ENHANCED HIGH TEMPERATURE PIEZOELECTRICS BASED ON $BiScO_3$-$PbTiO_3$ CERAMICS

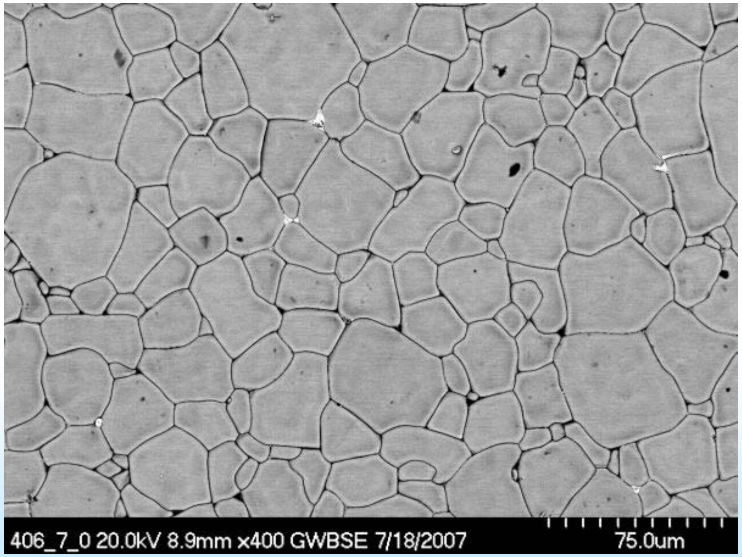
High-temperature piezoelectrics are a key technology for aeronautics and aerospace applications such as fuel modulation to increase the engine efficiency and decrease emissions. The principal challenge for the insertion of piezoelectric materials is the limitation on upper use temperature which is due to low Curie-Temperature (T_C) and increasing electrical conductivity. $BiScO_3$-$PbTiO_3$ (BS-PT) system is a promising candidate for improving the operating temperature for piezoelectric actuators due to its high T_C (>400^{o}C). Bi_2O_3 was shown to be a good sintering aid for liquid phase sintering resulting in reduced grain size and increased resistivity. Zr doped and liquid phase sintered BS-PT ceramics exhibited saturated and square hysteresis loops with enhanced remenant polarization (37 $\mu C/cm^2$) and coercive field (14 kV/cm). BS-PT doped with Mn showed enhanced field induced strain (0.27% at 50kV/cm). All the numbers indicated in parenthesis were collected at 100 ^oC.

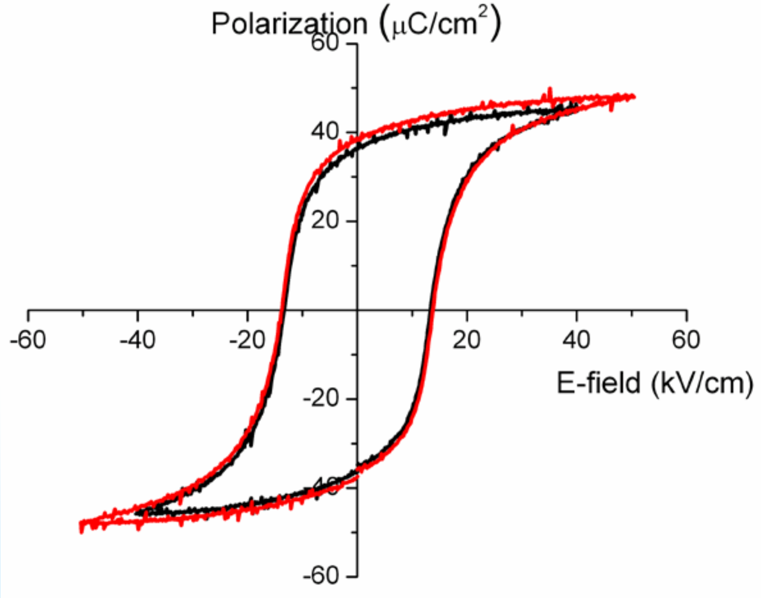
Enhanced High Temperature Piezoelectrics Based on $BiScO_3$-$PbTiO_3$ Ceramics

Alp Sehirlioglu[1], Ali Sayir[1,2] and Fred Dynys[2]

[1] Case Western Reserve University, Cleveland, OH
[2] NASA Glenn Research Center, Cleveland, OH

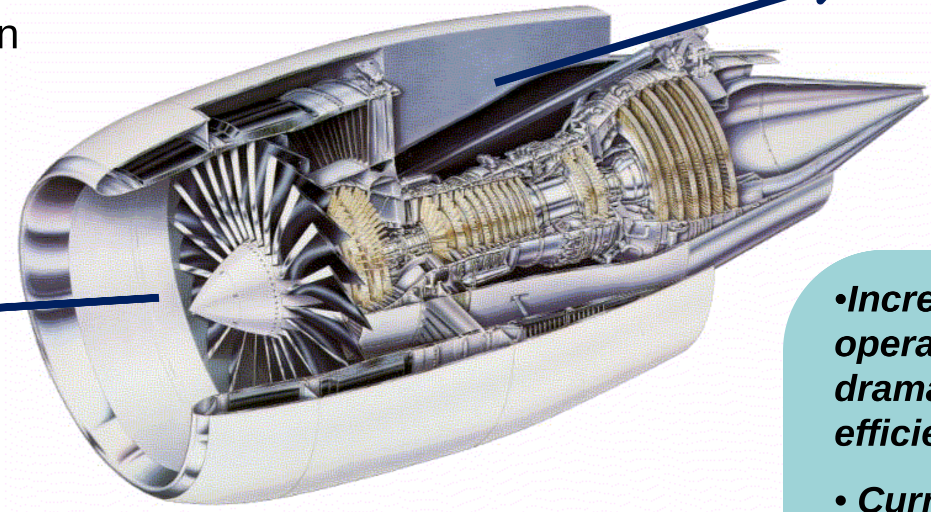
AFOSR FA 9550-06-1-0260





Green engines and morphing planes

Active and Passive Vibration Control of Fan Blade Using Piezoceramics



Fuel modulation:

–Increased engine efficiency

–Decreased NO_x gases

•Increased turbine engine operating temperate can dramatically increase fuel efficiency & reduce emissions

• Current DOD study shows only reasonable way to increase engine temperature is by advanced materials

• 2001 Stanford study shows a $1B/year fuel savings if engines run 1 degree C hotter

Advantages:

- Fast response time
- Generate large forces
- No gears or rotating shafts, no wear and tear.

Actuators for Aerospace and Aeronautics:

Fuel modulation, valves, micro-positioning devices, MEMS, active damping and energy harvesting.

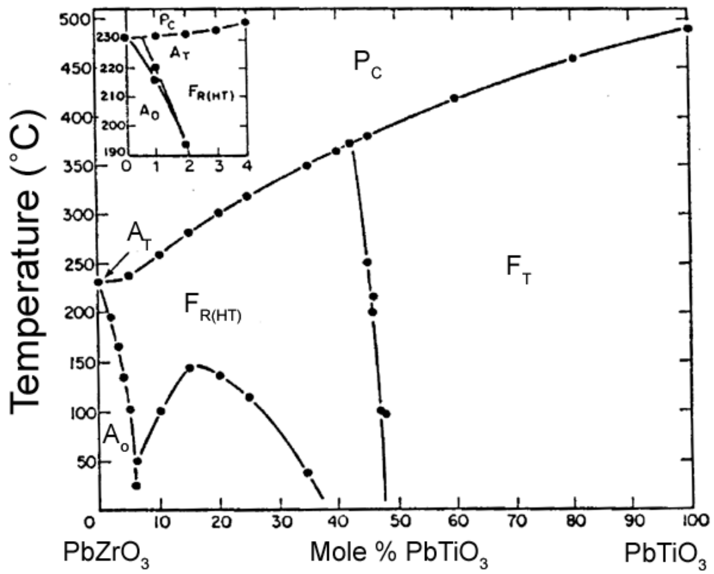
Sensors:

