

SOLID STATE GRAIN GROWTH OF PIEZOELECTRIC SINGLE CRYSTALS

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Abstract – The recent results related to development of the solid state crystal growth process, specially focusing on PMN-PT are presented. The processing parameters such as sintering atmosphere and growth temperature of crystal are discussed. The feasibility of using SSCG for the growth of high T_c piezoelectric materials such as $\text{BiScO}_3\text{-PbTiO}_3$ will be also presented. The hetero epitaxial nucleation and growth, are examined in $36\text{BiScO}_3\text{-64PbTiO}_3$ ceramics using SrTiO_3 and BaTiO_3 as template materials. The amount of excess PbO is correlated with the growth distance when BaTiO_3 single crystals are used as templates. More than $100\ \mu\text{m}$ of growth was observed at 1150°C after 16 hr heat treatment for this system. When tabular SrTiO_3 particles are used as template materials, elongated grains ~ 10 times larger than matrix grains were observed.

their use in low cost fabrication and commercial applications. Fabricating these materials by solid state grain growth resulting in single crystal (solid state conversion) or textured ceramics (templated grain growth) is a potential way around this problem.

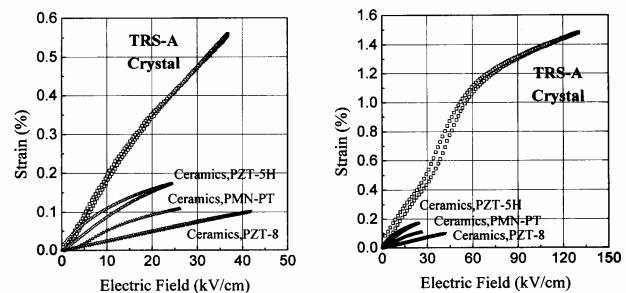


Figure 1. Strain vs. E field behavior for selected relaxor-PT crystals, PMN-PT ceramic, and PZT ceramic.

I. PIEZOELECTRIC SINGLE CRYSTAL AND SOLID STATE GRAIN GROWTH

Single crystal piezoelectrics in the relaxor- PbTiO_3 systems (such as PZN-PT and PMN-PT) have been found to exhibit order of magnitude improvements in strain over conventional ceramics. The very large strains ($> 1\%$) and exceptional piezoelectric properties ($d_{33} > 2000\ \text{pC/N}$, $k_{33} > 92\%$) of these crystals result from an “engineered” ferroelectric domain state associated with the $\langle 001 \rangle$ crystallographic direction [1]. Normal linear piezoelectric strains of up to 0.6% can be achieved at electric field levels typical of many actuator applications (left hand graph in Fig. 1). When a sufficiently high electric field is applied, the materials undergo a phase transition from rhombohedral to tetragonal crystal structures producing strains as high as 1.7% (right hand graph in Fig. 1). These high strains seem to be correlated to the lattice distortion during the phase transition (c/a ratio); however, currently data only exists for PZN-PT and PMN-PT.

Fig. 1 clearly demonstrates the significance of single crystals over conventional ceramics for many applications. Unfortunately, the cost of producing these crystals by the current high temperature flux and Bridgeman methods prohibit

The process of converting random ceramics in to single crystal without melting 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. Since this process is not only quite cost-effective but also good for mass production of large single crystals, many researchers have tried to grow single crystals by the SSCG method.

Templated grain growth (TGG) is another approach to obtain properties of single crystals by texturing the microstructure of ceramics. In this process, nucleation and growth of matrix material on oriented, isostructural single crystal templates results in an increased fraction of oriented grains after thermal processing. By increasing the fraction of crystallites or grains having desired orientation, it is possible to approach the properties of single crystals with a polycrystalline ceramic. In fact the TGG approach has been proven to be successful in obtaining textured microstructures in many ceramics including piezoelectrics such as PMN-PT. It has been reported that the piezoelectric coefficient of textured PMN-PT has been increased as much as twice that of untextured, randomly oriented ceramics.

Due to the fact that ceramic texturing still makes use of conventional processing, TGG possesses several advantages over conventional crystal growth. TGG processing is believed to be more cost-effective compared to conventional crystal growth, including Bridgman growth. Many single crystal compositions, particularly solid solutions such as PMN-PT and BS-PT, exhibit significant compositional variation due to solute segregation in the melt during the growth process. Oppositely, in the TGG process, the compositional variation is minimal because it relies on a powder process rather than melt processes. This also leads to improved impurity control compared to single crystal growth.

