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144055 Development of "n- and p-type Doped" Perovskite Single Crystals

Ho-Yong Lee
INDUSTRY-UNIVERSITY COOPERATION FOUNDATION.SUNMOON UNIV.

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Professor Ho-Yong Lee

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Sunmoon University
Department of Advanced Materials Engineering
Chungnam 336-708, Korea

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14. ABSTRACT

In this project the solid-state growth of “n- and p-type doped” perovskite single crystals [(1) paraelectric SrTiO3, (2) normal ferroelectric BaTiO3, (3) relaxor ferroelectric 0.85BaTiO3-0.15Bi(Mg0.5Ti0.5)O3, and (4) antiferroelectric PbZrO3] have been tried. Among them “n- and p-type doped” BaTiO3 single crystals have been successfully fabricated. And their bi-crystals containing a twin or twist boundary are also fabricated using diffusion bonding process of two single crystal plates. These results demonstrate that the SSCG (solid-state single crystal growth) technique are suitable to grow a variety of “n- and p-type doped” perovskite single crystals of complicated compositions. The Fe-doped (001) BaTiO3 single crystals show an ultrahigh strain of 0.8% at 1 kV/mm (Smax/Emax = 15,000 pm/V) which is 30 times higher than PZT ceramics and 7.5 times higher than PMN-PT single crystals. Therefore the BaTiO3 single crystals having “ultrahigh” unipolar strains will be used for actuator, sensor, and transducer applications. The research is anticipated to guide the practical development of functional perovskite single crystals.

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"Development of "*n*- and *p*-type Doped" Perovskite Single Crystals Using Solid-State Single Crystal Growth (SSCG) Technique"

Principal Investigator:
Prof. Ho-Yong Lee
Sunmoon University
Department of Advanced Materials Engineering
70, Sunmoon-Ro 221, Tangjeong-Myeon, Asan-si, Chungnam,
336-708 (Postal Code), KOREA
Tel) 82-41-530-2366 (Office); 82-10-3301-2366 (Mobile)
Fax) 82-41-584-2367
E-mail) hlee.ceracomp@gmail.com; hlee@sunmoon.ac.kr

Administrative Point of Contact:
Goang-Hyon Ryu
Sunmoon University
Industry-University Cooperation Foundation
Tel) 82-41-530-2641 (Office)
E-mail) ryu01@sunmoon.ac.kr

Submitted to:
Dr. Ken Caster
International Program Office
Asian Office of Aerospace Research & Development (AOARD)
Tokyo, Japan
E-mail) kenneth.caster@us.af.mil; kcchem83.japan@gmail.com

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Ho-Yong Lee
Ho-Yong Lee

September 01, 2017
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Abstract:

In this project the solid-state growth of “n- and p-type doped” perovskite single crystals [(1) paraelectric $SrTiO_3$, (2) normal ferroelectric $BaTiO_3$, (3) relaxor ferroelectric $0.85BaTiO_3$-$0.15Bi(Mg_{0.5}Ti_{0.5})O_3$, and (4) antiferroelectric $PbZrO_3$] have been tried. **Among them “n- and p-type doped” $BaTiO_3$ single crystals have been successfully fabricated.** And their bi-crystals containing a twin or twist boundary are also fabricated using diffusion bonding process of two single crystal plates. These results demonstrate that the SSCG (solid-state single crystal growth) technique are suitable to grow a variety of “*n*- and *p*-type doped” perovskite single crystals of complicated compositions.

The Fe-doped (001) $BaTiO_3$ single crystals show an ultrahigh strain of 0.8% at 1 kV/mm (S_{max}/E_{max} = 15,000 pm/V) which is 30 times higher than PZT ceramics and 7.5 times higher than PMN-PT single crystals. Therefore the $BaTiO_3$ single crystals having “ultrahigh” unipolar strains will be used for actuator, sensor, and transducer applications.

The research is anticipated to guide the practical development of functional perovskite single crystals of critical importance to the Air Force mission. The fundamental information gained will be presented and integrated into scientific workshops and symposia to catalyze expansion of the fundamental work and to also inspire practical solutions to developing improved non-linear dielectric materials for extreme environments.

1. Introduction

There are several classes of materials that can be used to develop new non-linear dielectrics for high-voltage and high-power applications. A major need is to better understand their individual limitations at high electric field strengths in terms of the high-field conductivity and electrical breakdown. The phenomena that lead to failure are complex and need more extensive scientific understanding, particularly in regard to polarization and conduction at interfaces, the specific charge transfer process, and point defect (and thus field) distributions in the vicinity of microstructural features and electrodes, how these are coupled, and how they evolve with time under electrical bias. Despite substantial work in non-linear dielectrics, such knowledge remains unknown and limits current strategies for improving high-temperature and high-field performance dielectrics.

In order to provide a fundamental, mechanistic understanding of interface-mediated polarization, conduction, degradation, and breakdown processes in non-linear dielectric materials, the majority of experiments utilize “n- and p-type doped” perovskite single crystals such as (1) paraelectric $SrTiO_3$, (2) normal ferroelectric $BaTiO_3$, (3) weakly coupled relaxor $0.85BaTiO_3$-$0.15Bi(Mg_{0.5}Ti_{0.5})O_3$ [BT-15BMT], and (4) antiferroelectric $PbZrO_3$ [PZ]. Bi-crystals of $SrTiO_3$ and $BaTiO_3$ will be used to conduct prototype experiments on artificial grain boundaries. However, it has been well known that it is very difficult or impossible to grow the single crystals. Therefore their bi-crystals cannot be easily made because of difficulty in growing the single crystals. So we need to use and develop a new single crystal growth method which is suitable to grow chemically uniform and large “n- and p-type doped” perovskite single crystals.

Figure 1 shows the methods of single crystal growth. The conventional crystal growth techniques for perovskite single crystals including flux technique or Bridgman method have critical limitations; high production cost and compositional inhomogeneity throughout the crystal. These limitations result from a complicated melting step of major constituents during crystal growth. Especially, it is very difficult to grow chemically uniform single crystals of $0.85BaTiO_3$-$0.15Bi(Mg_{0.5}Ti_{0.5})O_3$ (BT-15BMT) and $PbZrO_3$ (PZ), because of its high solid solubility (BT-15BMT) and incongruent melting behavior (PZ), by using the conventional crystal growth methods such flux and Bridgman methods. Therefore the successful growth of large and chemically uniform BT-15BMT and PZ single crystals has not been reported yet.

In this project, we will develop a more convenient and cost-effective fabrication process for growing perovskite single crystals with no melting step of major components. The perovskite single crystals will be directly grown from polycrystalline precursors by the SSCG method, as shown in Fig. 2. Since the growth of perovskite single crystals will proceed at a constant temperature without a melting step, the grown crystals are chemically homogeneous and the production cost becomes much lower.

Figure 3 shows the previous investigation of solid-state growth of $BaTiO_3$ single crystals. A small $BaTiO_3$ single crystal (as a seed) was diffusion bonded to a polycrystalline $BaTiO_3$ ceramics and heat-treated at an appropriate temperature for growth of the seed crystal. During the heat-treatment, however, the seed single crystal grew up to a few millimeters. The single crystal growth was very limited and the growth rate was very low. So in the previous investigation it was not possible to grow large $BaTiO_3$ single crystals by using the solid-state method because the abnormal grain growth was not controlled successfully.

During the heat-treatment of a polycrystalline material, a few grains sometimes grow extensively at the expense of fine matrix grains a process usually referred to as abnormal grain growth (AGG). Because of the appearance of large abnormal grains, the grain size distribution changes from uni-modal distribution of grain size to bimodal distribution of grain size, as shown in Fig. 4. During normal grain growth (NGG), however, the grain size distribution of a polycrystalline body does not change, as shown in Fig. 4. The rate of AGG is orders of magnitude higher than that of normal grain growth. Therefore, when the number of abnormal grains is strictly controlled, the single crystal can be grown with a relatively high rate in the solid state. For growing a single crystal by AGG, the number of “nuclei” for AGG should be minimal. For this purpose, the seeds for AGG may also be provided externally. This process is called the solid-state single crystal growth (SSCG) method, and its principle is rather simple: let an external single crystal seed grow by consuming the fine matrix grains without melting the major constituents, as shown in Fig. 2. Since this process is not only quite cost-effective but also good for mass production of large single crystals, many researchers tried to grow single crystals by the SSCG method. The possibility of growing a single crystal by the SSCG was already demonstrated by NGK (ferrite) in Japan and GE (Al_2O_3) in USA.

Ceracomp has demonstrated that the number density of abnormal grains in sintered $BaTiO_3$ ceramics can be controlled, as shown in Fig. 5. By controlling the number density of abnormal grains in sintered $BaTiO_3$ ceramics, a large single crystal can be grown in a polycrystalline ceramics.

Figure 6 shows the SSCG process of $BaTiO_3$ that has been successfully established by Ceracomp. A small (001) $BaTiO_3$ single crystal seed was placed on the top of a sintered ceramics and heat-treated. During the heat-treatment, the seed crystal grew in to the ceramics and became a large single crystal. It occurred without melting of $BaTiO_3$ because the heat-treatment temperature was much lower than the melting temperature of $BaTiO_3$.

By using the SSCG process, a transparent $BaTiO_3$ single crystal could be grown as shown in Fig. 7. A "unique" $BaTiO_3$ single crystal with the compositional gradient (A Mn-, Cr-, and Ce-doped $BaTiO_3$ single crystal) could be also fabricated by using a $BaTiO_3$ ceramics with the same compositional gradient (Fig. 8). This result has demonstrated that the SSCG method is very suitable to fabrication of doped" perovskite single crystals and makes it possible to grow compositionally uniform "n- and p-type doped" perovskite single crystals [(1) paraelectric $SrTiO_3$, (2) normal ferroelectric $BaTiO_3$, (3) relaxor ferroelectric $0.85BaTiO_3$-$0.15Bi(Mg_{0.5}Ti_{0.5})O_3$ [BT-15BMT], and (4) antiferroelectric $PbZrO_3$ [PZ]].

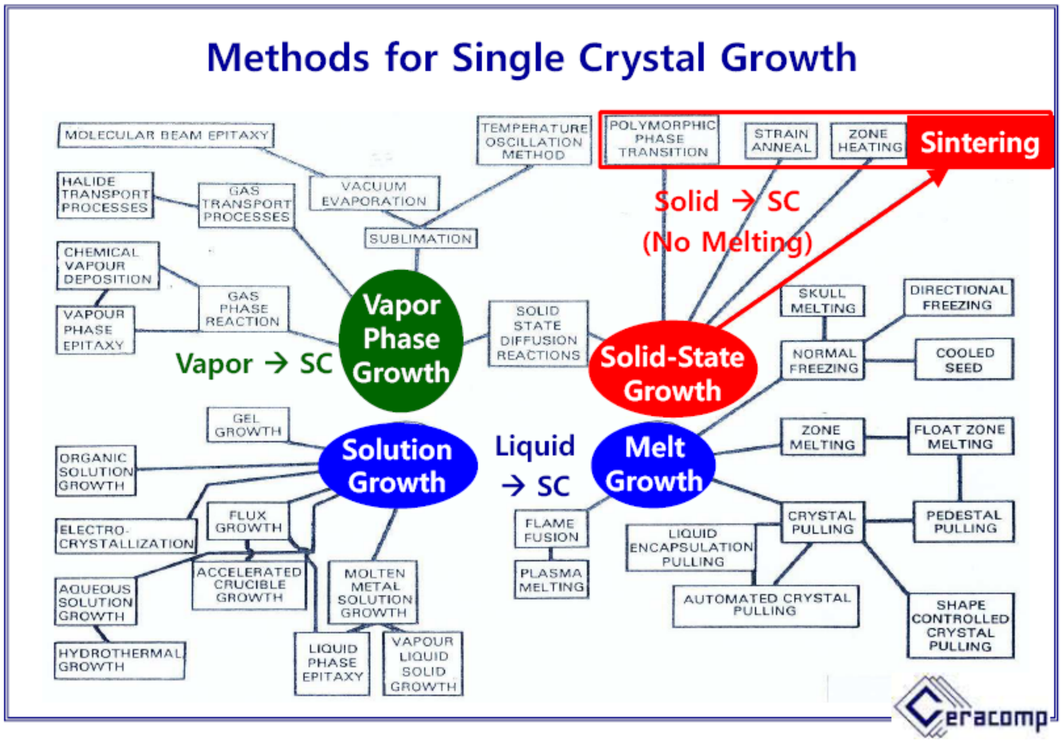
$Pb(Zr,Ti)O_3$ [PZT] ceramics have been the main stay for high performance piezoelectric applications. Compositionally PZT ceramics lie near the MPB between the tetragonal and rhombohedral phases and MPB compositions exhibit anomalously high dielectric and piezoelectric properties. Many attempts to grow single crystals of PZT and PZ have been made by numerous researchers, resulting in crystallites too small to allow adequate property measurements, as shown in Fig. 9. In contrast to relaxor-PT crystal growth, PZT and PZ cannot be readily grown in single crystal form because of incongruent melting behavior of PZ as well as evaporation of volatile PbO during melting process. During incongruent melting of PZ, PZ decomposes to liquid and solid phase ZrO_2. The solid phase ZrO_2 in the liquid phase prevents continuous growth of PZ single crystals. In order to grow large PZ or PZT single crystals, therefore, a melting step of PZ should be avoided in the crystal growth process.