Pressure sensors, passive damping

Challenges for High Temperature Applications

- Trade off between T_C and d_{33}
- Conductivity at elevated temperatures

	T_{limit} (°C)/(°F)	d_{33} (pC/N)
PZT Type II (PZT 5A)	350 / 662	374
PMN-PT single crystals	90 / 194	>2000
$BiScO_3$-$PbTiO_3$	450 / 842	401
$La_3Ga_{5.5}Ta_{0.5}O_{14}$ single crystal	N/A	7
$Na_{0.5}Bi_{4.5}Ti_4O_5$	650 / 1202	19
$La_2Ti_2O_7$	1482 / 2700	16



B. Jaffe, W. R. Cook and H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.

Approach and Outline

- Microstructure engineering

  Liquid phase sintering

- Compositional engineering
  - Isovalent doping (Yb, In)
  - Aliovalent doping (Sr, Zr)
  - Multivalent doping (Mn)
- Properties

Processing of BS-PT

Raw materials (Bi_2O_3, PbO, Sc_2O_3, TiO_2) ← Dopants

↓

Ball milling (15hrs)

↓

Drying (stirred)

↓

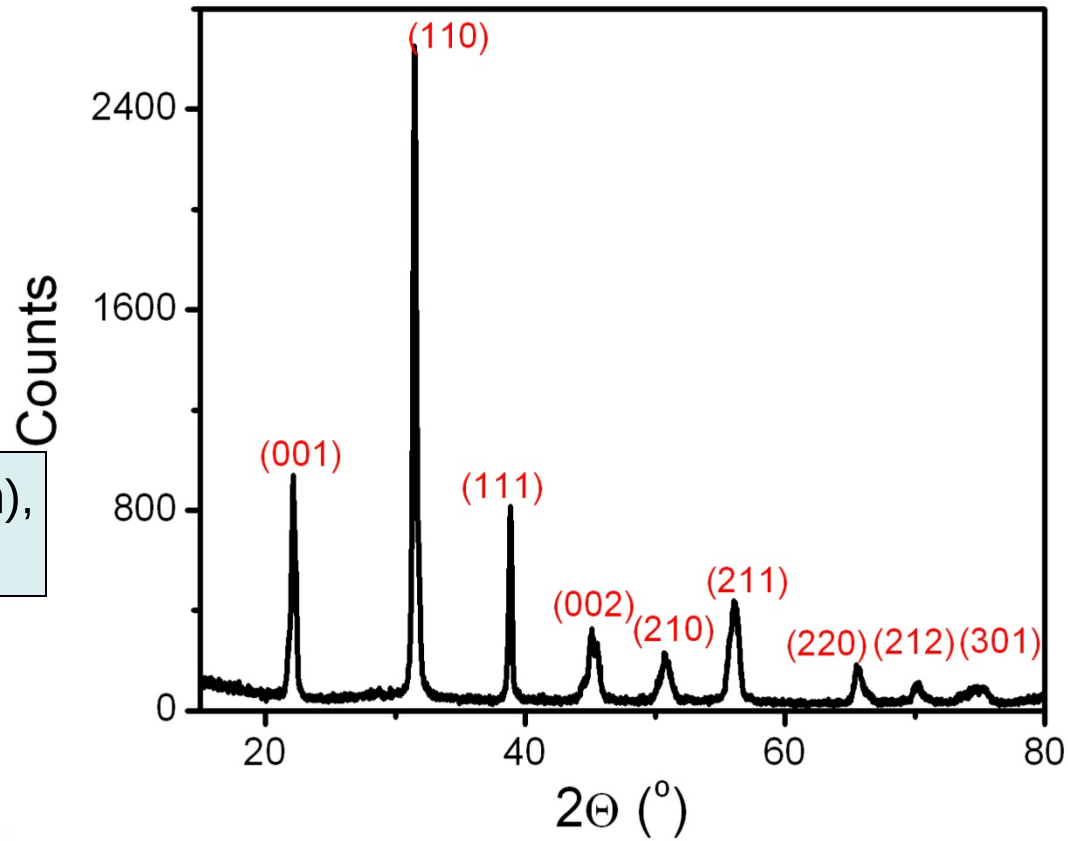
Calcination (750^oC, 3hrs, 5^oC/min), in air

