Office of Naval Research International Field Office

31. Solid State Growth of Piezo-Crystal

Dr. Jun Kameda

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or Email: *kamedaj@onrasia.navy.mil*

Contents:

***Key Words**: Solid–state single crystal growth (SSCG), PMN-PT, Lead-Free Ba(Ti,Zr)O_3, Curie temperature, Polarization*

1. Summary

Prof. Lee has developed a new solid-state single crystal growth (SSCG) technique, which draws strong interests from Drs. Smith and Wu, Scientific Officers of the Materials S&T Division (ONR 332) of ONR. He was invited to present his work at the DARPA PiezoCrystal meeting held in Washington DC on January 28-30. He was supported under the Visitor Support Program (VSP) of the ONRIFO. This report includes his presentation at the DARPA meeting.

2. Background

The development of advanced sonar materials with better capacity to construct three-dimensional images is underway. This requires the fabrication of single piezo-crystals with complex phases and a large size, which is a significant challenge. Bridgman and flux methods have been conventionally applied to accomplish it. Yet, the transformation from the liquid to solid phase makes it difficult to to fabricate single crystals with homogeneous chemical composition due to the segregation at the solid/liquid interface. Prof. Lee's SSCG technique enables us to overcome such problems though the crystal size is not yet very large.

3. Assessment

Prof. Lee's previous NICOP proposal was not selected last year though it was highly rated by the fellows at the ONR 332 and myself.

4. Points of Contact

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Recent Progress in Solid-State Single Crystal Growth of PMN-PT, Lead-Free Ba(Ti,Zr)O_3, and High Curie Temperature Piezoelectrics

DARPA PiezoCrystals PI Meeting

28-30 January 2003, Washington D.C., USA

Ho-Yong Lee

Ceracomp Co. Ltd., Asan, Korea

Seung-Eek "Eagle" Park

Fraunhofer-IBMT Technology Center Hialeah, Hialeah, FL

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DARPA PiezoCrystals PI Meeting

28-30 January 2003, Washington D.C., USA

Special Thanks to

Dr. Wallace A. Smith and Dr. Carl C. M. Wu

for inviting me to this meeting

and

the ONRIFO (Office of Naval Research International Field Office)

for the financial support through the visitor support program

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Three Topics of Presentation

1. Solid-State Growth and Piezoelectric Properties of PMN-PT Single Crystals

2. Solid-State Growth and Piezoelectric Properties of Lead-Free $Ba(Ti,Zr)O_3$ Single Crystals

3. Solid-State Growth of High Tc Piezoelectric Single Crystals

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Previous Works

Fully Dense and Chemically Homogeneous PMN-PT Single Crystals (> 1 inch) Grown by SSCG

Fully Dense or Hot Pressed Ceramics

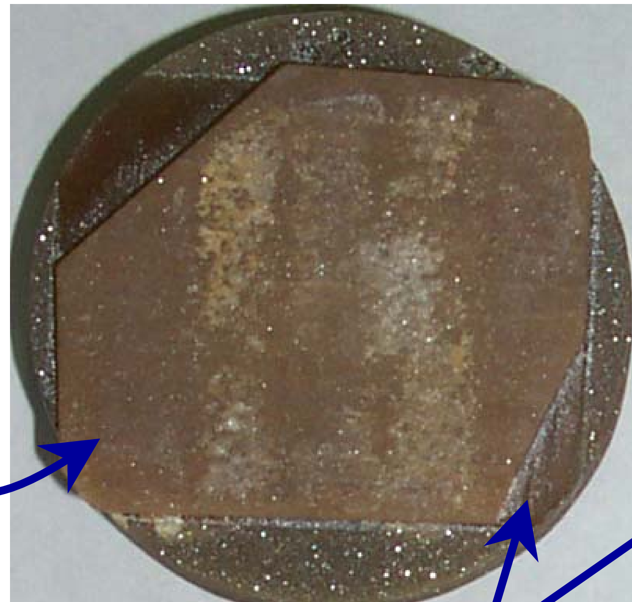
"+"

$BaTiO_3$ Seed Crystal

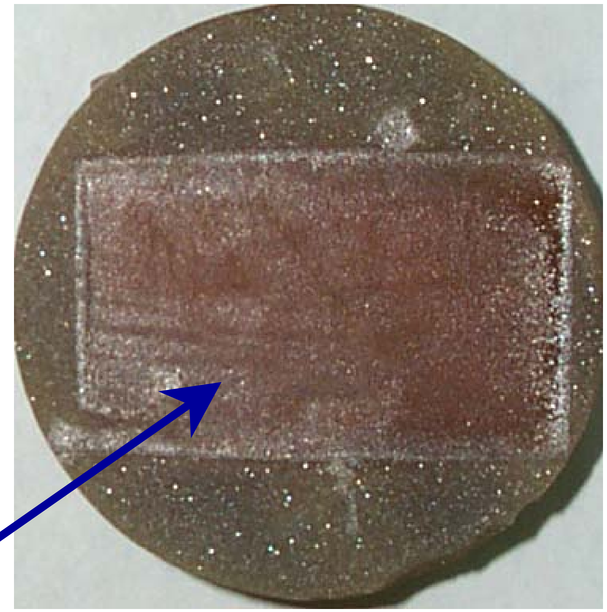
PMN-PT Ceramics

Side View

Top



Bottom



1 inch

Grown PMN-PT Single Crystal

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Fabrication of PMN-PT Single Crystals by SSCG