For the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ [PMN-PT] system containing volatile PbO, a $BaTiO_3$ single crystal obtained by the SSCG method (Fig. 6) was used as a seed crystal. When a $BaTiO_3$ single crystal was placed on the top of a PMN-PT ceramics and then heat-treated, a PMN-PT single crystal grew hetero-epitaxially at the surface of the $BaTiO_3$ single crystal. Figure 10 shows an experimental procedure for growing chemically homogeneous and fully dense PMN-PT single crystal. Hot pressing was very effective in densification of PMN-PT ceramics. When a seed crystal was grown in a hot-pressed ceramics, a fully dense PMN-PT single crystal was obtained as shown in Fig. 10.

Figure 11 shows the solid-state growth of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ [PMN-PZT] single crystals doped (a) Fe, (b) In, and (c) Mn. The PMN-PZT system includes a PZ component and thus shows incongruent melting behavior. Because of the incongruent melting of PZ as well as volatile PbO, the growth of large PMN-PZT single crystals has not been reported yet by using other crystal growth methods except the SSCG technique. Especially up to this time "n- or p-type doped" PMN-PZT single crystals could be grown only by the SSCG method.

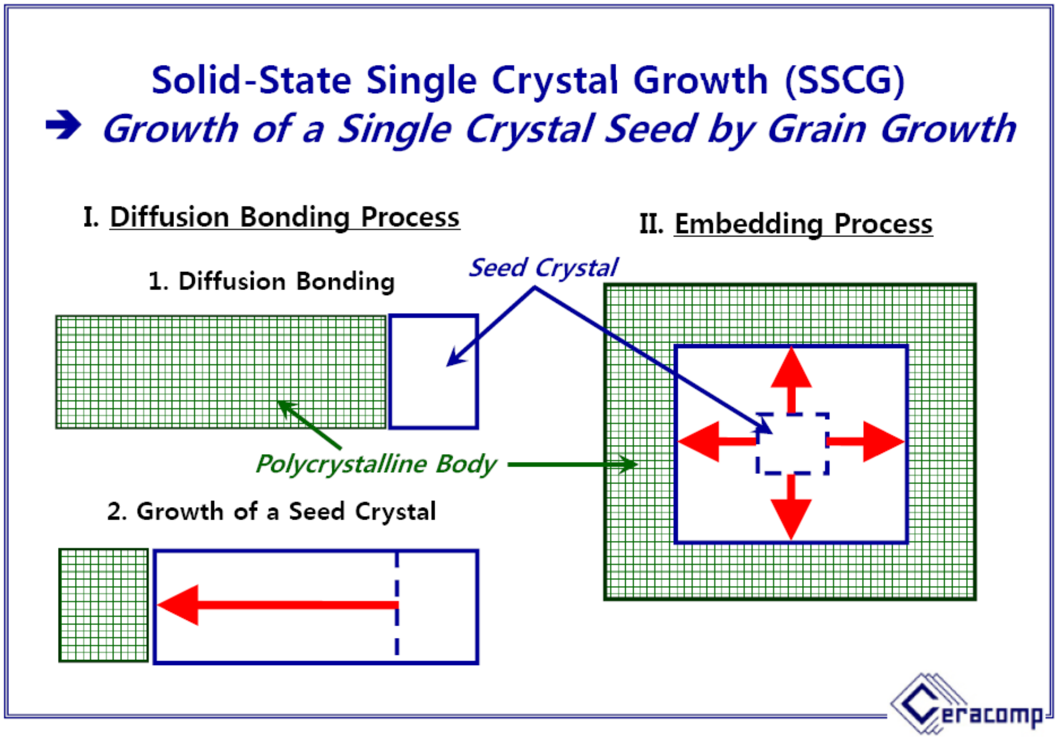
The application of conventional melt growth techniques to "n- and p-type doped" perovskite single crystals [(1) paraelectric $SrTiO_3$, (2) normal ferroelectric $BaTiO_3$, (3) relaxor ferroelectric $0.85BaTiO_3$-$0.15Bi(Mg_{0.5}Ti_{0.5})O_3$ [BT-15BMT], and (4) antiferroelectric $PbZrO_3$ [PZ]], such as flux, Czocharlski, zone melting, and Bridgman techniques, are limited by the several reasons shown in Fig. 12. The main reasons are (1) the destructive phase transition, (2) high PbO vapor pressure at the growth temperature, (3) incongruent melting behavior of PZ, and (4) phase stability, and (5) high solid solubility. These make the growth of "n- and p-type doped" perovskite single crystals complicated. Therefore the solid-state single crystal growth method could be the best way of growing compositionally uniform "n- and p-type doped" perovskite single crystals [(1) paraelectric $SrTiO_3$, (2) normal ferroelectric $BaTiO_3$, (3) relaxor ferroelectric $0.85BaTiO_3$-$0.15Bi(Mg_{0.5}Ti_{0.5})O_3$ [BT-15BMT], and (4) antiferroelectric $PbZrO_3$ [PZ]].

The bi-crystals of "n- and p-type doped" perovskite single crystals can be made by a simple diffusion bonding process, as shown in Fig. 13. Fig. 13 shows the vertical cross sections, thermally etched at 1550°C for 1 h, of the ***m*** plane of an Al_2O_3 single crystal diffusion-bonded to (A) the ***C*** plane of an Al_2O_3 single crystal located at the top [**Bi-crystal**] and (B) the sintered Al_2O_3 polycrystal located at the bottom. And Fig. 14 shows the microstructures of cross sections of diffusion couples (Fig. 13) after heat-treatment in the presence of Fe_2O_3 at 1550°C ((A) ***C-m*** **bi-crystal** and (B) ***m-P***). As shown in Figs. 13 and 14, the diffusion bonding process is very simple and effective to make bi-crystals containing a tilt or twist boundary.



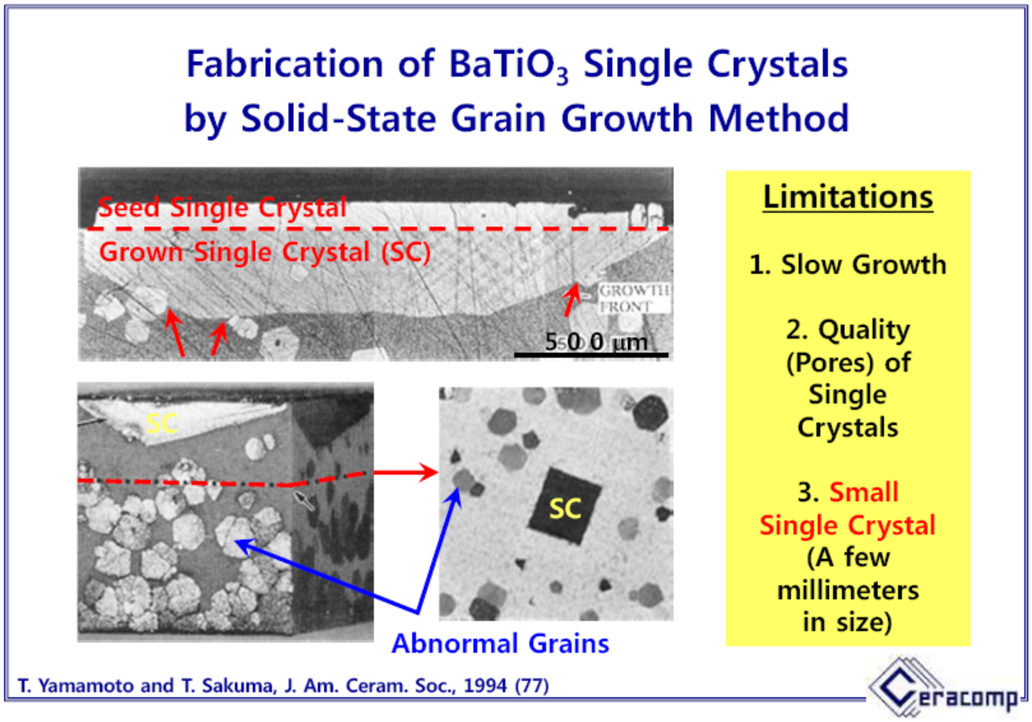
Methods for Single Crystal Growth

Fig. 1. Methods for single crystal growth
(Solid-state conversion from a polycrystalline ceramics to a single crystal).



Solid-State Single Crystal Growth (SSCG)
➔ *Growth of a Single Crystal Seed by Grain Growth*

Fig. 2. Schematic of the solid-state single crystal growth (SSCG) method.



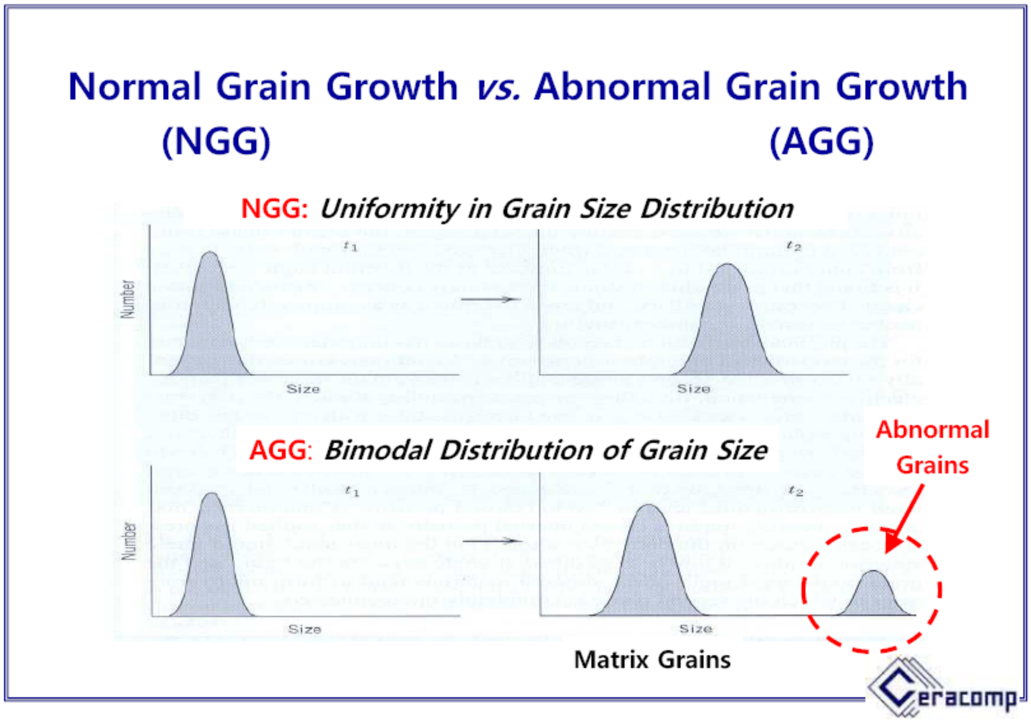
Fabrication of $BaTiO_3$ Single Crystals by Solid-State Grain Growth Method

Limitations

1. Slow Growth
2. Quality (Pores) of Single Crystals
3. Small Single Crystal (A few millimeters in size)

T. Yamamoto and T. Sakuma, J. Am. Ceram. Soc., 1994 (77)

Fig. 3. Solid-state growth of a $BaTiO_3$ single crystal in the previous study. In the previous study the abnormal grain growth was not successfully controlled.

