D. in Materials Science and Engineering in 1989 and 1993, respectively. He developed the “Solid-state Single Crystal Growth (SSCG) technique” for ferroelectric/piezoelectric materials such as BaTiO3, Ba(Ti,Zr)O3, PMN-PT, and PMN-PZT. He also contributed to the understanding of the single crystal growth mechanism in the SSCG process. In 2000, he founded a venture company (Ceracomp Co., Ltd.) to commercialize the SSCG technique. His research interests focus on the fabrication, characterization, and application of ferroelectric/piezoelectric single crystals.