1 inch - sized
PMN-PT Single Crystals

ϕ 30 x t 5 mm

(Produced by Ceracomp)

Problems to be solved

✓1. PMN-PT Single Crystal Sizes Required
- ➔ *For medical probes > 20x5x1 mm*
  For sonar > 15 x 15 x 1 mm

✓2. Size of Ceramics
- ➔ *Diameter > 40 mm; Thickness > 8 mm*

3. Compositions of PMN-PT Crystals
- ➔ *PMN/PT = 68/32 ~ 72/28*

4. Characterization of Properties
- ➔ $k_{33} \approx 0.9$; $k_{31} \approx 0.62$; $d_{33} \approx 1500$
  (Measured by "Eagle Park")
- ➔ *Look good, but still underway*

5. Scale-up Test (Future Plan)
- ➔ *is required for mass production.*
- ➔ *Production cost, reproducibility, and productivity will be evaluated.*

PMN-PT (68/32) Single Crystals Grown from PMN-PT Ceramics (≈ ϕ40 x t8 mm)

Fully Dense or Hot Pressed Ceramics

"+"=

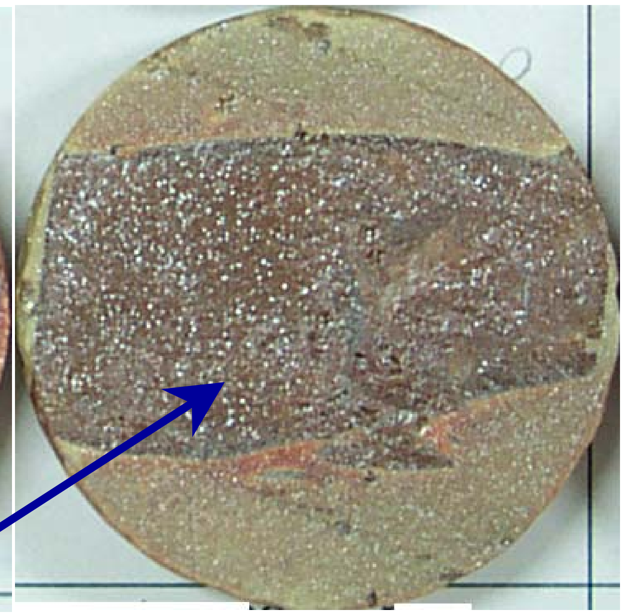
$BaTiO_3$ Seed Crystal

PMN-PT Ceramics

Side View

Top

Bottom

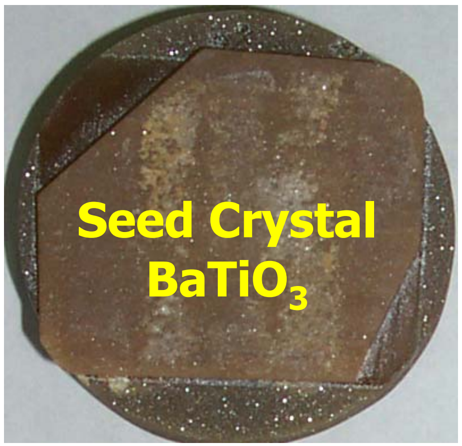


Grown PMN-PT Single Crystal

1.5 inch (≈ ϕ40 x t8 mm)

Growth of 1.5 Inches-Sized PMN-PT Single Crystals
: *Volume Increase → 3 Times Larger Than Before*

Old

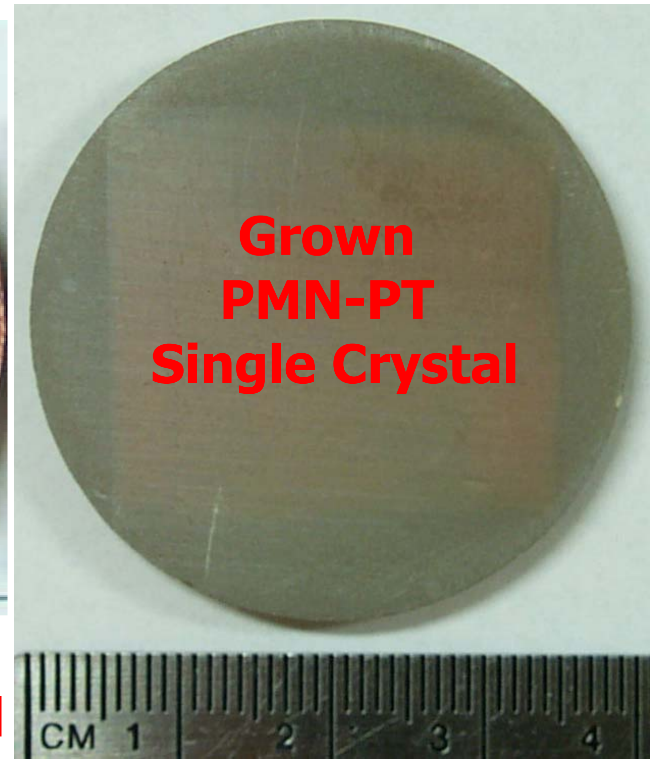


1 inch-sized Crystal
(Ceramics
≈ ϕ 30 x t 5 mm)

New !!!