II. HIGH T_c MATERIALS

At the Curie temperature (T_c), ferroelectrics undergo a thermally induced phase transition to a cubic paraelectric state that is no longer piezoelectric. The T_c therefore represents the theoretical maximum use temperature for piezoelectrics. Since piezoelectrics are ceramics consisting of randomly oriented grains or crystallites, the spontaneous polarization in each crystallite (embodied in the ferroelectric domains) must be oriented by applying a large electric field to the ceramic; a process known as poling. Poled ceramics are metastable; therefore, due to thermal fluctuations, maximum use temperatures are in practice typically 1/2 to 2/3 T_c . Because of the decay in polarization at temperatures above 1/2 T_c and the peak in dielectric constant at T_c , piezoelectric ceramics have a substantial temperature dependence of their piezoelectric and dielectric properties, which becomes worse as T_c is decreased.

It has been known for some time that there is a correlation between the Curie temperature of ABO_3 perovskite ferroelectrics and the Goldschmidt tolerance factor. The tolerance factor (t), is given by the expression;

$$t = \frac{r_a + r_o}{\sqrt{2}r_b + r_o} \quad (1)$$

where r_a is the ionic radius of A site cations, r_b is the ionic radius of B-site cations and r_o is the ionic radius of oxygen (perovskite stability is maximized for tolerance factors between 0.80 and 1.05). A correlation between the end member tolerance factor and the Curie temperature of the MPB composition has been proposed based on data for known $ABO_3 - PbTiO_3$ solid solution systems. As t decreases, the Curie temperature of the MPB composition increases. Bismuth based ABO_3 compounds in solution with $PbTiO_3$ were predicted to have much higher T_c 's than PZT. This prediction was verified when the $PbTiO_3 - BiScO_3$ system, was found to have an MPB composition (at 64% $PbTiO_3$) with a T_c of 450°C, 100° higher than PZT. Remarkably, despite the higher T_c , the material's piezoelectric properties were very similar to those of PZT (See Table I).

TABLE I: HIGH TEMPERATURE PIEZOELECTRIC MATERIALS [2]

Material	Structure	T_c (°C)	d_{33} (pC/N)
PZTs (MPB)	Perovskites	~330	~400
(Pb,Ba)Nb ₂ O ₆	Tungsten Bronze	~400	~85
PbTiO ₃	Perovskite	~470	56
Na _{0.5} Bi _{4.5} Ti ₄ O ₅	PLS	<600	18
LiNbO ₃	Corundum	1150	6
SiO ₂	α -Quartz (non-ferroelectric)	573 (α - β transition)	2 (d_{11})
PbTiO₃ - Bi(B)O₃			
BS-PT (MPB)	Perovskite	~450	~350
BS-PLT (La-doped MPB)	Perovskite	~385	~460
BI-PT (MPB)	Perovskite	~575	>200
BY-PT (MPB)	Perovskite	>600	>100

TABLE II: HIGH TEMPERATURE PIEZOELECTRIC PROPERTIES FOR BS-PT (MPB).

T	Dielectric Constant	k_p
RT	1860	0.51
225°C	3710	0.58

III. EXPERIMENTAL PROCEDURES

A. FABRICATION OF PMN-PT

The columbite precursor method was used to fabricate PMN-32PT. The first step in this synthesis is production of the $MgNb_2O_6$ precursor at 1100°C. Phase-pure $MgNb_2O_6$ precursor was formed by first mixing stoichiometric amounts of the raw materials ($MgCO_3$ and Nb_2O_5). The mixing steps were carried out using a vibratory mill for 24 hours. The slurries were dried and then ground and sieved through an 80 mesh. After sieving, the powder was calcined by heating to 1100°C for 12 hours. The phase purity was confirmed by X-ray diffraction. Mixing $MgNb_2O_6$ with PbO and TiO_2 for the formation of PMN-PT was same manner as formation of $MgNb_2O_6$ except for the calcination temperature 850°C.