↓

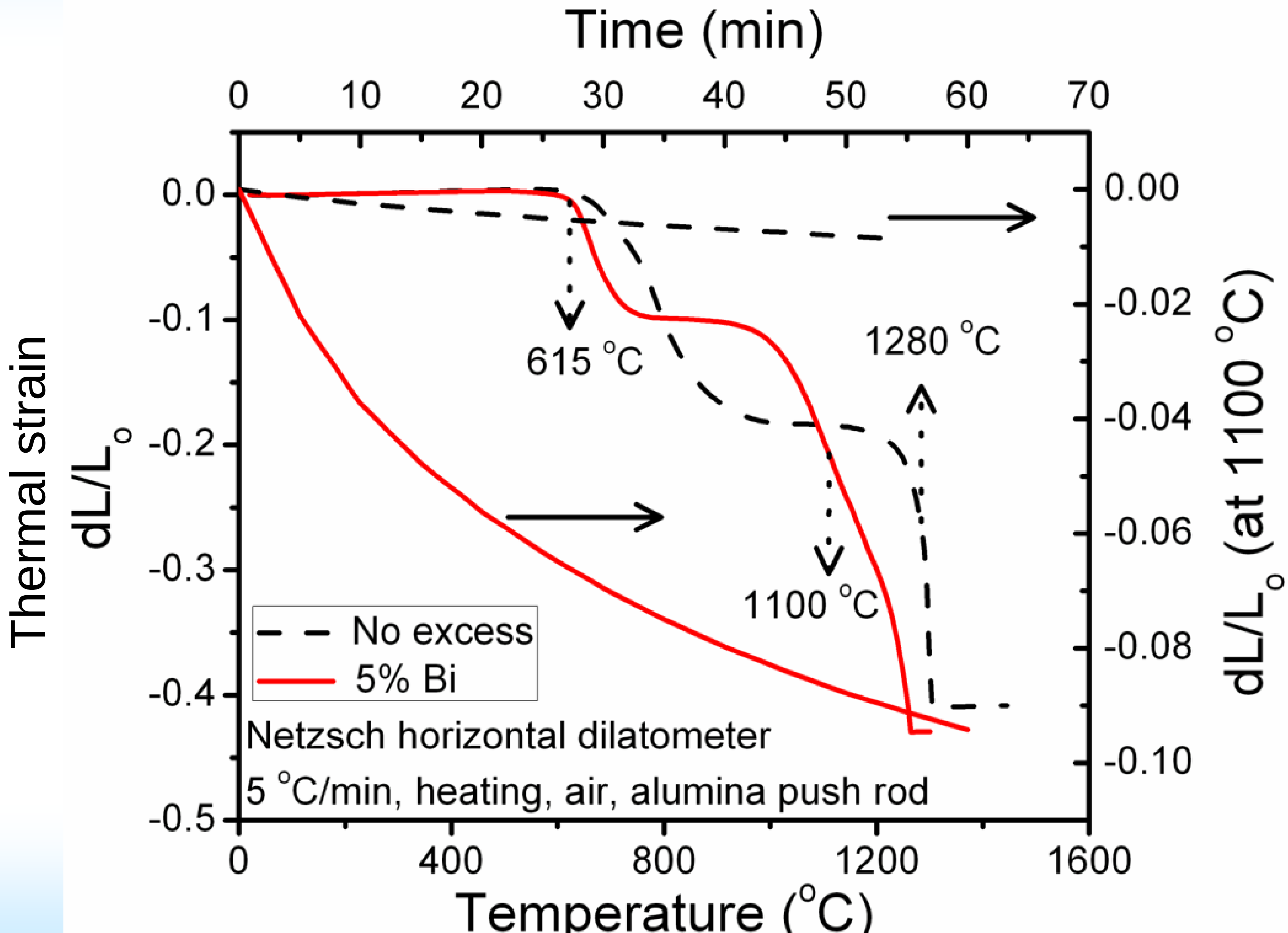
Ball milling (6hrs) ← Excess addition

↓

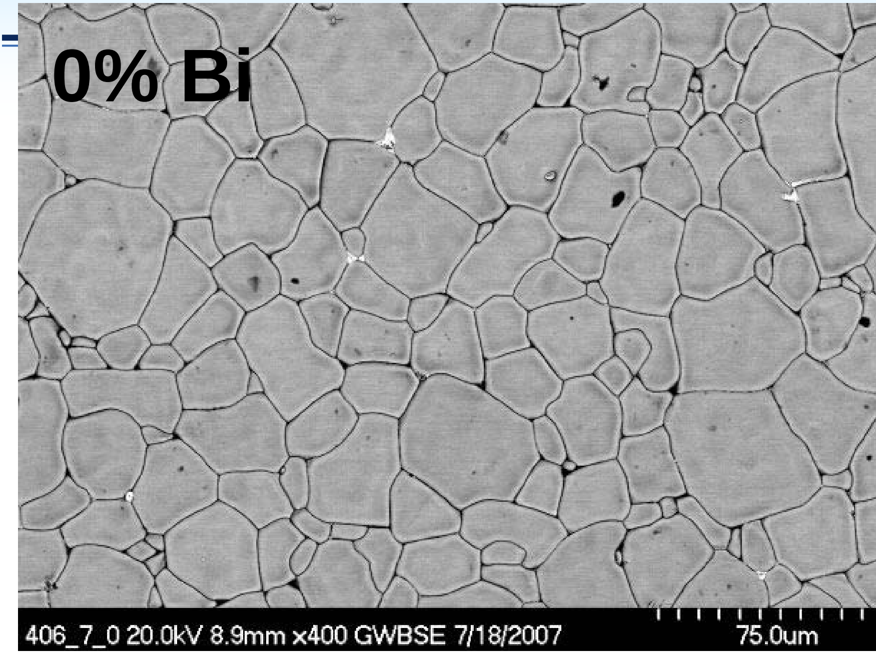
Pressing → Sintering (1100^oC, 1hr, 5^oC/min), in air