Top

Cut Surface



1.5 inches-sized Crystal
(Ceramics
≈ ϕ 40 x t 8 mm)

Fabrication of PMN-PT Single Crystals by SSCG

40 mm-sized
PMN-PT Single Crystals

ϕ 40 x t 7.5 mm

(Produced by Ceracomp)

Problems to be solved

1. PMN-PT Single Crystal Sizes Required
➔ ***For medical probes > 25x5x1 mm***
For sonar > 15 x 15 x 1 mm

2. Size of Ceramics
➔ ***Diameter > 40 mm; Thickness > 8 mm***

✓ **3. Compositions of PMN-PT Crystals**
➔ ***PMN/PT = 68/32, 69/31, 70/30, 71/29, 72/28***

4. Characterization of Properties
➔ $k_{33} \approx 0.9$; $k_{31} \approx 0.62$; $d_{33} \approx 1500$
(Measured by "Eagle Park")
➔ ***Look good, but still underway***

5. Scale-up Test (Future Plan)
➔ ***Production cost, reproducibility, and productivity will be evaluated.***

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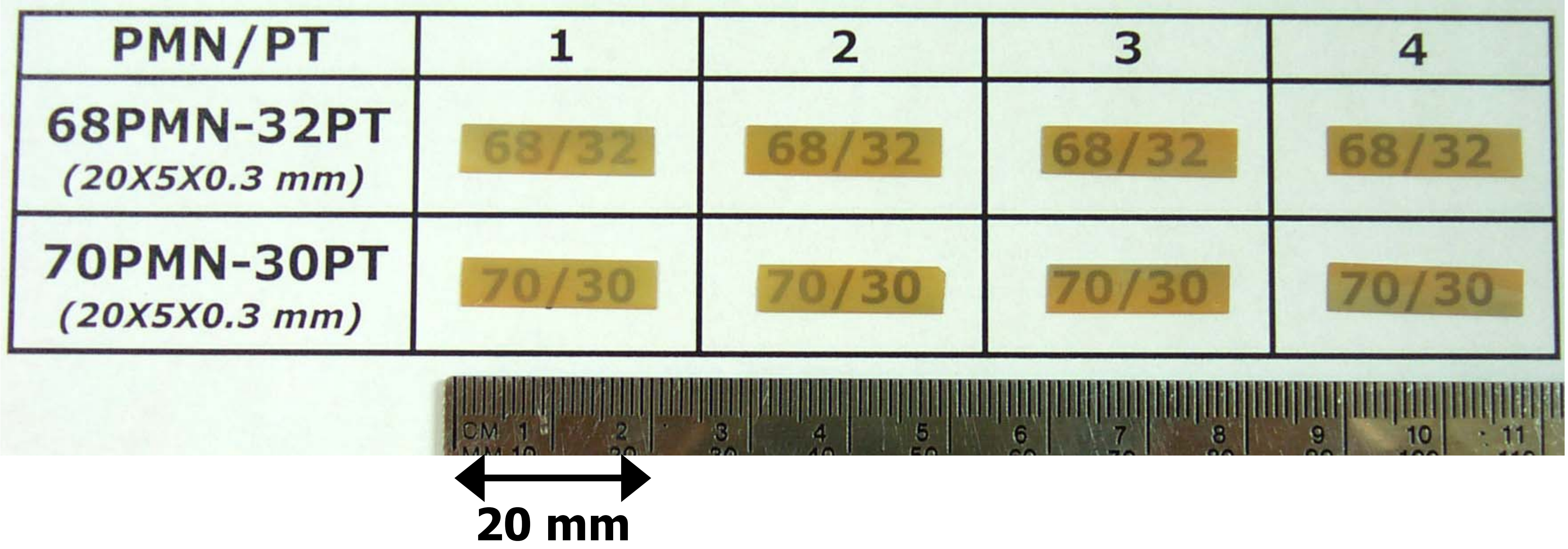
Polished PMN-PT Single Crystal Bars → *Transparent !*

(PMN/PT = 68/32, 70/30; 20x5x0.3 mm)

Cut from Grown Single Crystals



Fabrication of PMN-PT Single Crystals by SSCG

40 mm-sized
PMN-PT Single Crystals

ϕ 40 x t 7.5 mm

(Produced by Ceracomp)

Problems to be solved

1. PMN-PT Single Crystal Sizes Required
- ➔ *For medical probes > 25x5x1 mm*
  For sonar > 15 x 15 x 1 mm

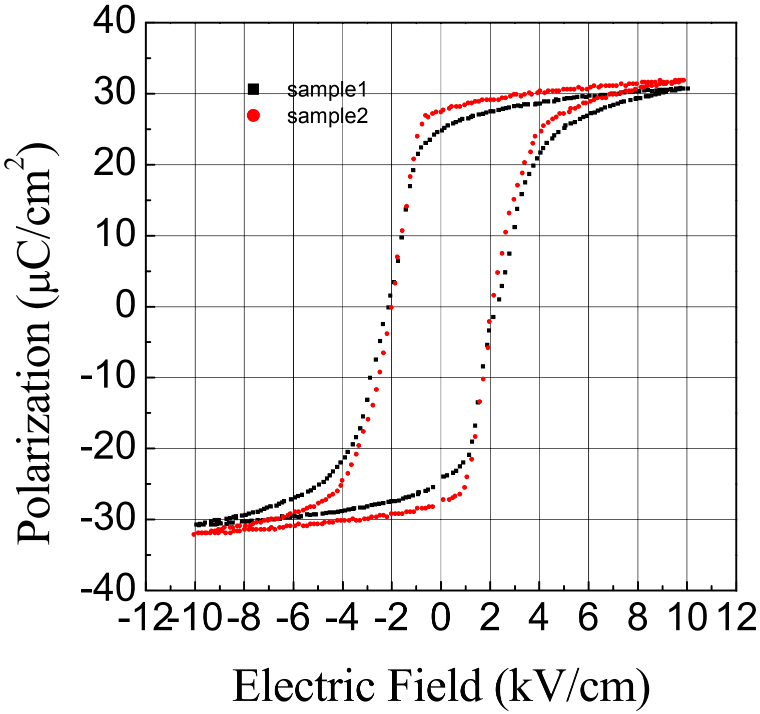
2. Size of Ceramics
- ➔ *Diameter > 40 mm; Thickness > 8 mm*