The last step in this process is the addition of the excess PbO required for the growth processes. Before re-milling PMN-PT batches, small amounts of PbO (8 mole%) were added. The powders were mixed with 3wt% polymer binder for the pressing.

B. FABRICATION OF BS-PT

The raw materials for $PbTiO_3$, titania and basic lead carbonate, were mixed using ball milling in deionized water. The dried cakes were then ground in a mortar and pestle and sieved. The synthesis was completed by calcination at 550°C for 4 hours. The phase-pure powders were then re-milled in ethanol (at 10v% solids loading) in a high-energy vibratory mill for 16 hrs.

For the formation of BS-PT, the raw materials, $PbTiO_3$, Bi_2O_3 , and Sc_2O_3 , were mixed by ball milling for 16 hrs. The dried cakes were then ground sieved and calcined as same method before and the calcination was carried out at 750°C. Excess lead oxide was added using the same method as in the PMN-PT case.

C. SOLID STATE GROWTH

For the crystal growth, 0.68PMN-0.32PT with 8 mole% excess PbO was uniaxially pressed at 10 MPa using a 50 mm diameter steel mold and then isostatically pressed (CIP) at 200 MPa. The polymer binder in samples was removed by slow heating to 500°C. Sintering was conducted in a box or tube furnace from 800 to 1150°C for 1 hr. A flowing oxygen atmosphere was used. Samples were HIPed at 800°C or 900°C for the sample sintered at higher than 900°C. Samples were attached to BaTiO₃ (BT) seed single crystals for heat treatments at temperatures from 1100 to 1200°C.

For the feasibility study using SSCG to grow single crystal BS-PT, 100 μm thick ~5 by 5 mm (100) BT single crystal was embedded in the middle of BS-PT powder compacts that were 12 mm in diameter. The pellets were cold isostatically pressed at 200 MPa and then sintered at 1150°. To determine the possibility of using SrTiO₃ (ST) as template material for TGG of BS-PT, tabular ST templates were mixed with BS-PT to verify the chemical stability of ST templates in the BS-PT matrix to measurement the amount of growth resulting from heat treatment.

IV. RESULTS

A. SOLID STATE CONVERSION OF PMN-PT

Sintering results showed that the maximum sintered density for PMN-PT with excess PbO is achieved at ~950°C. The sintering atmosphere has a great effect on the sintered and HIP'ed density as shown in Fig. 2. Even though samples produced in a box and tube furnace were both sintered in oxygen, a tube furnace provided much higher P_{O₂}, and therefore, higher density.

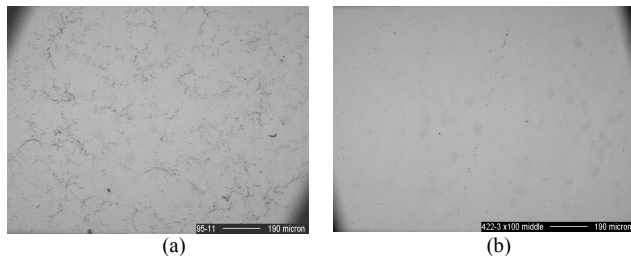


Figure 2: Polished cross sections of samples after HIP. Samples were sintered in a a) box furnace and b) tube furnace before HIP.

Fig. 3 illustrates the bottom view of the PMN-PT sample annealed at 1200°C for 200 hr. The sample is 5 mm thick and the grown crystal is through the whole sample thickness. The BT seed crystal is oriented in the <110> direction.

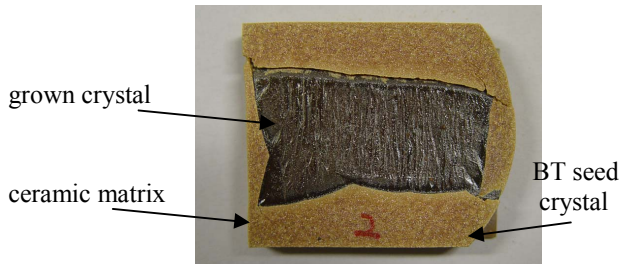


Figure 3 Bottom view of the annealed sample at 1200°C for 200 hr.