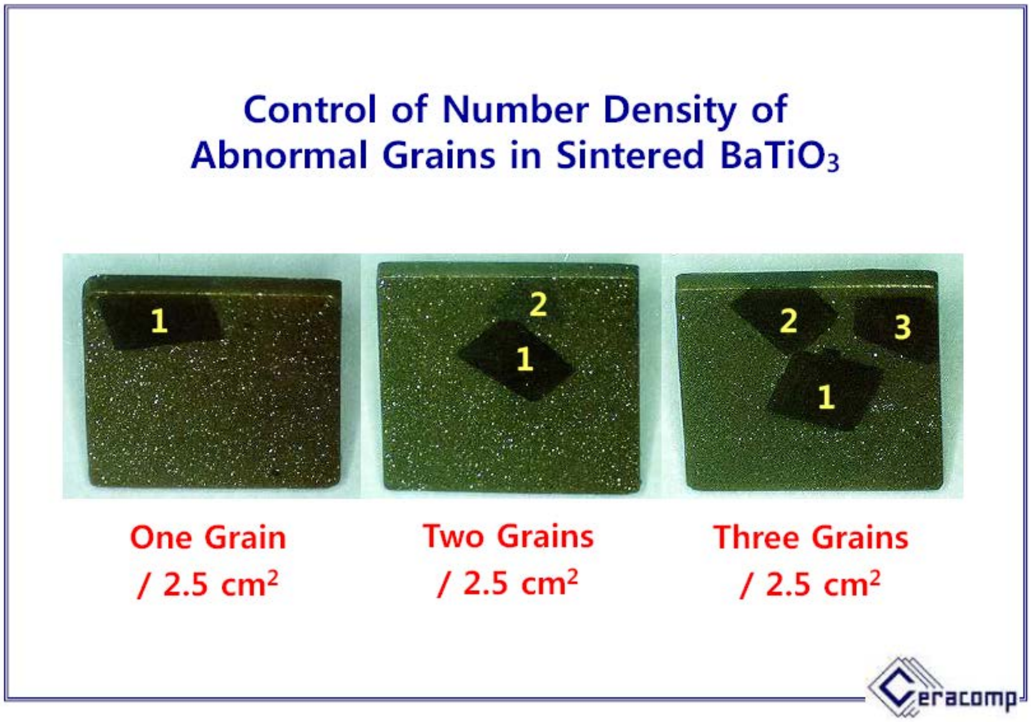


Normal Grain Growth *vs.* Abnormal Grain Growth (NGG) (AGG)

NGG: *Uniformity in Grain Size Distribution*

AGG: *Bimodal Distribution of Grain Size*

Fig. 4. Normal grain growth (NGG) *vs*. Abnormal grain growth (AGG).



Control of Number Density of
Abnormal Grains in Sintered $BaTiO_3$

One Grain / 2.5 cm^2

Two Grains / 2.5 cm^2

Three Grains / 2.5 cm^2

Fig. 5. Control of number density of abnormal grains in sintered $BaTiO_3$ ceramics.

"Solid-State Single Crystal Growth (SSCG)" Method

➔ *Growth of a Single Crystal in a Polycrystalline Body by Grain Growth*

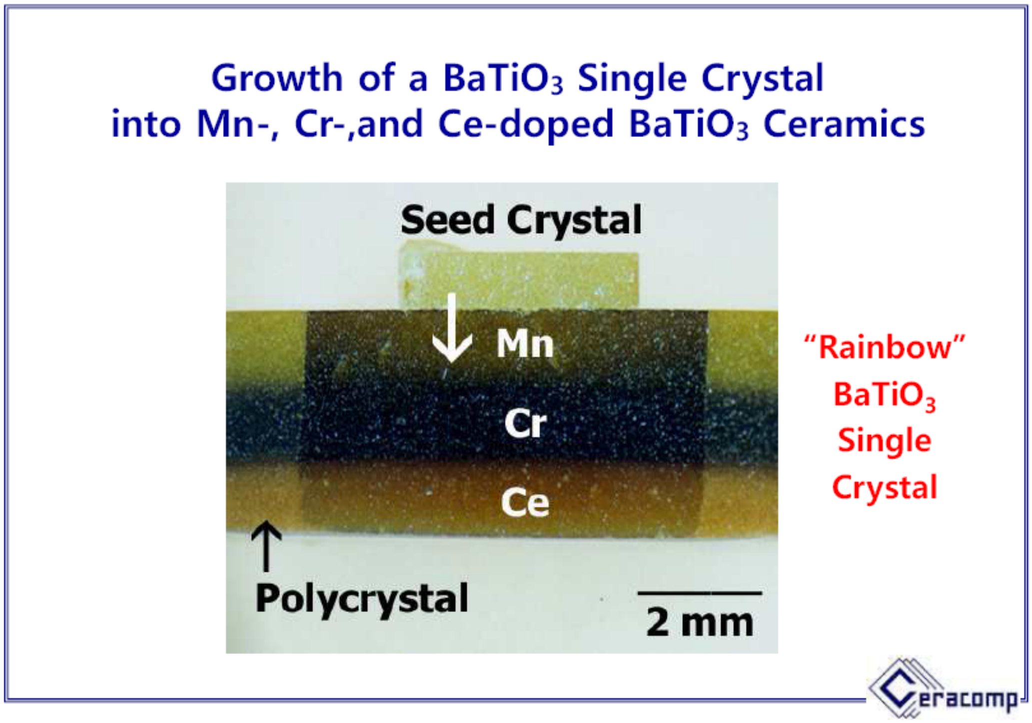
SSCG of $Ba(Ti,Zr)O_3$:
Growth of a (100) Seed

Fig. 6. SSCG of a $BaTiO_3$ single crystal in a polycrystalline precursor.
by Ceracomp

Transparent “High Density” $BaTiO_3$ Single Crystal Grown by SSCG Method

(001) Plate; [15x5x1 mm^3]

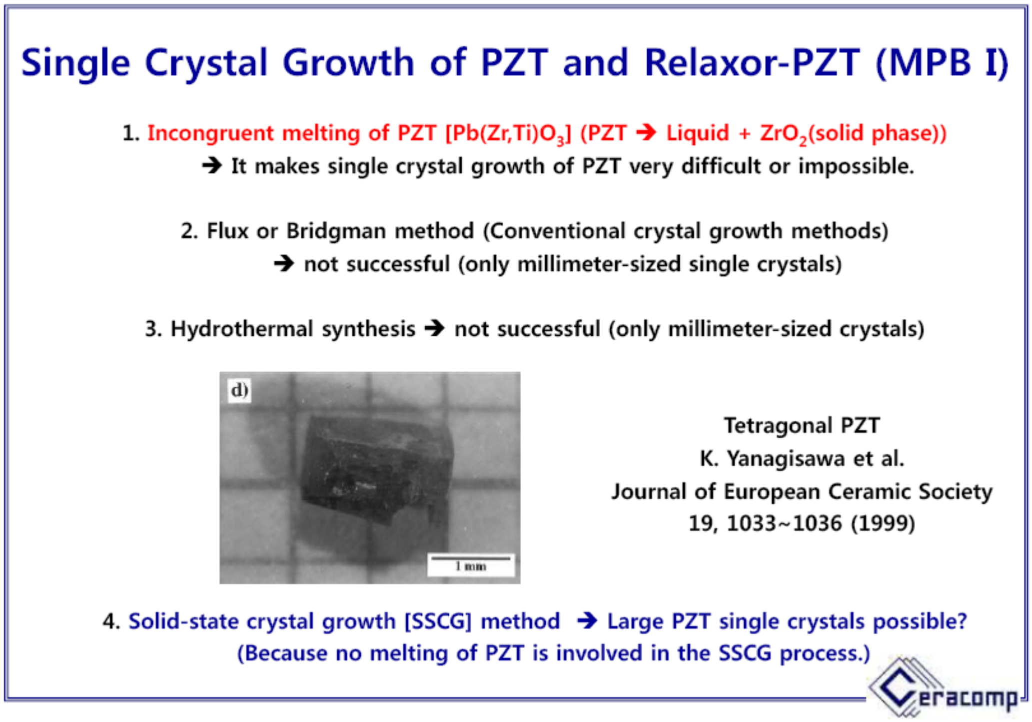
Fig. 7. Growth of a transparent $BaTiO_3$ single crystal by SSCG technique.



Growth of a $BaTiO_3$ Single Crystal into Mn-, Cr-,and Ce-doped $BaTiO_3$ Ceramics

“Rainbow” $BaTiO_3$ Single Crystal

Fig. 8. Cross-section of a $BaTiO_3$ single crystal with the compositional gradient. (A Mn-, Cr-, and Ce-doped $BaTiO_3$ single crystal)



Single Crystal Growth of PZT and Relaxor-PZT (MPB I)

1. Incongruent melting of PZT [Pb(Zr,Ti)O_3] (PZT → Liquid + ZrO_2(solid phase))
   → It makes single crystal growth of PZT very difficult or impossible.

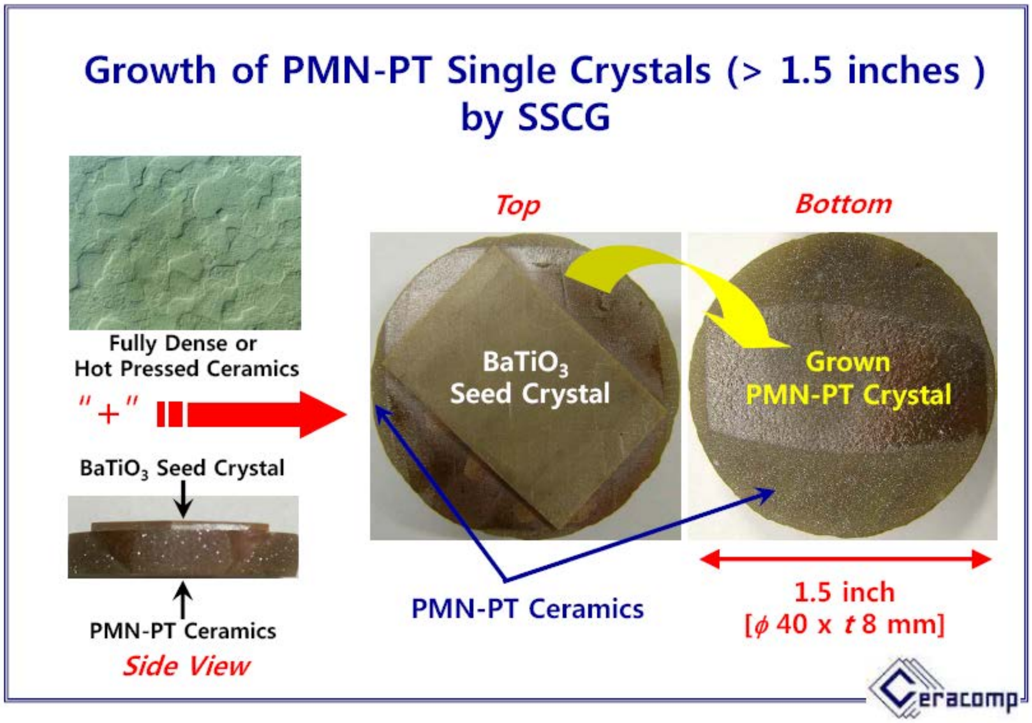
2. Flux or Bridgman method (Conventional crystal growth methods)
   → not successful (only millimeter-sized single crystals)

3. Hydrothermal synthesis → not successful (only millimeter-sized crystals)

Tetragonal PZT
K. Yanagisawa et al.
Journal of European Ceramic Society
19, 1033~1036 (1999)

4. Solid-state crystal growth [SSCG] method → Large PZT single crystals possible?
   (Because no melting of PZT is involved in the SSCG process.)

Fig. 9. Previous studies of Pb(Zr,Ti)O_3 [PZT] single crystal growth.