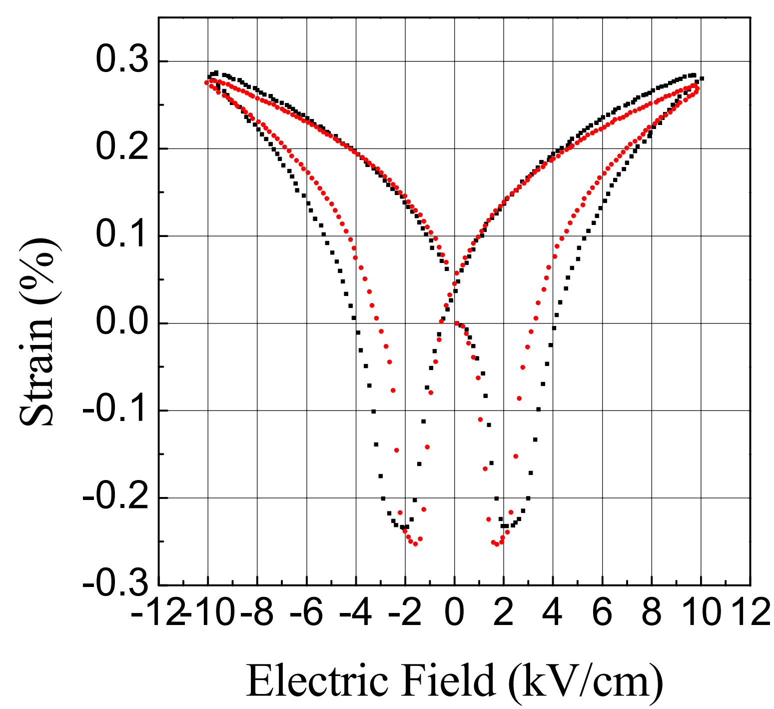
3. Compositions of PMN-PT Crystals
- ➔ *PMN/PT = 68/32, 70/30, 72/28*

✓**4. Characterization of Properties**
- ➔ *$k_{33} \approx 0.9$; $k_{31} \approx 0.62$; $d_{33} \approx 2500$*
  (68PMN-32PT;Measured by "Eagle Park")
- ➔ *Look good, but still underway*

5. Scale-up Test (Future Plan)
- ➔ *is required for mass production.*
- ➔ *Production cost, reproducibility, and productivity will be evaluated.*

Polarization Curve and Bipolar Strain of (001) 68PMN-32PT Single Crystals





<u>Polarization</u> : 30 ~ – 30 μC/cm²
<u>Coercive Electric Field</u> ≈ 2 kV/cm

<u>Bipolar Strain</u> :
0.28% at +10 kV/cm
➔ – 0.26% at – 2 kV/cm

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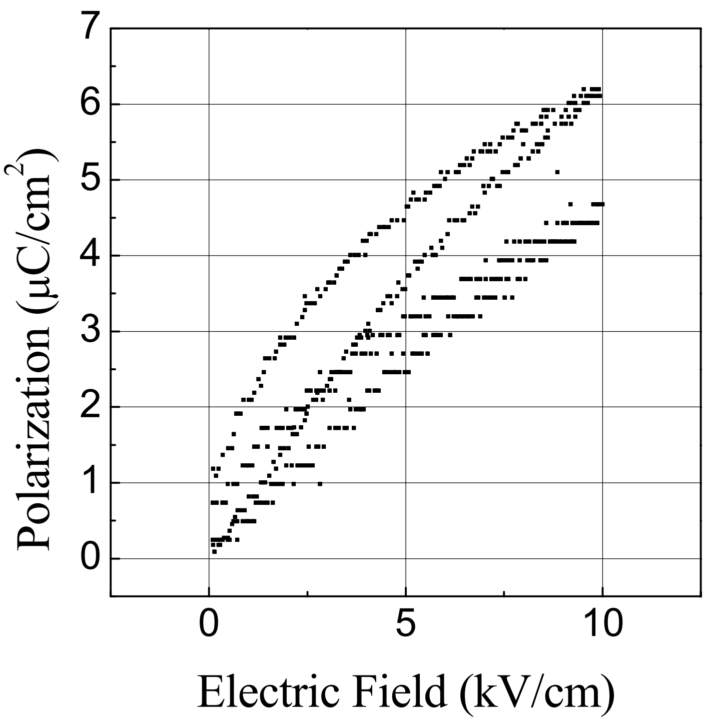
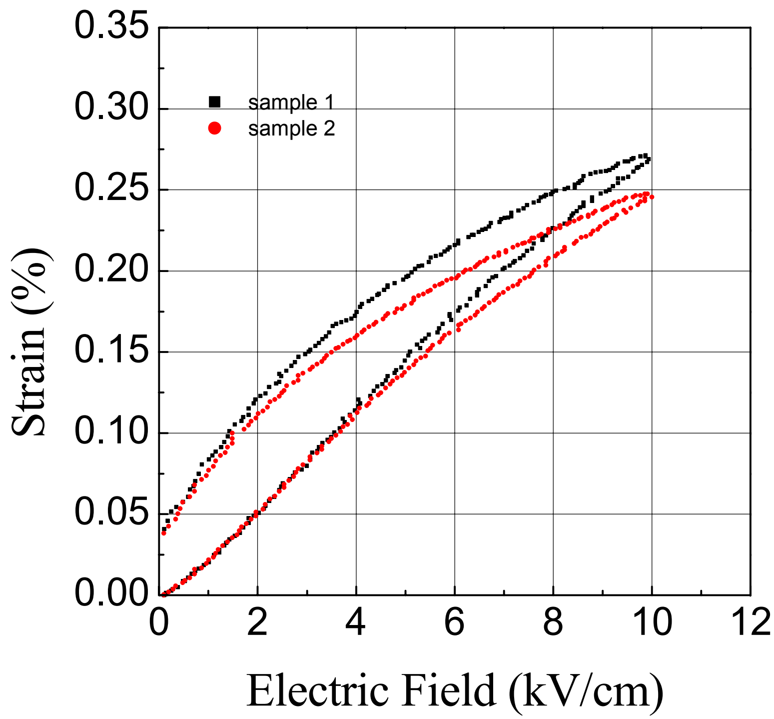
Polarization Curve and Unipolar Strain of (001) 68PMN-32PT Single Crystals