Due to the characteristics of solid state conversion method which are similar to conventional ceramic processing, these results strongly show that single crystal PMN-PT can be grown by the solid state conversion method. Thus, the SSG method shows great promise for reducing the cost of crystals over that of melt growth techniques such as the Bridgman method.

B. TEMPLATED GRAIN GROWTH OF BS-PT

Fig. 4 shows the polished and etched cross sections of samples containing <001> BT single crystal sintered at 1150°C for 16 h. For the sample without excess PbO, there was very little growth of BS-PT on the BT crystal. Also there were multiple nucleations from the BT crystals. It is apparent that BS-PT growth is enhanced with the amount of excess PbO. For 2% excess PbO in the BS-PT matrix, there is ~ 30 μm growth from <001> plane of the BT seed (top and bottom of BT crystal) and from the side direction.

The growth is much more enhanced in the 5% excess PbO sample. There is more than 50 μm growth from the <001> plane and ~ 200 μm growth from the side. The matrix grains also grew larger as the content of excess PbO increased. They were ~20 μm, ~30 μm, and ~40 μm for 0, 2 and 5% excess PbO, respectively. This embedding experiment result is especially promising for solid state conversion of BS-PT. It is believed that with modification of liquid phase content and other important parameters, SSCG can be an effective method to grow single crystals of BS-PT starting with ceramic precursors as has been demonstrated with PMN-PT [3].

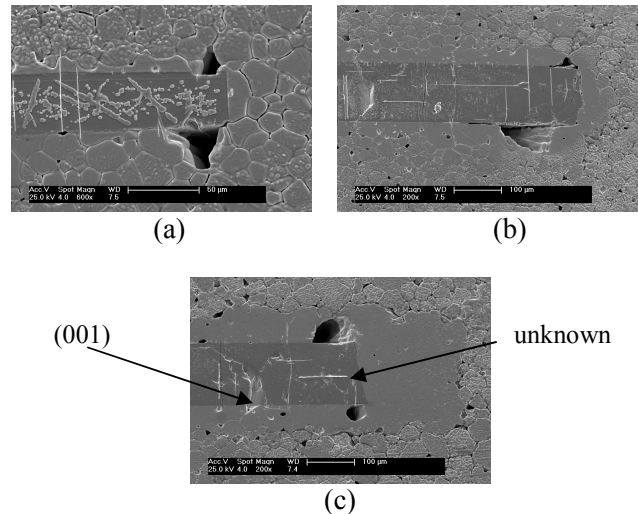


Figure 4 Polished and thermally etched surface of BS-PT cross section containing BT single crystal. The excess amount of PbO is (a) 0% (b) 2% and (c) 5%. Samples were etched at 1080°C for 30 min.

The chemical stability of template material and growth from the templates are key issues in texturing ceramics by TGG. In order to verify whether TGG is applicable for BS-PT, tabular ST templates were dispersed in the BS-PT ceramics. Fig. 5 shows a thermally etched surface of a polished sample sintered at 1150°C for 16 hr. There are several, ~30 μm sized, elongated grains, which are believed to be grown from the ST

templates. The orientation of the elongated grains is random because the template particles were mixed without alignment. In this sample, EDS analysis did not detect the existence of ST templates as discrete grains and Sr is rather uniformly dispersed in the sample. It is assumed that the ST template was incorporated into the ceramic matrix due to the long sintering time at high temperature. This ST template dispersing study result showed the feasibility of using the TGG approach for the texturing BS-PT using ST templates.

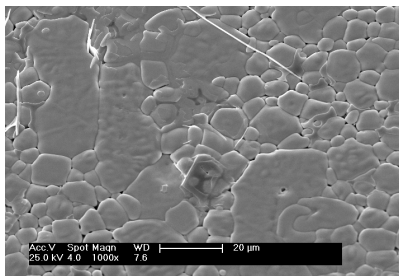


Figure 5. Polished and thermally etched surface of BS-64PT and 5% ST template mixture sintered at 1150°C for 16 hr.

V. CONCLUSIONS

Solid state conversion can be used to fabricate PMN-PT single crystals. This method can be also used for high T_c piezoelectrics such as BS-PT. The excess PbO amount is an important factor for the SSCG, and the feasibility of texturing BS-PT ceramics using ST templates was shown.

VI. ACKNOWLEDGEMENTS

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VII. REFERENCES

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