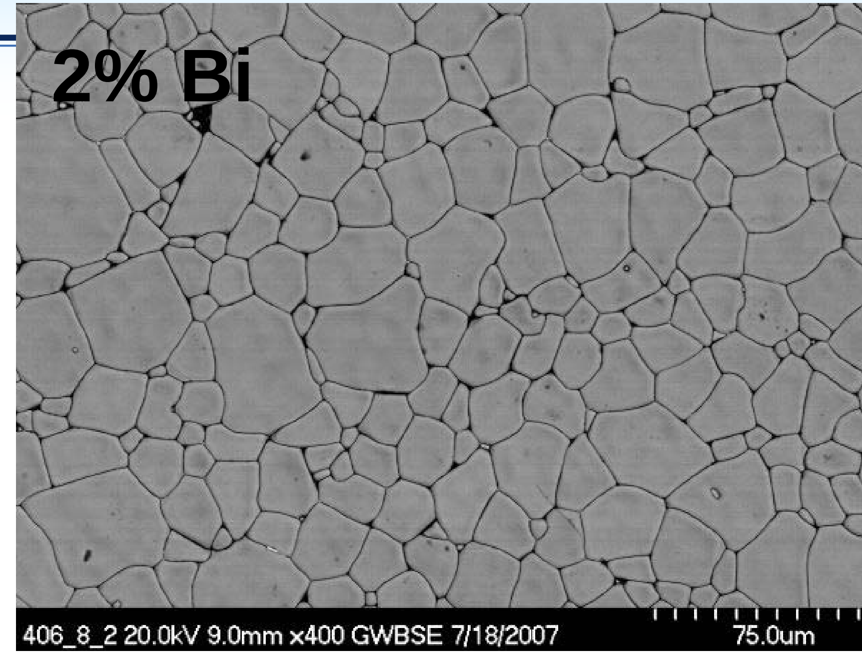


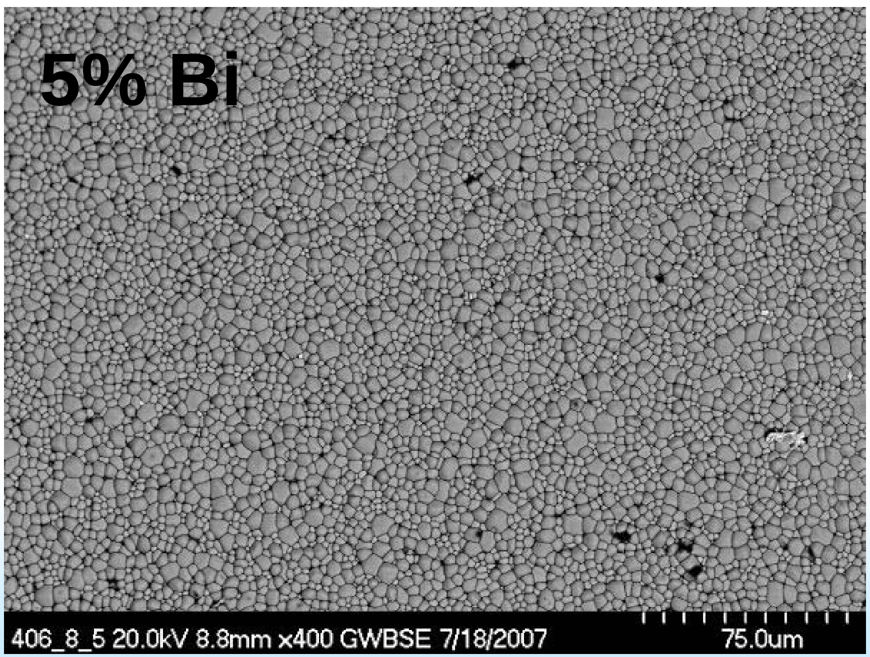
Sintering conditions

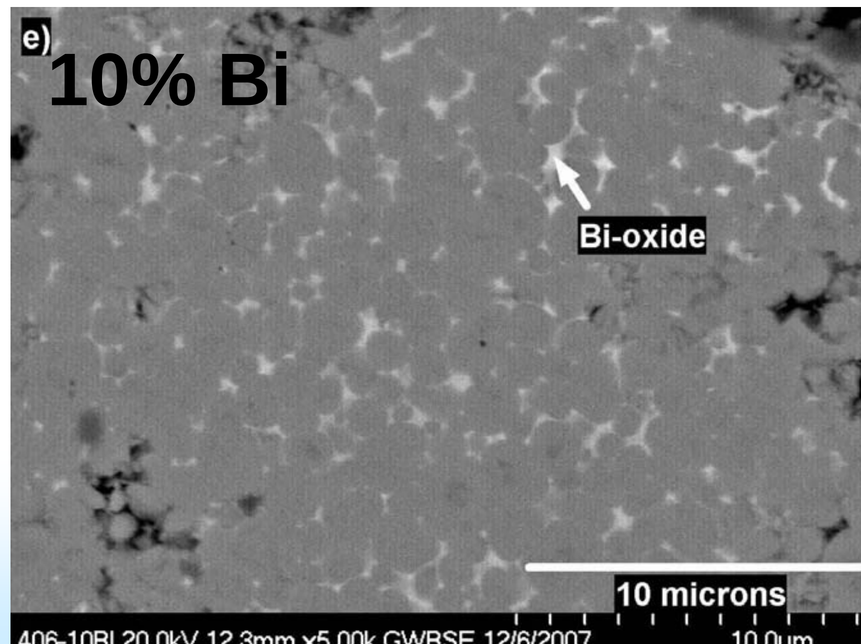


Effect of Liquid Phase Sintering (via Bi_2O_3)on microstructure

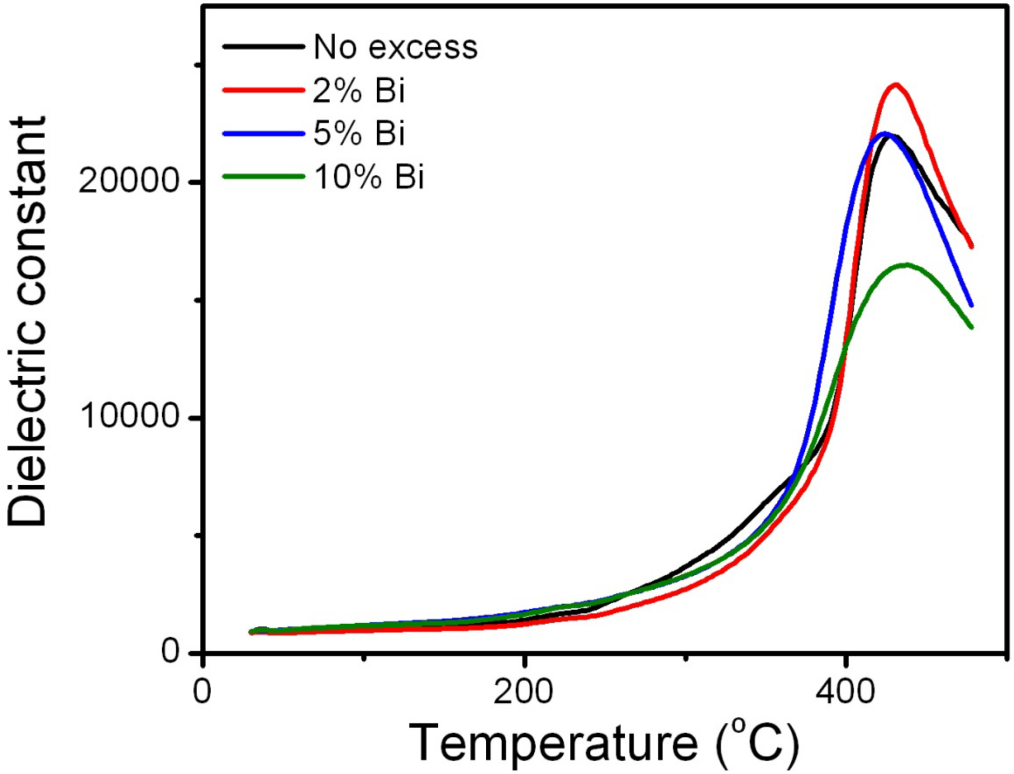


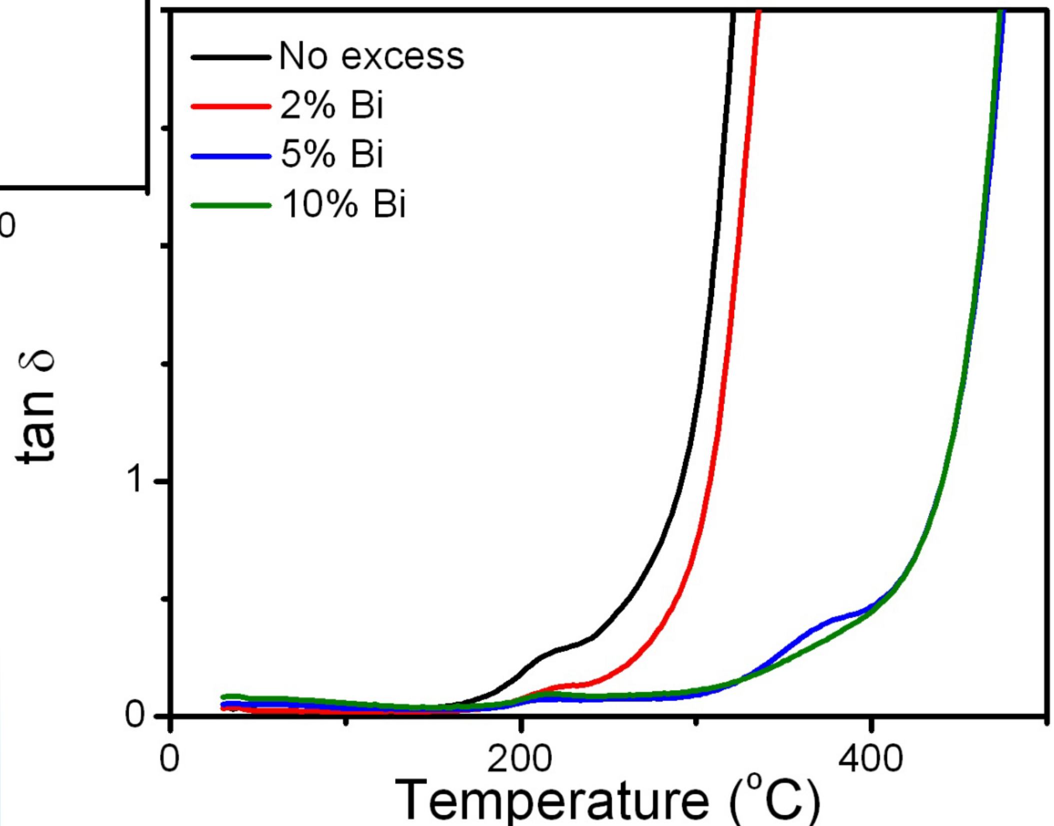






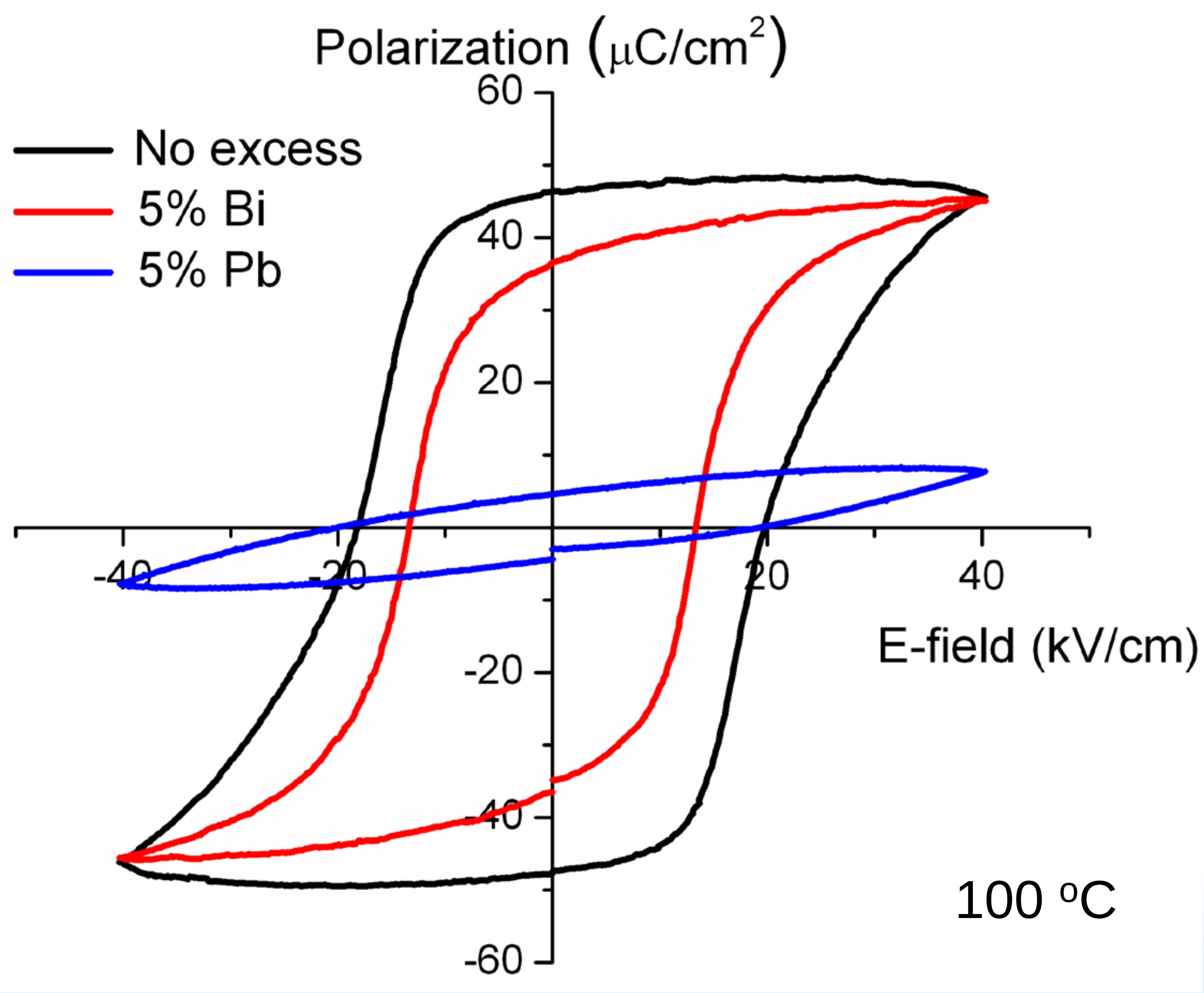
Effects of Liquid Phase Sintering in BS-PT