Polarization :
5 ~ 6 μC/cm² at 10kV/cm

Unipolar Strain : 0.25% at 10 kV/cm
➔ d_{33} = 2500 pC/N

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Fabrication of PMN-PT Single Crystals by SSCG

40 mm-sized
PMN-PT Single Crystals

ϕ **40 x t 7.5 mm**

(Produced by Ceracomp)

Problems to be solved

1. PMN-PT Single Crystal Sizes Required
➔ *For medical probes > 25x5x1 mm*
For sonar > 15 x 15 x 1 mm

2. Size of Ceramics
➔ *Diameter > 40 mm; Thickness > 8 mm*

3. Compositions of PMN-PT Crystals
➔ *PMN/PT = 68/32, 70/30, 72/28*

4. Characterization of Properties
➔ $k_{33} \approx 0.9$; $k_{31} \approx 0.62$; $d_{33} \approx 1500$
(Measured by "Eagle Park")
➔ *Look good, but still underway*

✓ **5. Scale-up Test (Future Plan)**
➔ *is required for mass production.*
➔ *Production cost, reproducibility, and productivity will be evaluated.*

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Three Topics of Presentation

1. Solid-State Growth and Piezoelectric Properties of PMN-PT Single Crystals

2. Solid-State Growth and Piezoelectric Properties of Lead-Free Ba(Ti,Zr)O_3 Single Crystals

3. Solid-State Growth of High Tc Piezoelectric Single Crystals

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Fabrication of Large $Ba(Ti,Zr)O_3$ Single Crystals

1. **Remarkable piezoelectric properties**
   - ➔ At low temperature (0°C),
     $k_{33} > 0.85$; $d_{33} > 500$ pC/N
     (Superior to PZT at the low temp.)
   - ➔ At room temperature,
     Orthorhombic or rhombohedral
     $BaTiO_3$, stabilized by proper
     dopants such as Zr
     $k_{33} > 0.75$ (?); $d_{33} > 340$ (?) pC/N
   - ➔ High-performance non-lead
     piezoelectrics

2. **Attractive photo-refractive properties**
   - ➔ for optical information processing
     and computing applications

3. **Lead-free and non-toxic**
   - ➔ Political regulation on materials
     containing lead (Pb)

Growth Method

Top-Seeded Solution Growth (TSSG)

The commercial cost is high and the supply is low, because of difficulties of the TSSG method.

➔

An alternative cost-effective growth method

➔

Solid-State Single Crystal Growth (SSCG)