Growth of PMN-PT Single Crystals (> 1.5 inches) by SSCG

Fully Dense or
Hot Pressed Ceramics

"+"

$BaTiO_3$ Seed Crystal

PMN-PT Ceramics

Side View

Top

Bottom

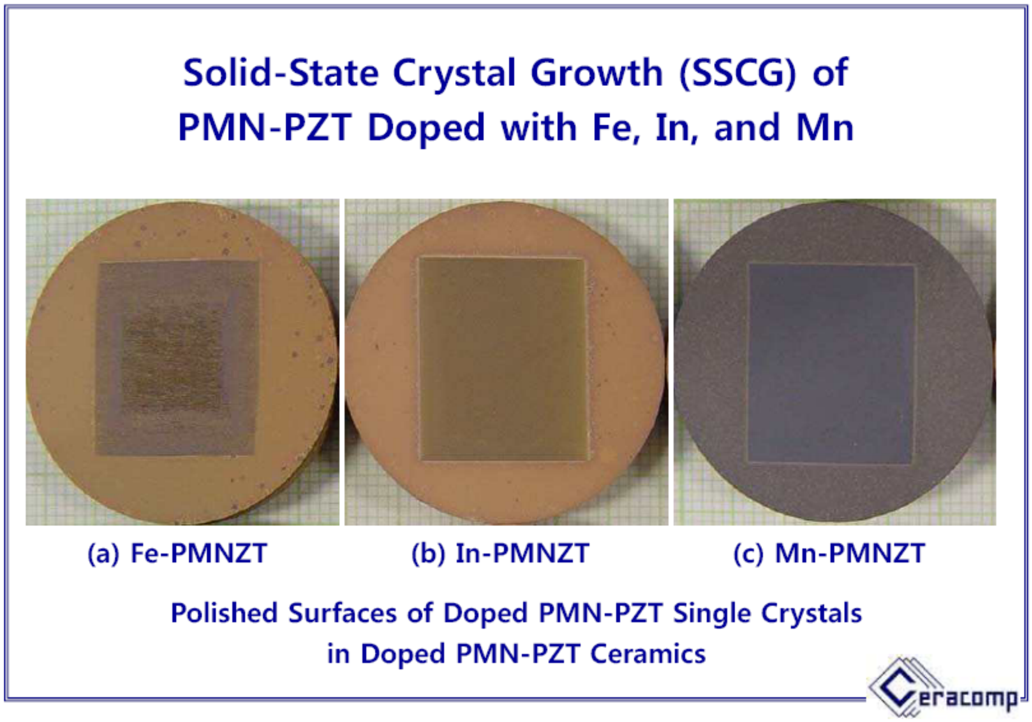
$BaTiO_3$
Seed Crystal

Grown
PMN-PT Crystal

PMN-PT Ceramics

1.5 inch
[ϕ 40 x t 8 mm]

Fig. 10. Experimental procedure for SSCG of a PMN-PT single crystal.

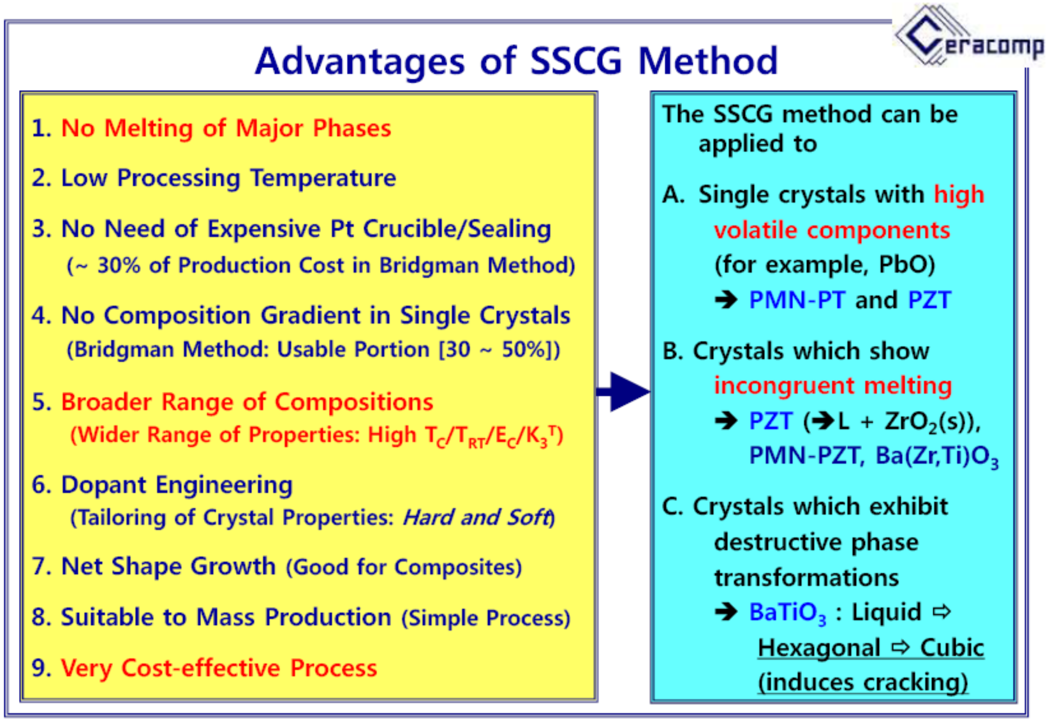


Solid-State Crystal Growth (SSCG) of PMN-PZT Doped with Fe, In, and Mn

(a) Fe-PMNZT (b) In-PMNZT (c) Mn-PMNZT

Polished Surfaces of Doped PMN-PZT Single Crystals in Doped PMN-PZT Ceramics

Fig. 11. Solid-state growth of PMN-PZT single crystals doped (a) Fe, (b) In, and (c) Mn.



Advantages of SSCG Method

1. No Melting of Major Phases
2. Low Processing Temperature
3. No Need of Expensive Pt Crucible/Sealing
   (~ 30% of Production Cost in Bridgman Method)
4. No Composition Gradient in Single Crystals
   (Bridgman Method: Usable Portion [30 ~ 50%])
5. Broader Range of Compositions
   (Wider Range of Properties: High $T_C/T_{RT}/E_C/K_3^T$)
6. Dopant Engineering
   (Tailoring of Crystal Properties: *Hard and Soft*)
7. Net Shape Growth (Good for Composites)
8. Suitable to Mass Production (Simple Process)
9. Very Cost-effective Process

The SSCG method can be applied to

A. Single crystals with high volatile components (for example, PbO)
   ➔ PMN-PT and PZT
B. Crystals which show incongruent melting
   ➔ PZT (➔L + ZrO_2(s)), PMN-PZT, $Ba(Zr,Ti)O_3$
C. Crystals which exhibit destructive phase transformations
   ➔ $BaTiO_3$: Liquid ⇨ Hexagonal ⇨ Cubic (induces cracking)

Fig. 12. Advantages of the SSCG method.

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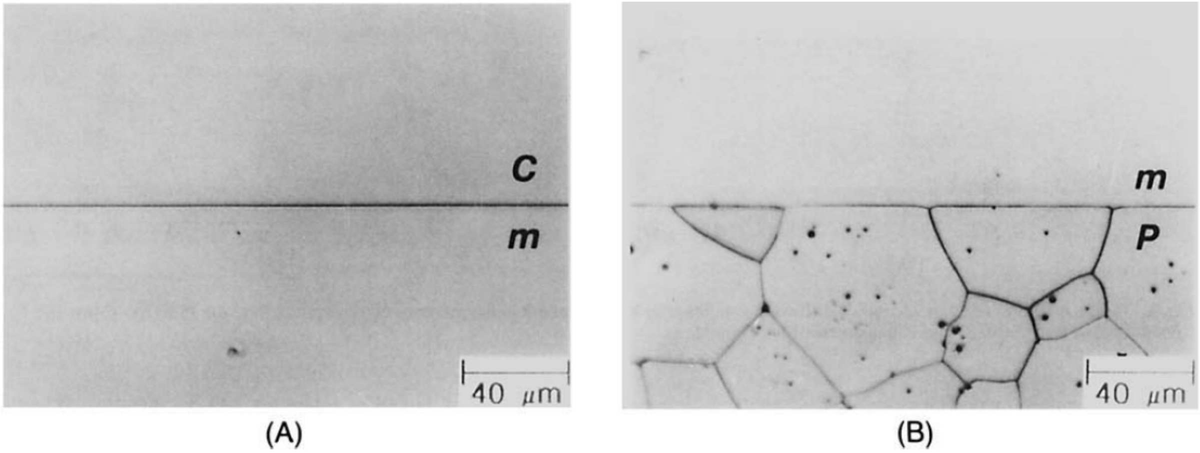


Fig. 13. Vertical cross sections, thermally etched at 1550°C for 1 h, of the *m* plane of an Al_2O_3 single crystal diffusion-bonded to (A) the *C* plane of an Al_2O_3 single crystal located at the top [**Bi-crystal**] and (B) the sintered Al_2O_3 polycrystal located at the bottom.

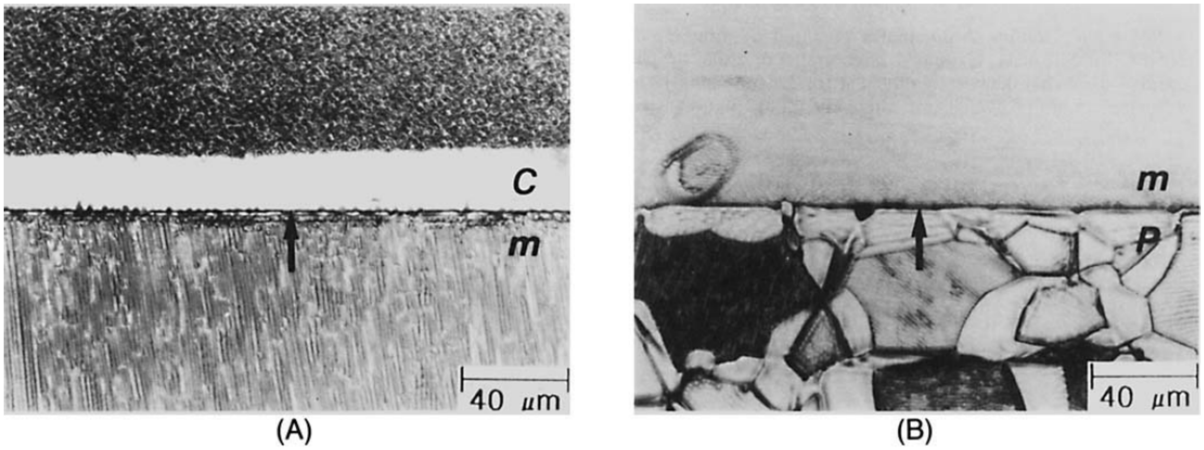


Fig. 14. Microstructures of cross sections of diffusion couples (Fig. 13) after heat-treatment in the presence of Fe_2O_3 at 1550°C ((A) *C*-*m* **bi-crystal** and (B) *m*-*P*). The arrow in each figure indicates the initial boundary.

3. Experimental Results and Discussion

In this project several different kinds of “n- and p-type doped” perovskite single crystals [(1) paraelectric $SrTiO_3$, (2) normal ferroelectric $BaTiO_3$, (3) relaxor ferroelectric $0.85BaTiO_3$-$0.15Bi(Mg_{0.5}Ti_{0.5})O_3$, and (4) antiferroelectric $PbZrO_3$] have been tried to grow by using solid-state single crystal growth (SSCG) technique. And their bi-crystals containing a twin or twist boundary are also fabricated using diffusion bonding process of two single crystal plates. The focus of this effort will also include the characterization of both “n- and p-type doped” perovskite single crystals and their bi-crystals.

3-1. $BaTiO_3$ single crystals

3-1-1. Experimental Process

“n- and p-type doped” $BaTiO_3$ single crystals used in the present study were prepared by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of $BaCO_3$, TiO_2 and several dopants (Ca, Ce, Co, Cr, Fe, La, Mg, Mn, Nb, and Nd), “n- and p-type doped” polycrystalline $BaTiO_3$ ceramics were obtained through a general sintering process. After weighing each raw material powder for “n- and p-type doped” $BaTiO_3$ compositions, they were mixed for 24 hours using ball-milling process, and calcined at 1,000℃ following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a $BaTiO_3$ seed single crystal was placed on the sintered body of “n- and p-type doped” $BaTiO_3$, and the second heat treatment for solid-state single-crystal growth was carried out for 200 hours at different temperatures.

The $BaTiO_3$ seed single crystal was continuously grown into the “n- and p-type doped” polycrystalline $BaTiO_3$ body during the heat treatment process for single-crystal growth, and “n- and p-type doped” $BaTiO_3$ single crystals of a size larger than 25x25x5 mm^3 were prepared as a result. Since no melting in $BaTiO_3$ occurred during single-crystal manufacturing process in the single-crystal growth method, composition gradients were not observed within the grown manufactured single crystal, giving rise to a chemical homogeneity. Thus-prepared single crystals larger than 25x25x5 mm^3 in size were cut into a plate shape(specimen of [3x3x0.5(t) m^3] for thickness mode measurement) and a square-column shape(specimen of [1x1x5(t) m^3] for 33 mode measurement) single-crystal specimens, and an Au electrode was formed on the cut single-crystal plate by using vacuum deposition method. Dielectric and piezoelectric properties of the manufactured “n- and p-type doped” $BaTiO_3$ single crystals and polycrystalline ceramics were measured in accordance with the IEEE standard.