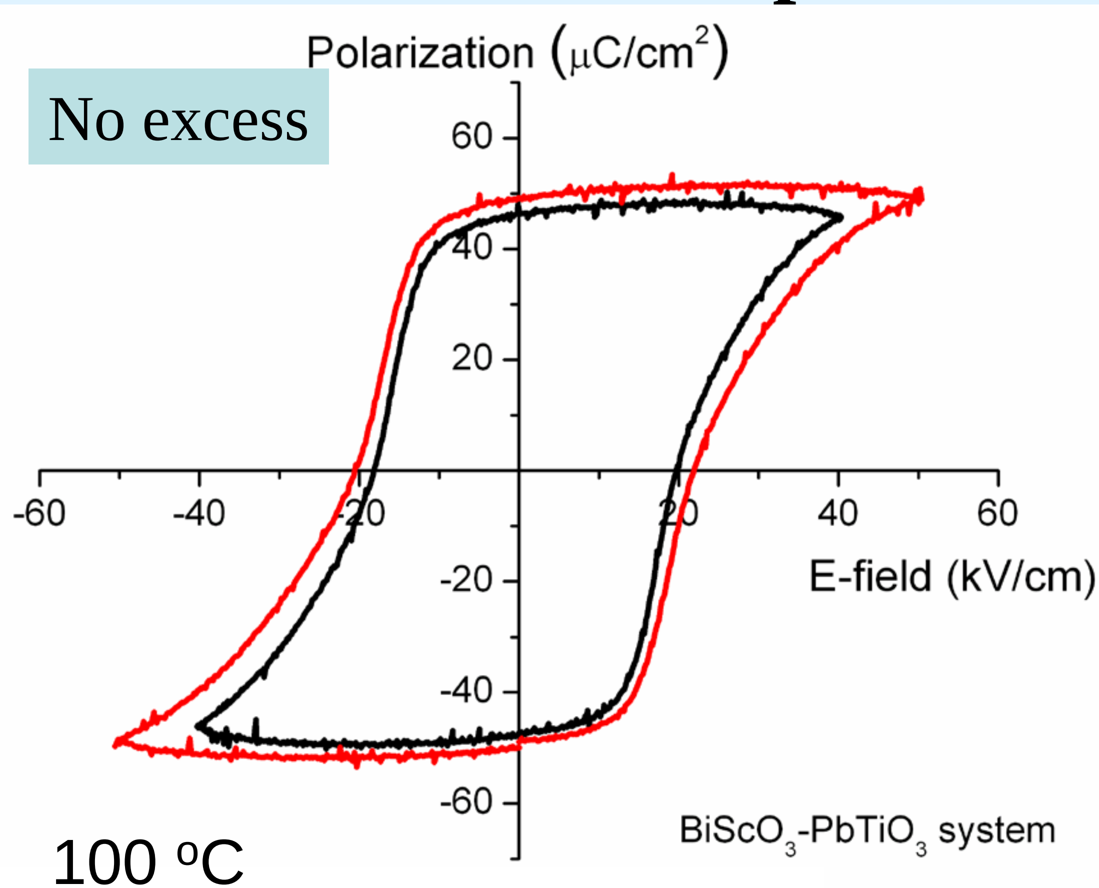


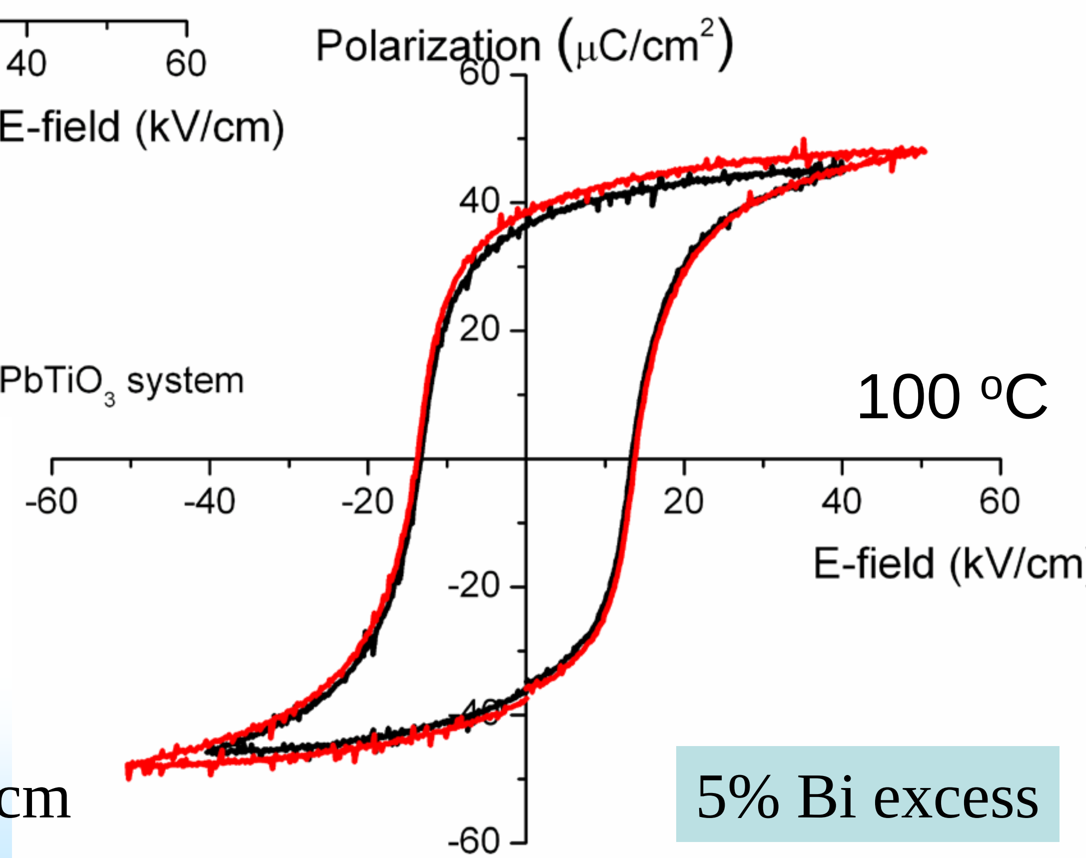
1 kHz, 0.5 V/mm ac, in air

Ferroelectric and piezoelectric properties



Ferroelectric Properties





E_C = 13.5 kV/cm

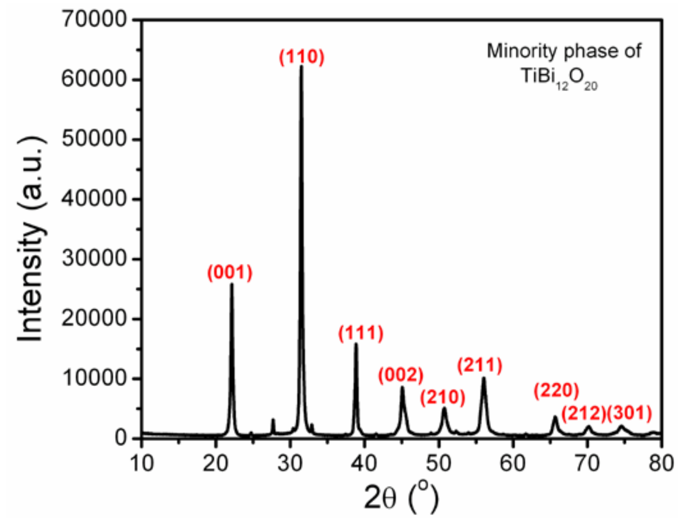
Effects of Zr-doping

Batched composition $0.37Bi(Sc_{0.98},Zr_{0.02})O_3$-$0.63PbTiO_3$

	Undoped	Doped
Bi/(Pb+Bi)	≈36	≈36
Sc/(Sc+Ti)	≈38	≈37.5
Volatilization during sintering	91Pb-9Bi	90Pb-10Bi
Weight loss during sintering (%) by TG	0.17	0.18
Weight change during sintering (%) (real sample)	- <2%	+0.15-0.30
Grain size (μm)	>20 (bimodal)	≈ 2