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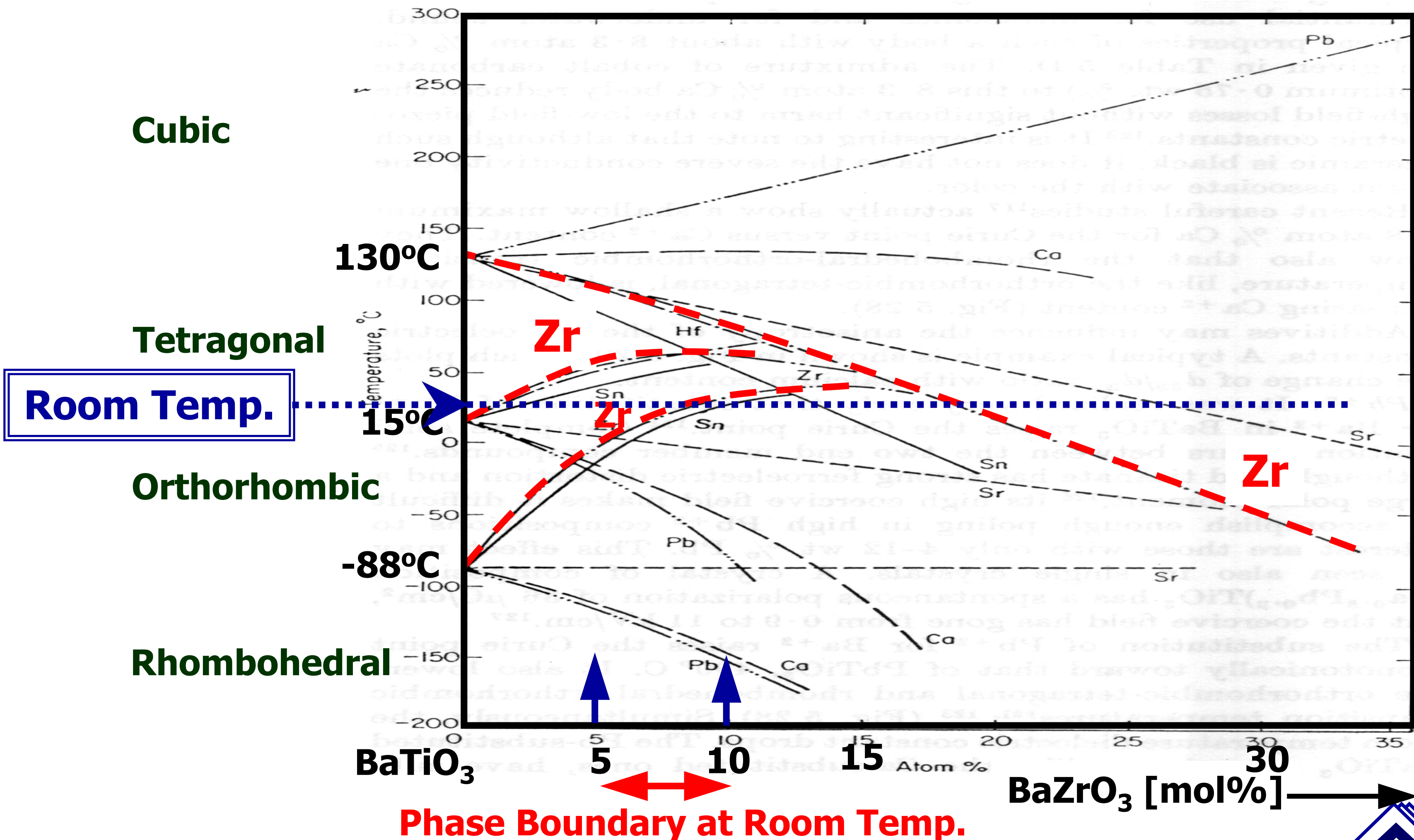
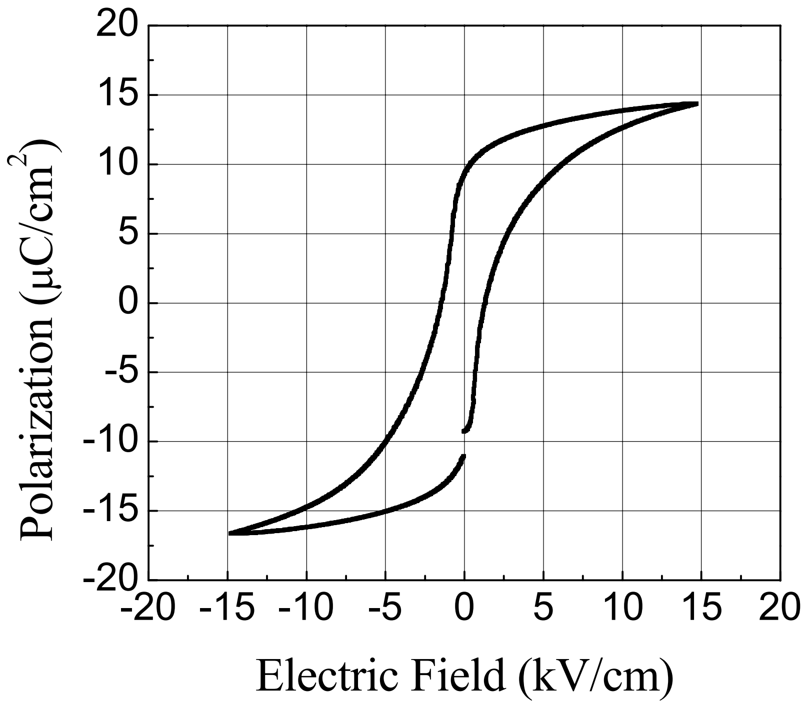
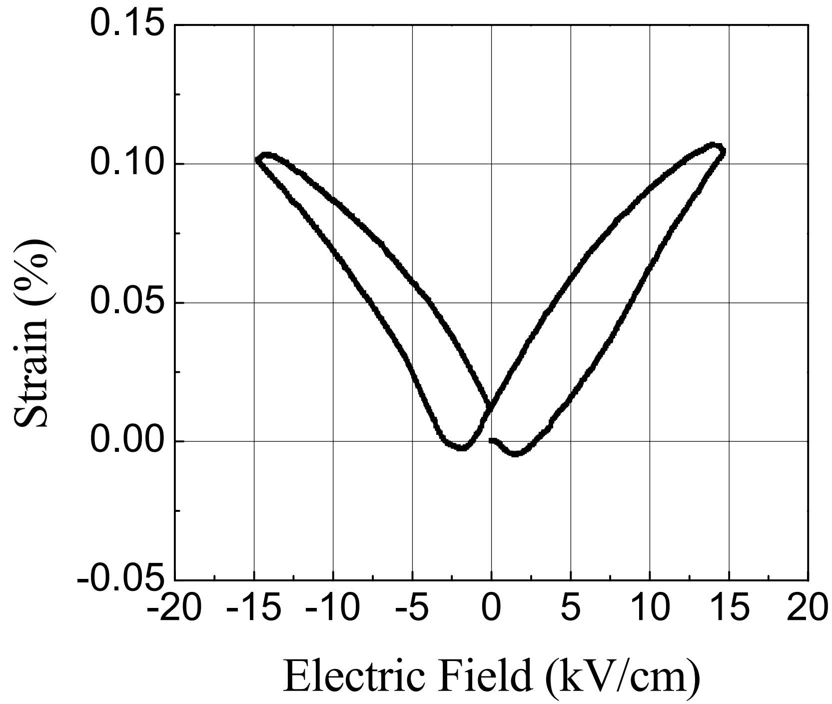
Effect of Zirconium Addition on Transition Temperatures of $BaTiO_3$