3-1-2. Experimental Results

All "*n*- and *p*-type doped" $BaTiO_3$ single crystals fabricated grown in this program are listed in Fig. 15. As shown in Fig. 15, **undoped, isovalent ion-doped (Ca, Ce, and Zr), *n*-type doped (La, Nb, Nd), and *p*-type doped (Cr, Co, Fe, Mg, and Mn) $BaTiO_3$ single crystals** are successfully grown by the SSCG technique.

Figure 16 shows the solid-state growth of "Cr"-doped $BaTiO_3$ single crystals. The (001) and (111) single crystals of "Cr"-doped $BaTiO_3$ are successfully grown from (001) and (111) seed crystals, respectively.

Figure 17 shows "5x5x1(t) mm_3" plates of "Fe"- and "Nb"-doped $BaTiO_3$ single crystals grown by the SSCG technique. And "5x5x1(t) mm^3" plates of "Mn"-, "Mg"-, and "Co"-doped $BaTiO_3$ single crystals are also shown in Fig. 18.

The density of $BaTiO_3$ single crystals can be increased by increasing the density of polycrystalline ceramics before SSCG process. The HP (hot press) process is very effective in increasing densities or decreasing porosities of polycrystalline ceramics. So in this study the HP process was used to increasing densities of polycrystalline ceramics as well as SSCG single crystals. Figure 19 shows the schematics of controlling the density and porosity of $BaTiO_3$ single crystals by using HP process. The "high density" $BaTiO_3$ single crystal fabricated by using HP (Hot Press) process is shown in Fig. 20. Because the $BaTiO_3$ single crystal is fully densified, it is transparent as shown in Fig. 20.

Figure 21 shows the polarization behaviors of (a) undoped, (b) Fe (Acceptor)-doped and (c) Nb (Donor)-doped (001) $BaTiO_3$ single crystals. Compared to undoped $BaTiO_3$ single crystals, Fe (Acceptor)-doped $BaTiO_3$ single crystals show the higher polarization. However, Nb (Donor)-doped $BaTiO_3$ single crystals show the lower polarization.

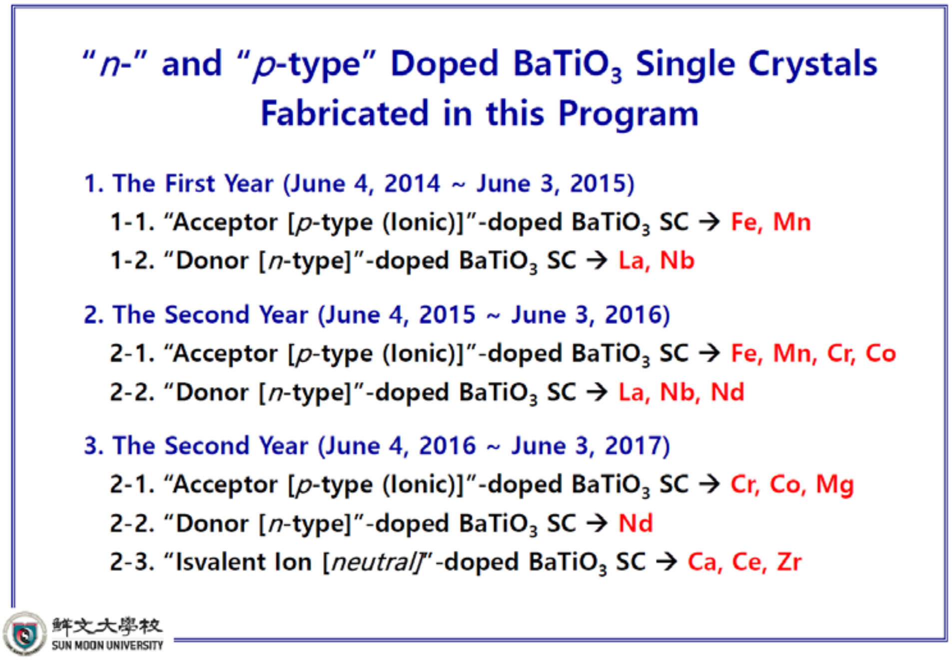
Figure 22 shows the bipolar strains of (a) undoped, (b) Fe (Acceptor)-doped and (c) Nb (Donor)-doped (001) $BaTiO_3$ single crystals. Compared to undoped $BaTiO_3$ single crystals, Fe (Acceptor)-doped $BaTiO_3$ single crystals show the higher bipolar strain. However, Nb (Donor)-doped $BaTiO_3$ single crystals show the lower bipolar strain.

Figure 23 shows the unipolar strains of (a) undoped, (b) Fe (Acceptor)-doped and (c) Nb (Donor)-doped (001) $BaTiO_3$ single crystals. Compared to undoped $BaTiO_3$ single crystals, Fe (Acceptor)-doped $BaTiO_3$ single crystals show the higher unipolar strain. However, Nb (Donor)-doped $BaTiO_3$ single crystals show the lower unipolar strain.

In order to compare unipolar strains of (001) $BaTiO_3$ single crystals undoped, acceptor-doped and donor-doped, doped $BaTiO_3$ single crystals are prepared and their unipolar strains are measured, as shown in Fig. 24. Among all doped $BaTiO_3$ single crystals, Fe (Acceptor)-doped $BaTiO_3$ single crystals show the largest unipolar strain of 0.8% at 1 kV/mm. However, Nb (Donor)-doped $BaTiO_3$ single crystals show the lower unipolar strain.

Figure 25 shows the ultrahigh unipolar strains of (001) $BaTiO_3$ single crystals doped with Fe. **The unipolar strain was about of 0.8% at 1 kV/mm and thus its S_{max}/E_{max} was calculated to be about 15,000 pm/V.** When the unipolar strains of PZT ceramics (d ~ 500 pC/N), PMN-PT single crystals (d_{33} ~ 2,000 pC/N), and Fe-doped $BaTiO_3$ single crystals (S_{max}/E_{max} = 15,000 pm/V) are compared as shown in Fig. 26, the Fe-doped $BaTiO_3$ single crystals show the highest unipolar strain of 0.8% at 1 kV/mm which is 30 times higher than PZT ceramics and 7.5 times higher than PMN-PT single crystals. **This result demonstrates that Fe-doped $BaTiO_3$ single crystals (S_{max}/E_{max} = 15,000 pm/V) can be used for actuator application.**

Figure 27 shows 1-3 single crystal-epoxy composites and “flexible” SFC composites of Fe-doped $BaTiO_3$ single crystals. The $BaTiO_3$ single crystals having “ultrahigh” unipolar strains will be used for actuator, sensor, and transducer applications.



“*n*-” and “*p*-type” Doped $BaTiO_3$ Single Crystals Fabricated in this Program

1. The First Year (June 4, 2014 ~ June 3, 2015)
   - 1-1. “Acceptor [*p*-type (Ionic)]”-doped $BaTiO_3$ SC → Fe, Mn
   - 1-2. “Donor [*n*-type]”-doped $BaTiO_3$ SC → La, Nb
2. The Second Year (June 4, 2015 ~ June 3, 2016)
   - 2-1. “Acceptor [*p*-type (Ionic)]”-doped $BaTiO_3$ SC → Fe, Mn, Cr, Co
   - 2-2. “Donor [*n*-type]”-doped $BaTiO_3$ SC → La, Nb, Nd
3. The Second Year (June 4, 2016 ~ June 3, 2017)
   - 2-1. “Acceptor [*p*-type (Ionic)]”-doped $BaTiO_3$ SC → Cr, Co, Mg
   - 2-2. “Donor [*n*-type]”-doped $BaTiO_3$ SC → Nd
   - 2-3. “Isvalent Ion [*neutral]*”-doped $BaTiO_3$ SC → Ca, Ce, Zr

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Fig. 15. “*n*- and *p*-type doped” $BaTiO_3$ single crystals grown in this program

“Cr”-doped $BaTiO_3$ Single Crystals Grown by SSCG

Growth from (001) Seed

Growth from (111) Seed

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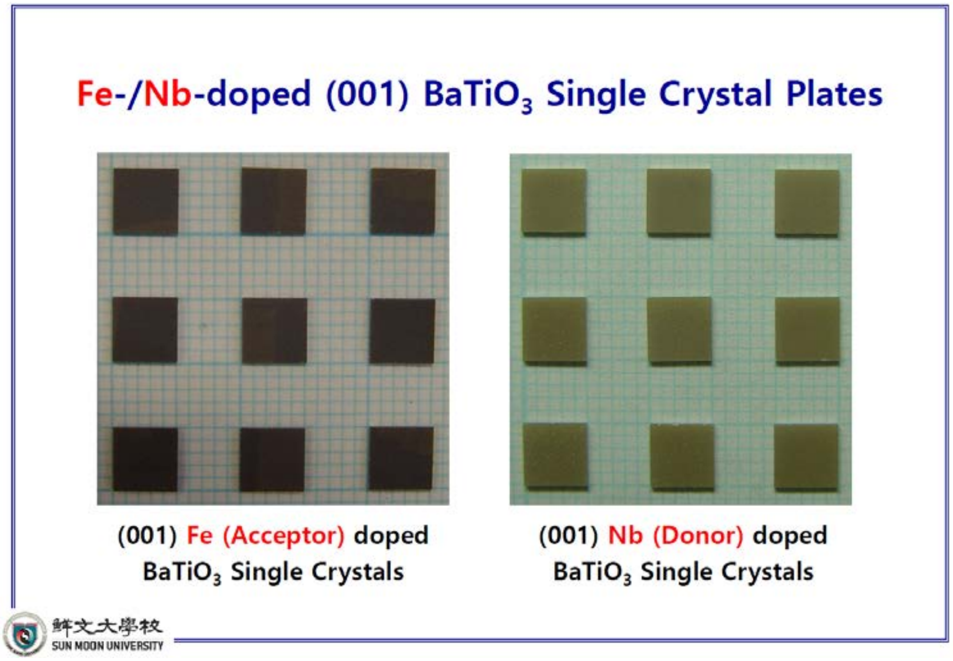
Fig. 16. “Cr”-doped $BaTiO_3$ single crystals grown by using (001) and (111) seed crystals



Fe-/Nb-doped (001) $BaTiO_3$ Single Crystal Plates

(001) Fe (Acceptor) doped
$BaTiO_3$ Single Crystals

(001) Nb (Donor) doped
$BaTiO_3$ Single Crystals

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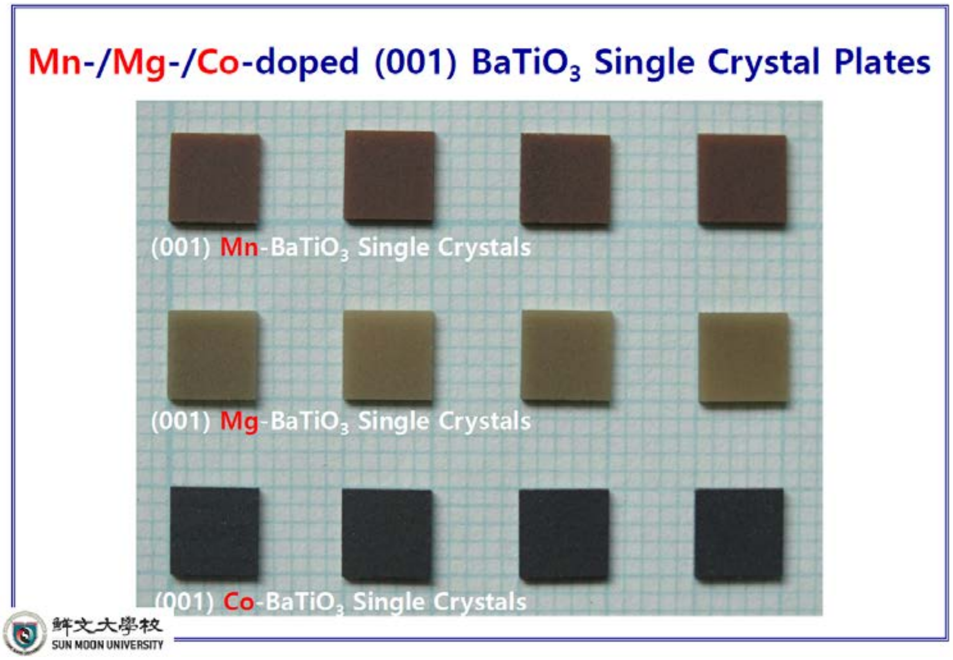
Fig. 17. “Fe”- and “Nb”-doped $BaTiO_3$ single crystals grown by SSCG technique