Theoretical: Zr mol% = 0.148

ICP calcined: Zr mol% = 0.144

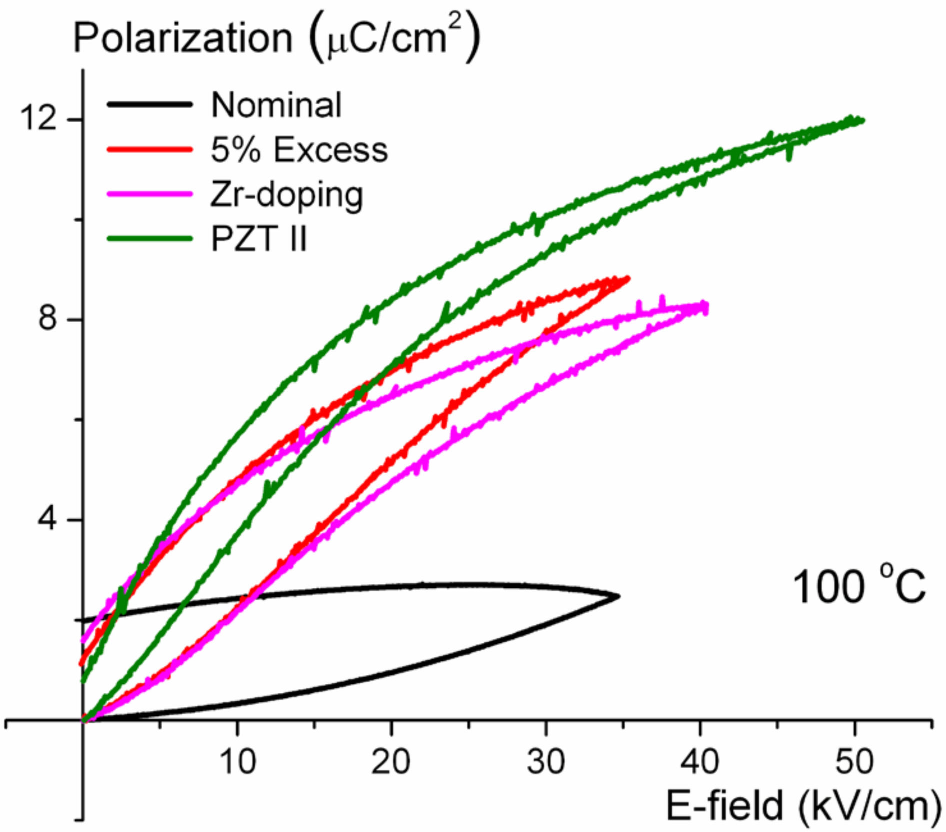


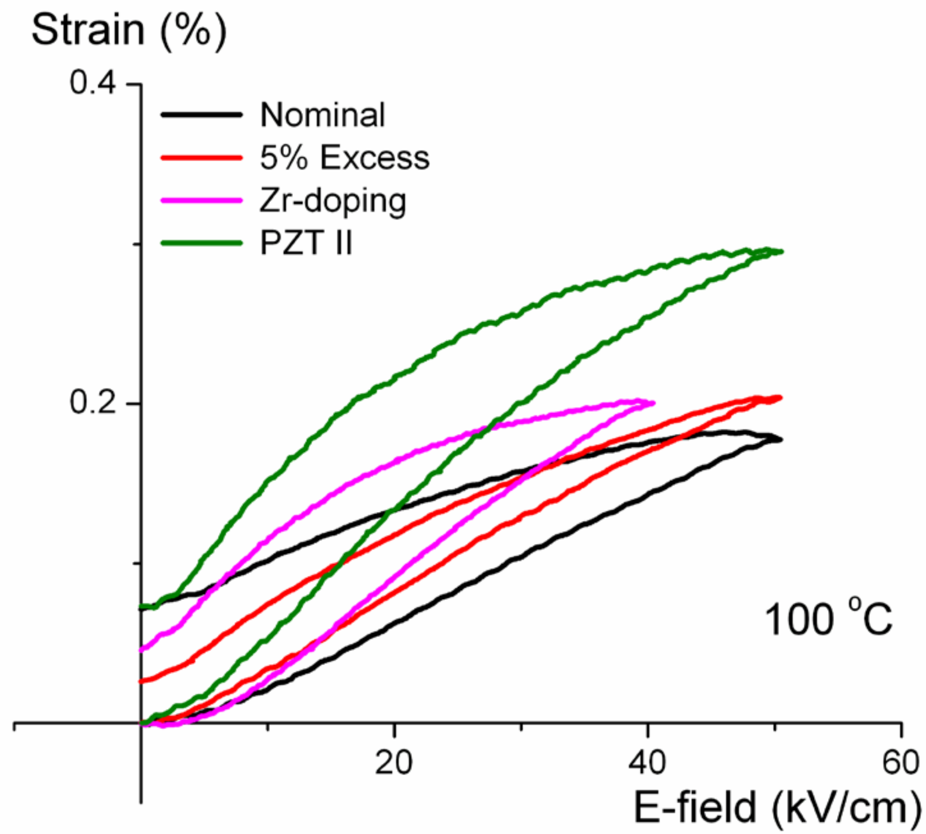
	tetragonal perovskite		rhombohedral perovskite		Ti $Bi_{12}O_{20}$
	a (Å)	c (Å)	a (Å)	α ( )	a (Å)
Zr-doped	3.997	4.052	4.027	90.16	10.198
Undoped	3.988	4.055	4.019	89.80	10.191

Relative ratio	Tetragonal	Rhombohedral
Zr-doped	0.29	0.71
Undoped	0.47	0.53

$$Zr_{Sc}^{\bullet} \Longrightarrow V_{Pb}^{//},\ V_{Bi}^{///},\ O_v^{//},\ Pb_{Bi}^{/}$$