Polarization Curve and Bipolar Strain of (001) $Ba(Ti_{0.925}Zr_{0.075})O_3$ Single Crystals





Polarization : 15 ~ – 15 μC/cm²
Coercive Electric Field ≈ 2 kV/cm

Bipolar Strain :
0.11% at +14 kV/cm
➔ – 0.01% at – 2 kV/cm

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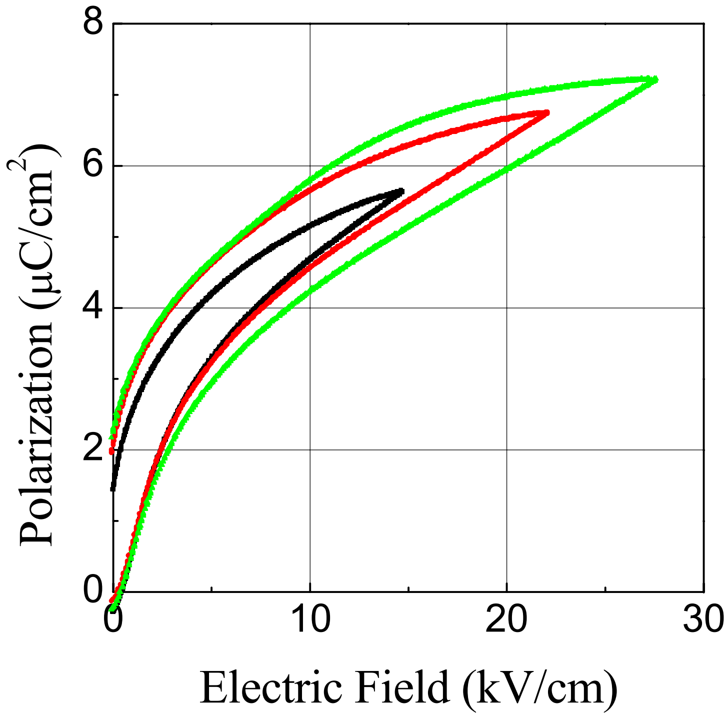
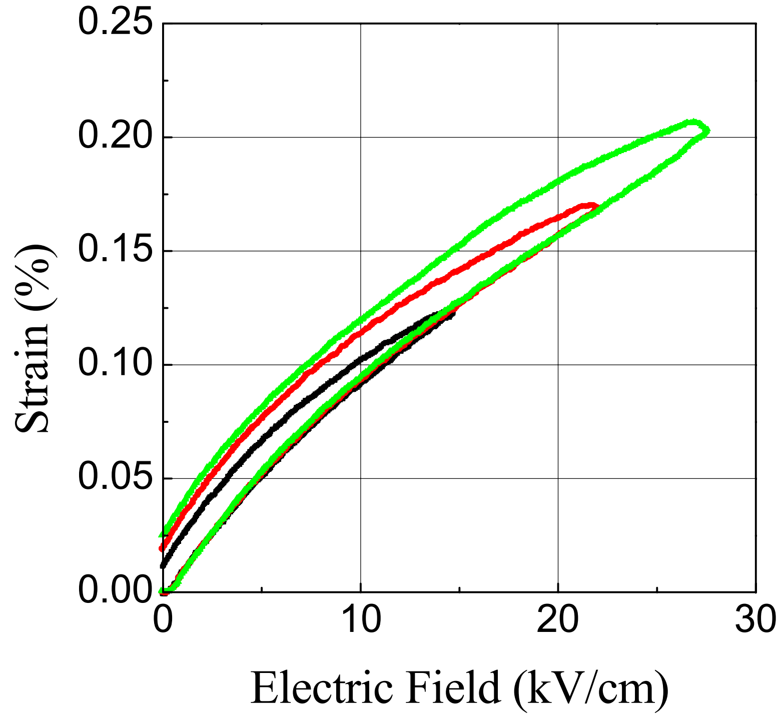
Polarization Curve and Unipolar Strain of (001) $Ba(Ti_{0.925}Zr_{0.075})O_3$ Single Crystals: ***E < 20 kV/cm***





Unipolar Strain : 0.1% at 10 kV/cm

➔ d_{33} = 1000 pC/N

k_{33} = 0.86

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Three Topics of Presentation

1. Solid-State Growth and Piezoelectric Properties of PMN-PT Single Crystals

2. Solid-State Growth and Piezoelectric Properties of Lead-Free Ba(Ti,Zr)O_3 Single Crystals

3. Solid-State Growth of High Tc Piezoelectric Single Crystals

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Fabrication of High Tc Piezoelectric Single Crystals

BUT !