Mn-/Mg-/Co-doped (001) $BaTiO_3$ Single Crystal Plates

(001) Mn-$BaTiO_3$ Single Crystals

(001) Mg-$BaTiO_3$ Single Crystals

(001) Co-$BaTiO_3$ Single Crystals

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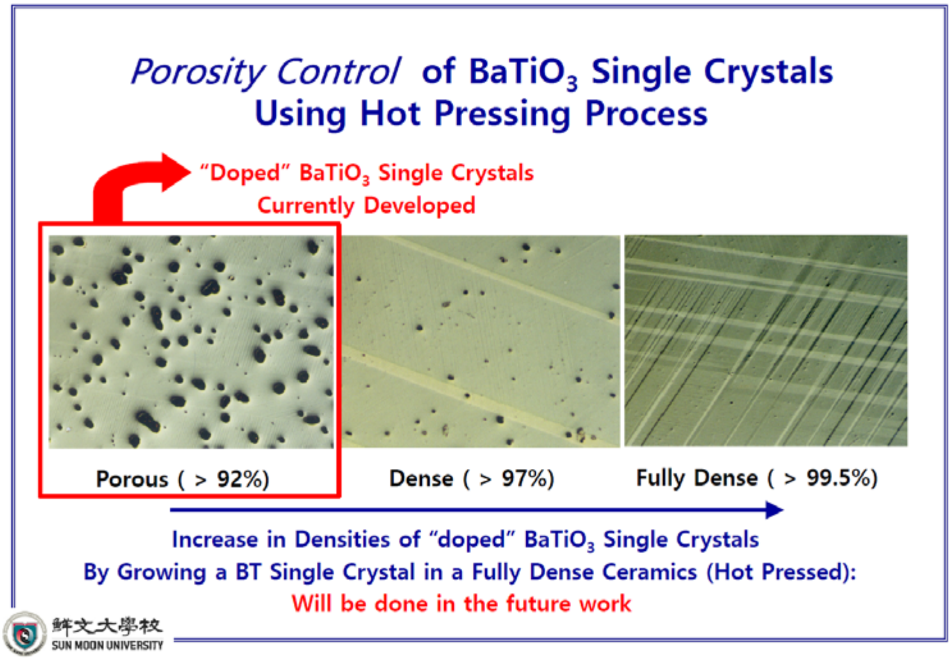
Fig. 18. “Mn”-, “Mg”-, and “Co”-doped $BaTiO_3$ single crystals grown by SSCG technique



Porosity Control **of $BaTiO_3$ Single Crystals Using Hot Pressing Process**

"Doped" $BaTiO_3$ Single Crystals
Currently Developed

Porous (> 92%)

Dense (> 97%)

Fully Dense (> 99.5%)

Increase in Densities of "doped" $BaTiO_3$ Single Crystals
By Growing a BT Single Crystal in a Fully Dense Ceramics (Hot Pressed):
Will be done in the future work

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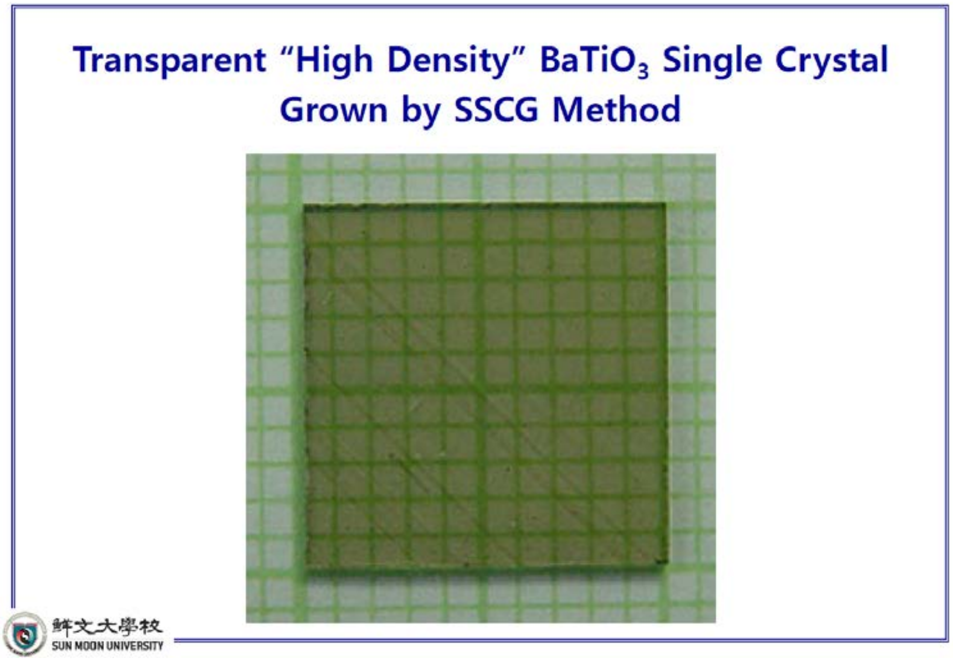
Fig. 19. Porosity Control of $BaTiO_3$ single crystals by using HP (Hot Press) process



Transparent "High Density" $BaTiO_3$ Single Crystal Grown by SSCG Method

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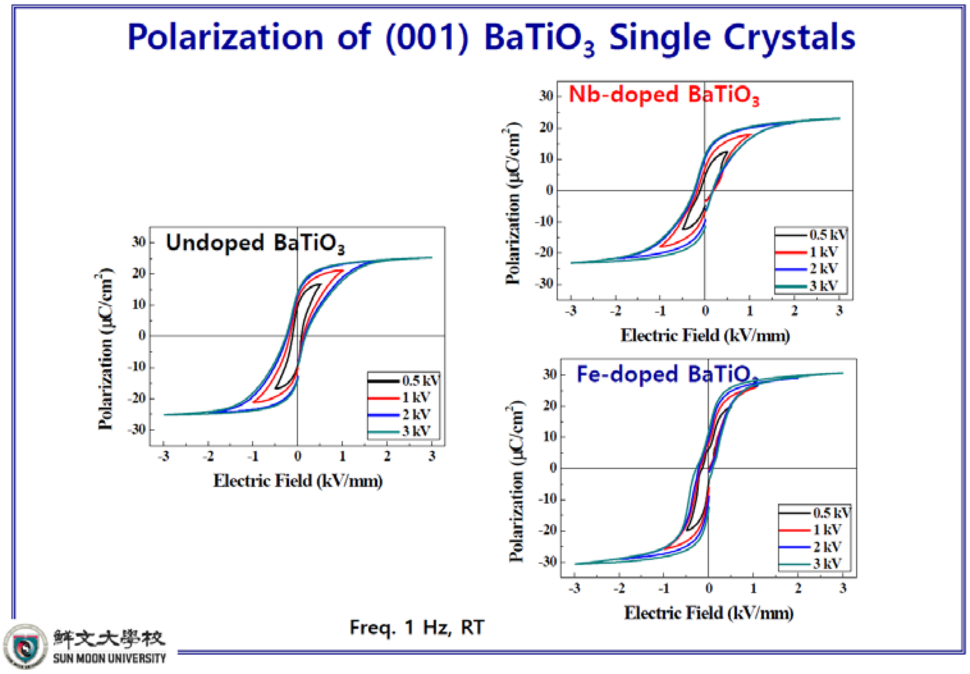
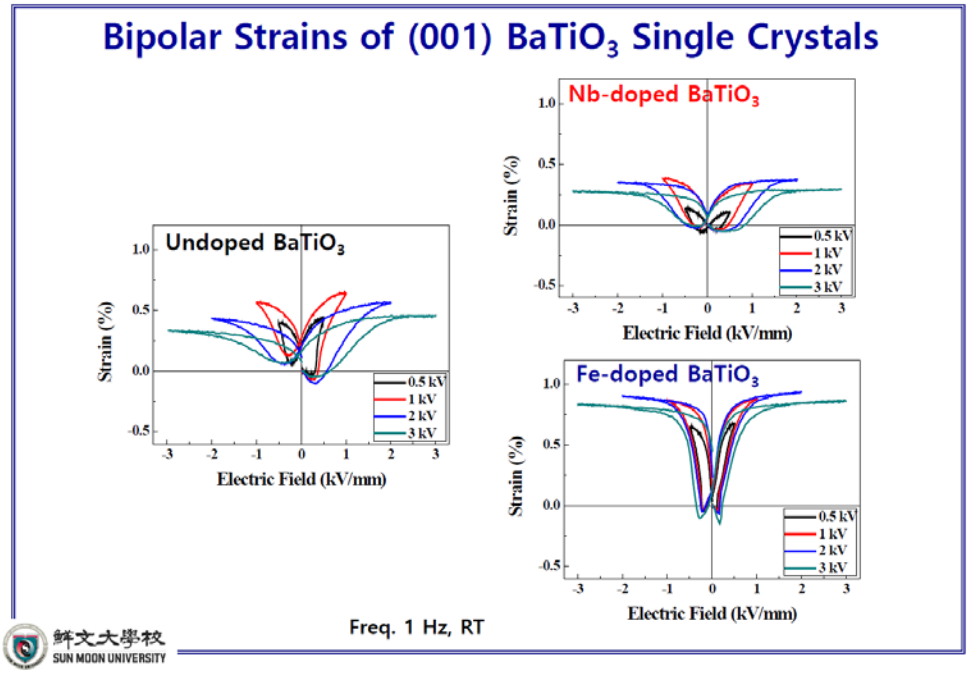
Fig. 20. Transparent "high density" $BaTiO_3$ single crystals
Fabricated by using HP (Hot Press) process



Polarization of (001) $BaTiO_3$ Single Crystals

Freq. 1 Hz, RT

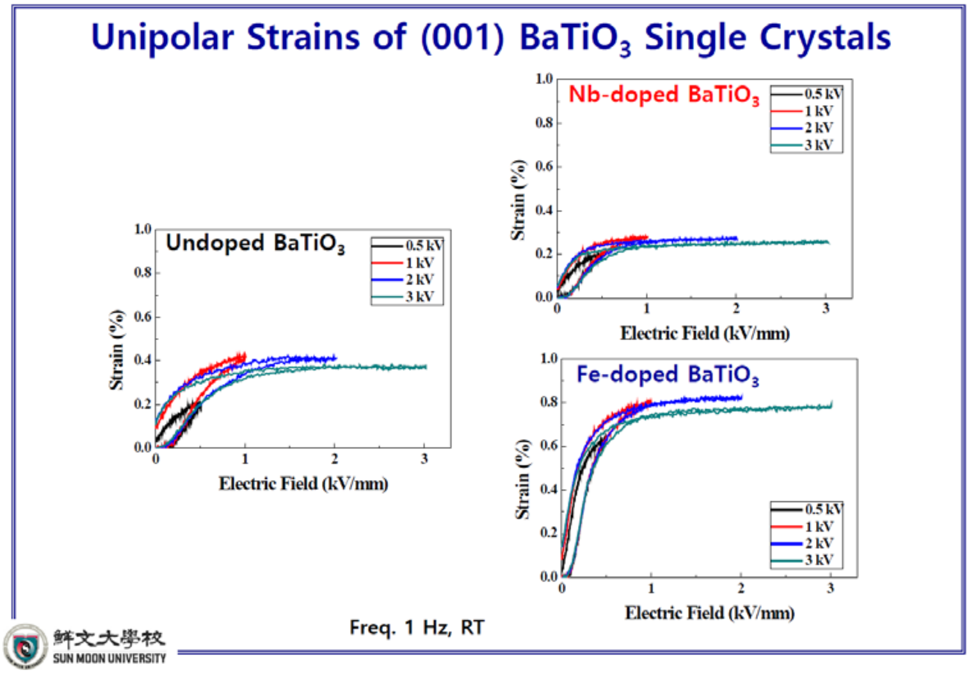
Fig. 21. Polarization vs. Electric Field of (a) undoped, (b) Fe (Acceptor)-doped and (c) Nb (Donor)-doped (001) $BaTiO_3$ single crystals