Doping comparison

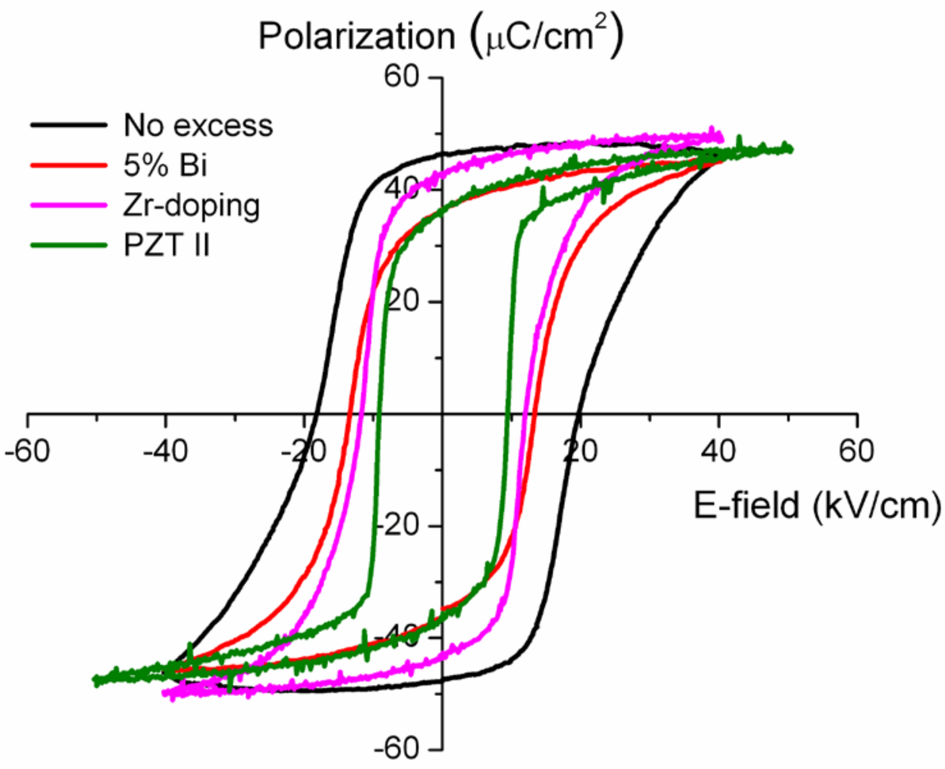


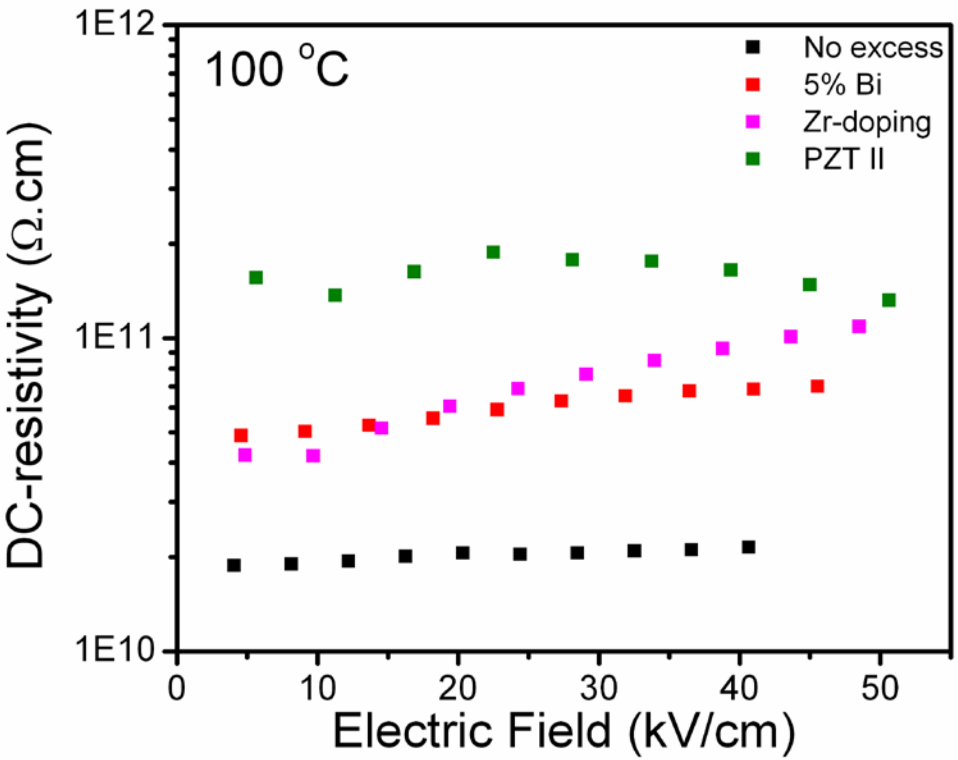


	Nominal	5% Bi	Zr-doping	PZT II
$d\varepsilon_{max}/dE_{max}$ (pm/V)	354	408	500	585

PZT II by Piezo Kinetics, Inc

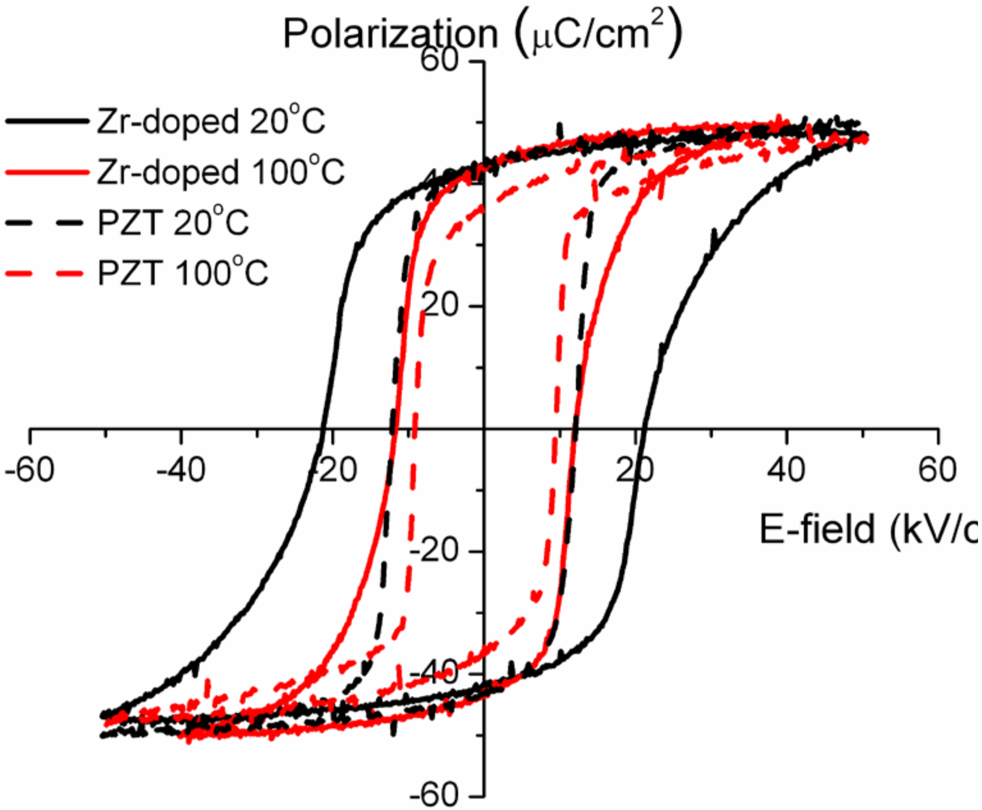
Doping comparison (2)





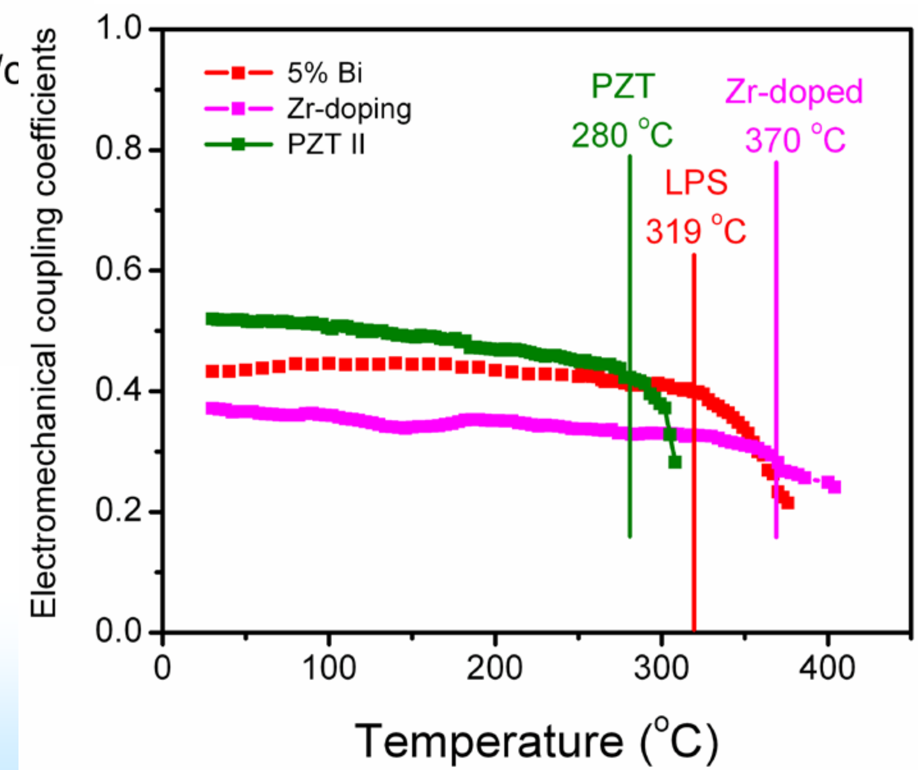
	Nominal	5% Bi	Zr-doping	PZT II
P_r ($\mu C/cm^2$)	46.4	36.6	43	36.4
E_C (kV/cm)	19	13.3	11.8	9.25