Remarkable Piezoelectric Properties

1. PMN-PT and PZN-PT

- **Electromechanical Coupling Factor** $k_{33} > 0.92$
- **Piezoelectric Coefficient** $d_{33} > 2000$ *pC/N*
- **Unipolar Strain** $\varepsilon > 1\%$

2. Non-lead Piezoelectrics

2-1. $BaTiO_3$

- **At low temperatures (0°C)**
  $k_{33} > 0.85$; $d_{33} > 500$ *pC/N*
  (Superior to PZT at low temp.)

2-2. $Ba(Ti,Zr)O_3$ **and Others**

- **At room temperature**
  $k_{33} > 0.75$; $d_{33} > 340$ *pC/N*

Limitations

1. **Low Curie Temperature**
2. **Temperature Usage Limited to** $T_{Rhom\text{-}Tet}$
3. **Strong Curvature of MPB**
4. **Low Coercive Electric Field** (E_C)
5. **Low Mechanical Quality Factor (Q)**

↓

Development of New Compositions

High Tc Piezoelectrics

PYbN-PT; PIN-PT; BS-PT

PZT; PZT Solid Solutions

+

Development of Crystal Growth Method

Suitable to New Compositions, PMN-PT, and Non-lead Piezoelectrics

↓

Solid-State Single Crystal Growth

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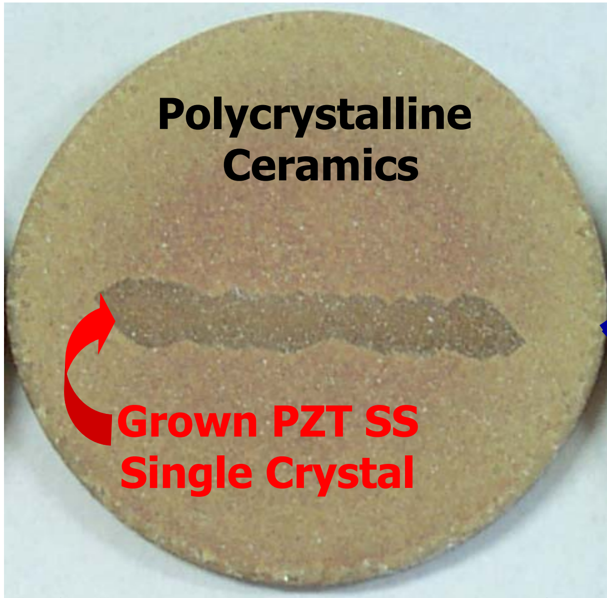
Solid-State Single Crystal Growth of PZT SS
→ The Only Way to Grow PZT SS Single Crystals

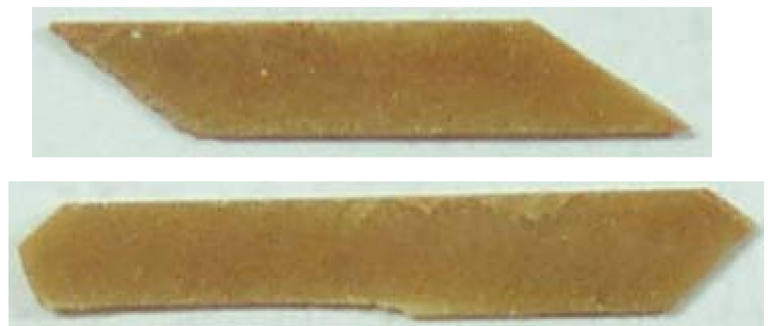


25 mm

Surface Microstructure of Sintered PZT SS Ceramics with a $BaTiO_3$ Seed Crystal inside

Cross Section

Grown Single Crystals Cut from Ceramics



18 mm

SUMMARY

1. **Solid-State Growth of Large PMN-PT Single Crystals**

   PMN/PT = 68/32, 69/31, 70/30, 71/29, 72/28; Relative density > 98.5%;

   Available crystal size ≈ 40x10x1 or 25x25x1 mm; Transparent Crystals;

   $k_{33} \approx 0.9$, $k_{31} \approx 0.62$, strain ≈ 0.25% at 10 kV/cm, $d_{33} \approx 2500$;

   ➔ Scale-up test will be done at Ceracomp.

   (to check reproducibility, productivity, and production cost, etc.)

2. **Non-lead piezoelectric single crystals grown by SSCG method:**

   Zirconium-doped $Ba(Ti_{1-x}Zr_x)O_3$ single crystals;

   x=0.05, 0.075, 0.085 and 0.1; Bigger than 25x25x5 mm;

   Relative density > 98.5%; Transparent single crystals;

   $Ba(Ti_{0.925}Zr_{0.075})O_3$ single crystals (x = 0.075) ➔ $k_{33} \approx 0.86$, $d_{33} \approx 1000$.

3. **High Curie Temperature Piezoelectric Single Crystals (PZT and PYN-PT):**

   PZT solid solutions single crystals;

   Bigger than 15 mm; Property measurement ➔ *underway*.

4. **The SSCG method will be a primary single crystal growth method for $BaTiO_3$, $Ba(Ti_{1-x}Zr_x)O_3$, PMN-PT, and high Curie temperature piezoelectrics (PZT, PYN-PT, and BS-PT, etc.).**

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