Bipolar Strains of (001) $BaTiO_3$ Single Crystals

Freq. 1 Hz, RT

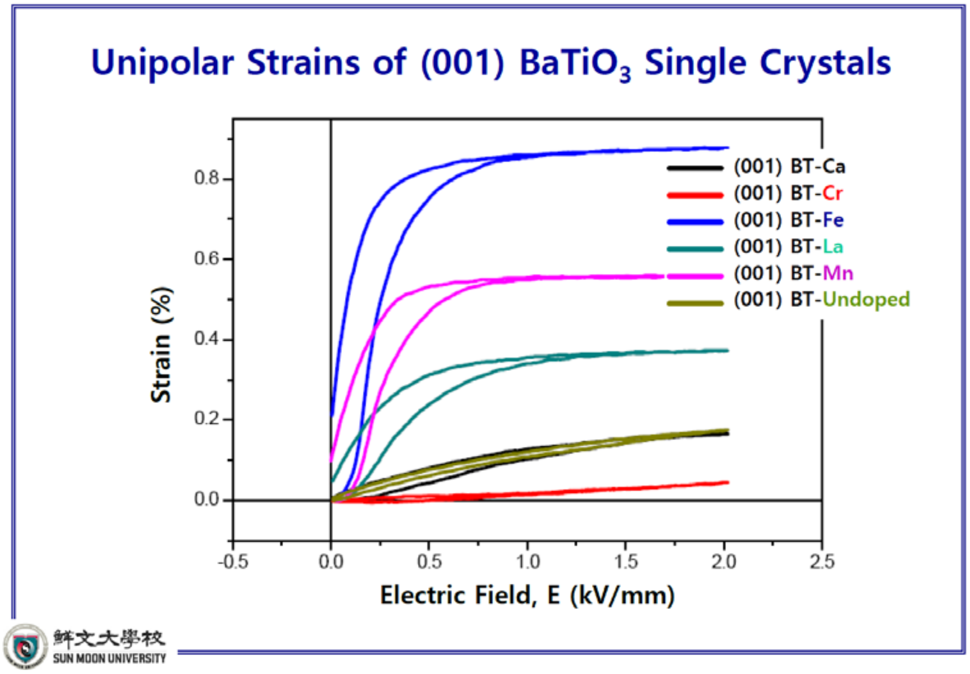
Fig. 22. Bipolar strains of (001) $BaTiO_3$ single crystals:
(a) undoped, (b) Nb-doped, and (c) Fe-doped



Unipolar Strains of (001) $BaTiO_3$ Single Crystals

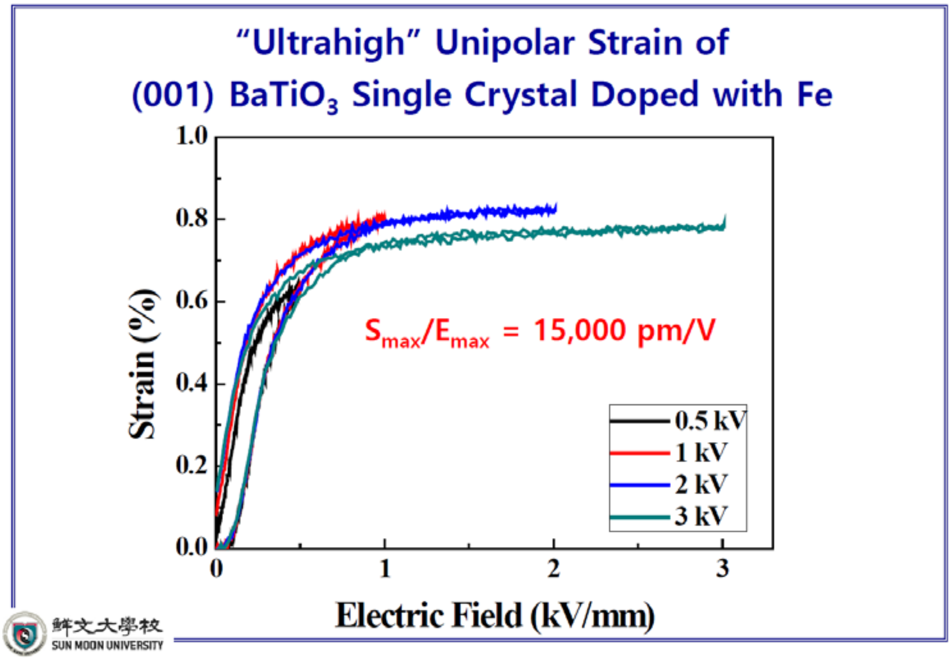
Freq. 1 Hz, RT

Fig. 23. Unipolar strains of (001) $BaTiO_3$ single crystals:
(a) undoped, (b) Nb-doped, and (c) Fe-doped



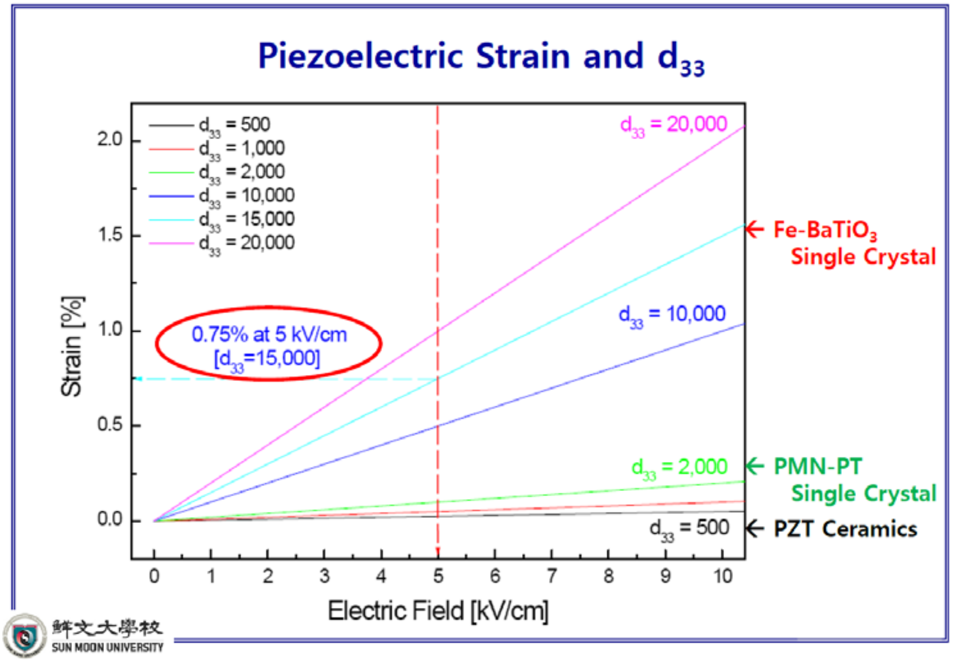
Unipolar Strains of (001) $BaTiO_3$ Single Crystals

Fig. 24. Unipolar strains of (001) $BaTiO_3$ single crystals doped with (a) No doping, (b) Ca, (c) Cr, (d) Fe, (e) La, and (f) Mn



"Ultrahigh" Unipolar Strain of (001) $BaTiO_3$ Single Crystal Doped with Fe

Fig. 25. "Ultrahigh" unipolar strains of (001) $BaTiO_3$ single crystals doped with Fe: S_{max}/E_{max} = 15,000 pm/V



Piezoelectric Strain and d_{33}

← Fe-$BaTiO_3$ Single Crystal

← PMN-PT Single Crystal

← PZT Ceramics

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Fig. 26. "Ultrahigh" unipolar strains of (001) $BaTiO_3$ single crystals doped with Fe: PZT ceramics (d ~ 500 pC/N), PMN-PT single crystals (d_{33} ~ 2,000 pC/N), Fe-doped $BaTiO_3$ single crystals (S_{max}/E_{max} = 15,000 pm/V)

High Performance doped $BaTiO_3$ Single Crystals:

Single Crystal-Epoxy Composite

1-3 Single Crystal-Epoxy Composite

Single Crystal "Flexible" Composite (SFC)

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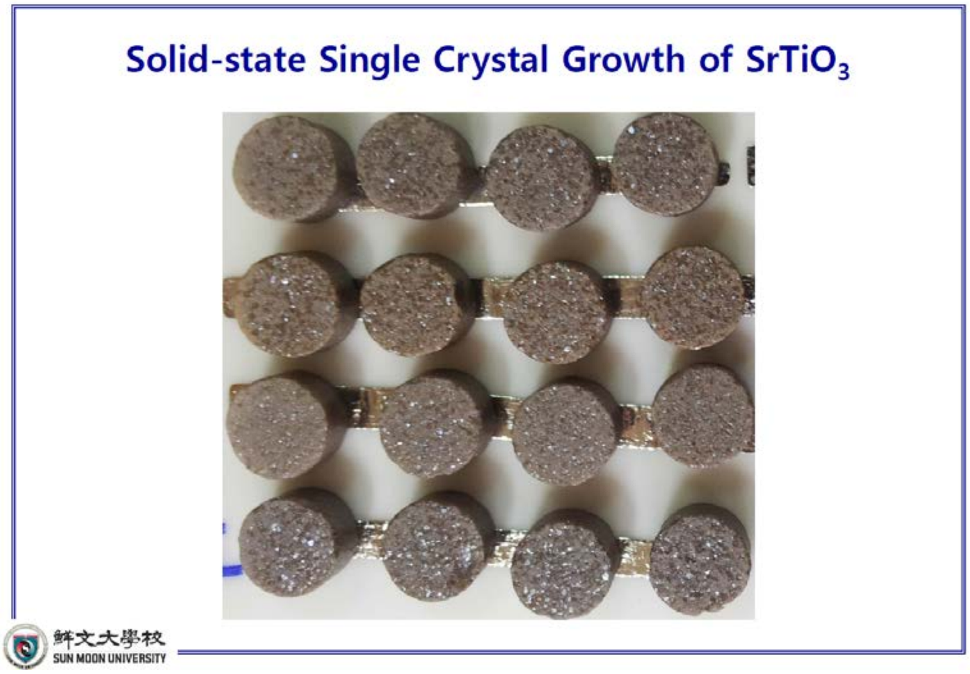
Fig. 27. Application of (001) $BaTiO_3$ single crystals having "ultrahigh" unipolar strains: 1-3 single crystal-epoxy composites and "flexible" SFC composites

3-2. $SrTiO_3$ single crystals

The single crystal growth of "*n*- and *p*-type doped" $SrTiO_3$ single crystals have been tried by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of $SrCO_3$, TiO_2, and several dopants (Ca, Ce, Co, Cr, Fe, La, Mg, Mn, Nb, and Nd), "*n*- and *p*-type doped" polycrystalline $SrTiO_3$ ceramics were obtained through a general sintering process. After weighing each raw material powder for "*n*- and *p*-type doped" $SrTiO_3$ compositions, they were mixed for 24 hours using ball-milling process, and calcined at 1,000℃ following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a $BaTiO_3$ seed single crystal was placed on the sintered body of "*n*- and *p*-type doped" $SrTiO_3$, and the second heat treatment for solid-state single-crystal growth was carried out for 200 hours, as shown in Fig. 28.

The $BaTiO_3$ seed single crystal was placed inside $SrTiO_3$ ceramics and heat-treated for 200 hours. However, the growth of $SrTiO_3$ single crystals from the $BaTiO_3$ seed single crystal was very limited, as shown in Fig. 28. So the growth of $SrTiO_3$ single crystals was not successfully.



Solid-state Single Crystal Growth of $SrTiO_3$

Fig. 28. Single crystal growth of $SrTiO_3$ from a $BaTiO_3$ single crystal seed inside $SrTiO_3$ ceramics

3-3. $PbZrO_3$ single crystals

The single crystal growth of “*n*- and *p*-type doped” PZ single crystals have been tried by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of PbO, ZrO_2 and several dopants (Ca, Ce, Co, Cr, Fe, La, Mg, Mn, Nb, and Nd), “*n*- and *p*-type doped” polycrystalline PZ ceramics were obtained through a general sintering process. After weighing each raw material powder for “*n*- and *p*-type doped” PZ compositions, they were mixed for 24 hours using ball-milling process, and calcined at 850℃ following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a $BaTiO_3$ seed single crystal was placed on the sintered body of “*n*- and *p*-type doped” PZ, and the second heat treatment for solid-state single-crystal growth was carried out for 200 hours, as shown in Fig. 29.