Doping comparison (3)



E_c for PZT at 20°C = E_c for Zr-doped at 100°C

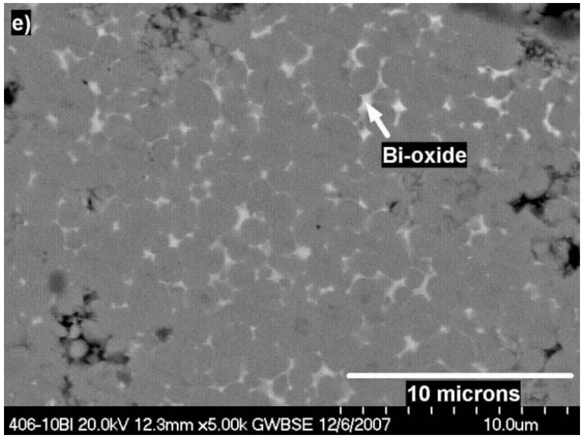
Next step is to increase k_p

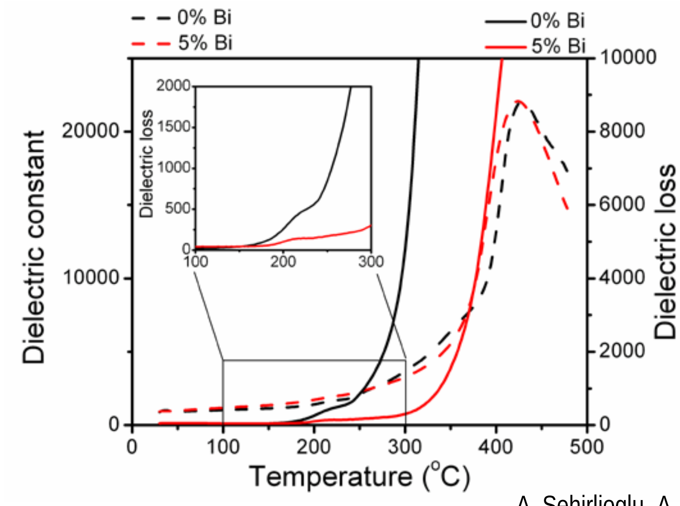


Effect of liquid phase sintering

Micro-structural Engineering : Liquid phase sintering

Bi_2O_3 is added as a liquid phase sintering aid





Improved dielectric loss at elevated temperatures

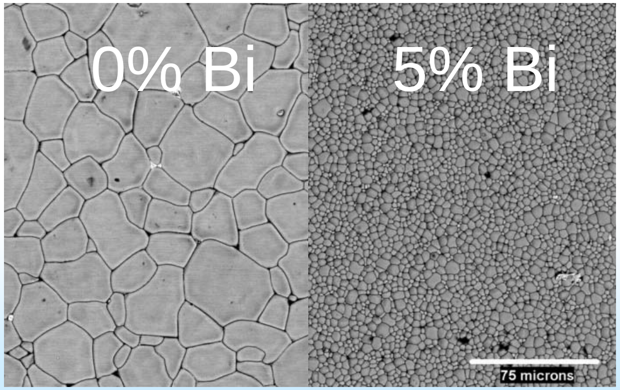
High Curie Temperature remain unchanged

A. Sehirlioglu, A. Sayir and F. Dynys, J. Am. Ceram. Soc., 91 [9], 2910 (2008).

Faster densification

Smaller grain size

Non-continuous grain boundary phase



	LPS $BiScO_3$-$PbTiO_3$	PZT-Type II
T_C (°C)	430	315
d_{33} (pC/N)	408	585
E_C (kV/cm)	13	9
P_R (μC/cm^2)	37	36
ρ_{DC} (Ω.cm)	≈ 10^{11}	≈ 10^{11}

High field d_{33} is an approximation of max induced strain / max field

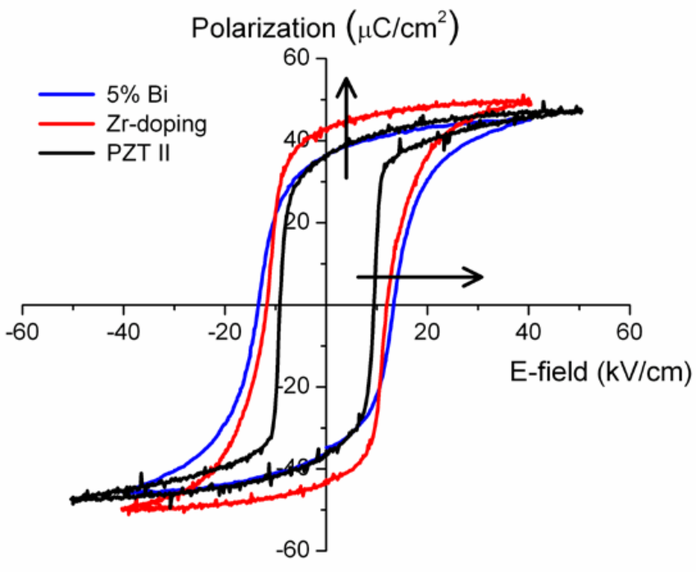
at 100 °C

Effect of compositional modification

Compositional Engineering : Donor doping

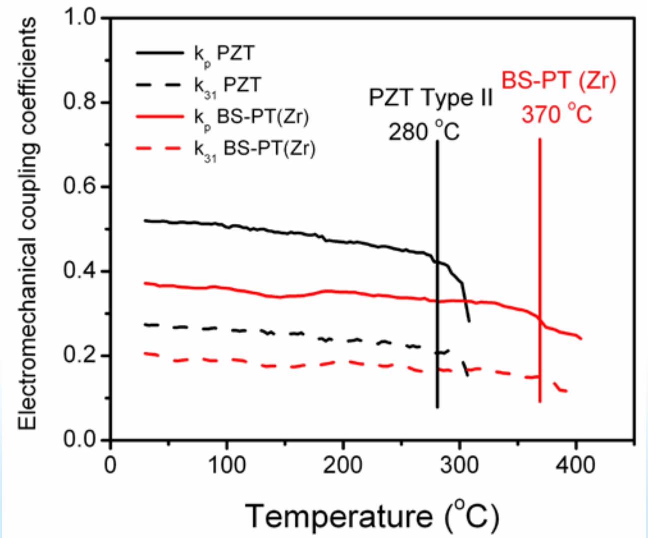
Zr^{4+} is added as a donor in place of Sc^{3+}

$0.37Bi(Sc_{0.98}Zr_{0.02})O_3\text{-}0.63PbTiO_3$



	Zr-doped BS-PT	LPS BS-PT	PZT Type II
T_C (°C)	404	430	315
d_{33} (pC/N)	500	408	585
E_C (kV/cm)	21	23	12
P_R (μC/cm²)	43	24	44
ρ_{DC} (Ω.cm)	≈ 10^{11}	≈ 10^{11}	≈ 10^{11}

High field d_{33} is an approximation of max induced strain / max field



Improved operating temperature

Improved coercive field

Improved remenant polarization

Acknowledgements

Dr. Nathan S. Jacobson

Tom Sabo

Rick Rodgers

Dereck Johnson

Anna Palczer

Raymond Babuder