The $BaTiO_3$ seed single crystal was placed inside PZ ceramics and heat-treated for 200 hours. However, the growth of PZ single crystals from the $BaTiO_3$ seed single crystal was very limited, as shown in Fig. 29. So the growth of PZ single crystals was not successfully.

Solid-state Single Crystal Growth of $PbZrO_3$

Fig. 29. Single crystal growth of PZ from a $BaTiO_3$ single crystal seed inside PZ ceramics

3-4. BT-BMT single crystals

The single crystal growth of "*n*- and *p*-type doped" BT-BMT single crystals have been tried by using solid-state single-crystal growth (SSCG) method. First, by using raw material powders of $BaCO_3$, TiO_2, Bi_2O_3, $MgCO_3$ and several dopants (Ca, Ce, Co, Cr, Fe, La, Mg, Mn, Nb, and Nd), "*n*- and *p*-type doped" polycrystalline BT-BMT ceramics were obtained through a general sintering process. After weighing each raw material powder for "*n*- and *p*-type doped" BT-BMT compositions, they were mixed for 24 hours using ball-milling process, and calcined at 800℃ following drying. The calcined powders were subjected to the second ball-milling, forming under uniaxial compression following drying, and then sintered. After the first sintering, a $BaTiO_3$ seed single crystal was placed on the sintered body of "*n*- and *p*-type doped" BT-BMT, and the second heat treatment for solid-state single-crystal growth was carried out for 200 hours, as shown in Fig. 30.

The $BaTiO_3$ seed single crystal was placed inside BT-BMT ceramics and heat-treated for 200 hours. However, the growth of BT-BMT single crystals from the $BaTiO_3$ seed single crystal was very limited, as shown in Fig. 30. So the growth of BT-BMT single crystals was not successfully.

Solid-state Single Crystal Growth of BT-BMT

Fig. 30. Single crystal growth of BT-BMT from a $BaTiO_3$ single crystal seed inside BT-BMT ceramics

3-5. Bi-crystals

The bi-crystals containing a twin or twist boundary have been fabricated by using (1) SSCG process and (2) diffusion-bonding process.

Figure 31 shows (a) the growth of one large single crystal from one small single crystal seed as well as (b) the growth of one large bi-crystal from one small bi-crystal seed. As shown in Fig. 31, one large bi-crystal can be easily grown from one small bi-crystal by SSCG process. However, in this process it was difficult to control a misorientation angle between two single crystals.

In order to control a misorientation angle between two single crystals more precisely, the diffusion bonding process has been developed. In this diffusion bonding process, two single crystal plates of specific crystallographic orientations are bonded under pressure at high temperature.

Figure 33 shows a process for making twist boundaries by diffusion bonding of two “same” single crystal plates of specific crystallographic orientations. In this process it was easy to control a misorientation angle between two single crystals.

Figure 34 shows a process for making twist boundaries by diffusion bonding of two “different” single crystal plates of specific crystallographic orientations. In this process it was easy to control a misorientation angle between two single crystals.

By using the diffusion bonding process developed in the program, a variety of bi-crystals are fabricated, as shown in Figs. 33 and 34.

A Bi-Crystal of $BaTiO_3$ Made by SSCG Process

A Single Crystal Seed

A Bi-Crystal Seed

Making a Bi-Crystal of $BaTiO_3$ by Using SSCG Process

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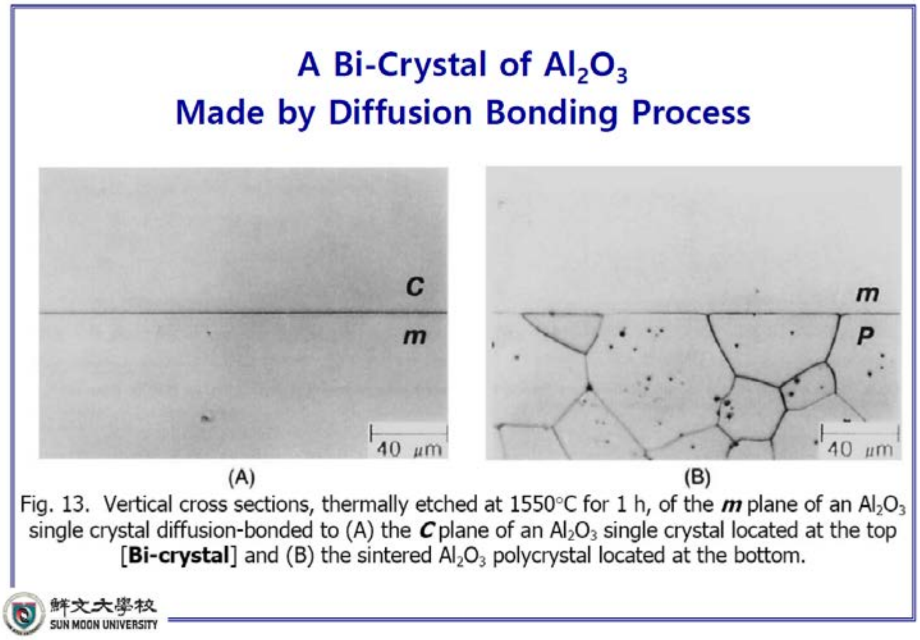
Fig. 31. Solid-state crystal growth of (a) one single crystal seed and (b) one bi-crystal seed: One large bi-crystal can be grown from one small bi-crystal by SSCG process.



A Bi-Crystal of Al_2O_3 Made by Diffusion Bonding Process

(A) (B)

Fig. 13. Vertical cross sections, thermally etched at 1550°C for 1 h, of the ***m*** plane of an Al_2O_3 single crystal diffusion-bonded to (A) the ***C*** plane of an Al_2O_3 single crystal located at the top [**Bi-crystal**] and (B) the sintered Al_2O_3 polycrystal located at the bottom.

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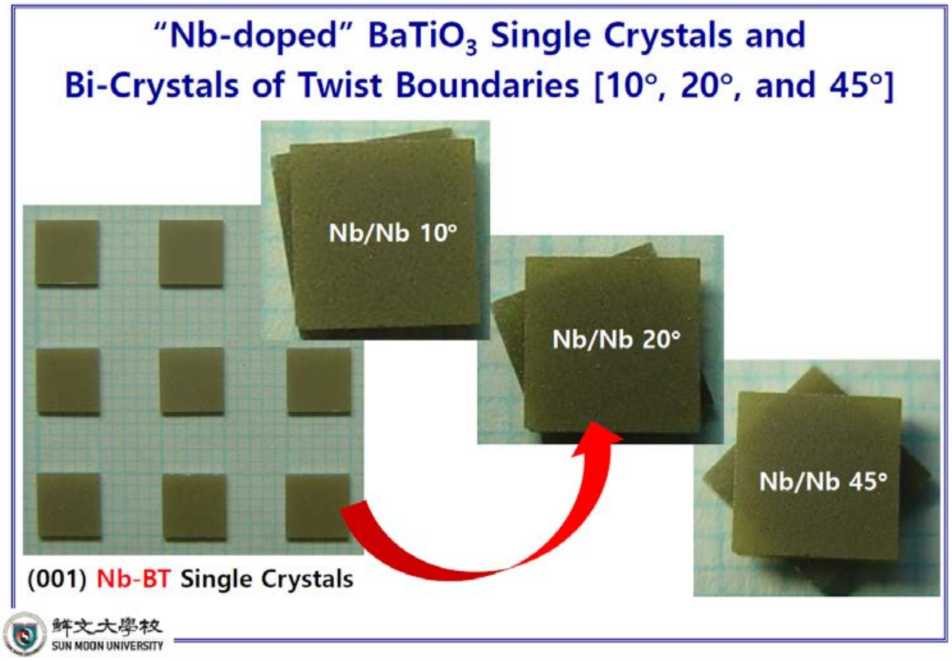
Fig. 32. Diffusion bonding process for making a bi-crystal: Two single crystal plates are bonded under pressure at high temperature



“Nb-doped” BaTiO$_3$ Single Crystals and
Bi-Crystals of Twist Boundaries [10°, 20°, and 45°]

Nb/Nb 10°

Nb/Nb 20°

Nb/Nb 45°

(001) Nb-BT Single Crystals

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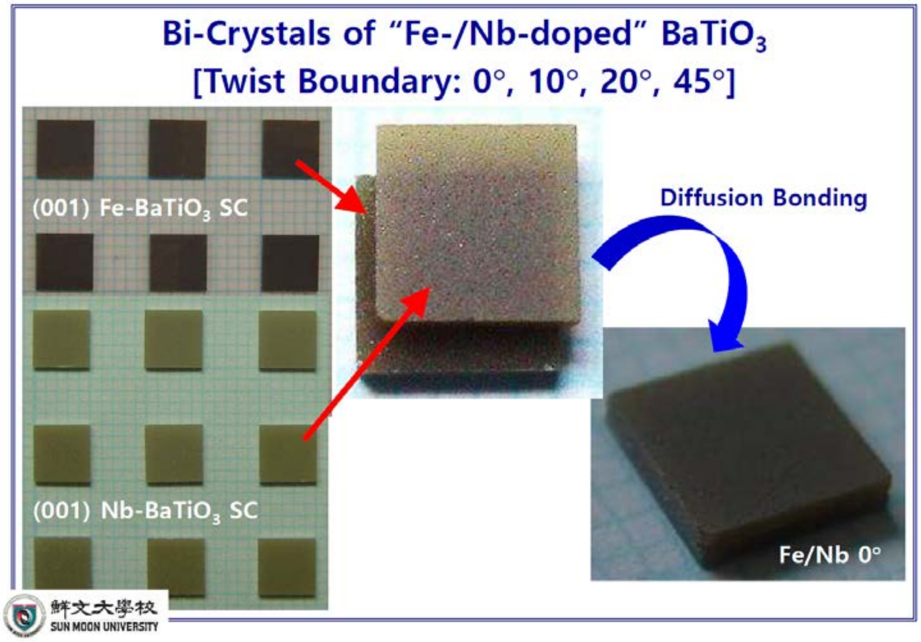
Fig. 33. Making twist boundaries by diffusion bonding of two “same” single crystal plates with specific misorientation angles



Bi-Crystals of “Fe-/Nb-doped” BaTiO$_3$
[Twist Boundary: 0°, 10°, 20°, 45°]

(001) Fe-BaTiO$_3$ SC

(001) Nb-BaTiO$_3$ SC

Diffusion Bonding

Fe/Nb 0°

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Fig. 34. Making twist boundaries by diffusion bonding of two “different” single crystal plates with specific misorientation angles

4. Conclusion

In this project the solid-state growth of “n- and p-type doped” perovskite single crystals [(1) paraelectric $SrTiO_3$, (2) normal ferroelectric $BaTiO_3$, (3) relaxor ferroelectric $0.85BaTiO_3$-$0.15Bi(Mg_{0.5}Ti_{0.5})O_3$, and (4) antiferroelectric $PbZrO_3$] have been tried. Especially “n- and p-type doped” $BaTiO_3$ single crystals have been successfully fabricated. And their bi-crystals containing a twin or twist boundary are also fabricated using diffusion bonding process of two single crystal plates. These results demonstrate that the SSCG (solid-state single crystal growth) technique are suitable to grow a variety of “*n*- and *p*-type doped” perovskite single crystals. The principles and demonstrations are well described in the paper of Fig. 35.

The Fe-doped (001) $BaTiO_3$ single crystals show an ultrahigh strain of 0.8% at 1 kV/mm (S_{max}/E_{max} = 15,000 pm/V) which is 30 times higher than PZT ceramics and 7.5 times higher than PMN-PT single crystals. Therefore the $BaTiO_3$ single crystals having “ultrahigh” unipolar strains will be used for actuator, sensor, and transducer applications.

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journal

Solid-State Conversion of Single Crystals: The Principle and the State-of-the-Art

Suk-Joong L. Kang[‡,†] Ji-Hoon Park[‡] Seok-Young Ko[‡] and Ho-Yong Lee[§]

[‡]Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Yuseong-gu, Daehak-ro 291, Daejone 305-701, Korea

[§]Department of Materials Science and Engineering, Sun Moon University, Asan 336-708, Korea

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.[1–4] 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.[5,6] 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.[1–4] 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.[1–4] 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.[7,8] 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.[7,8]

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

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[†] Author to whom correspondence should be addressed. e-mail: sjkang@kaist.ac.kr

Fig. 35. Solid-state conversion of single crystals: The principle and the state-of-the-art (J. Am. Ceram. Soc., 98[2], 347-360 (2015))