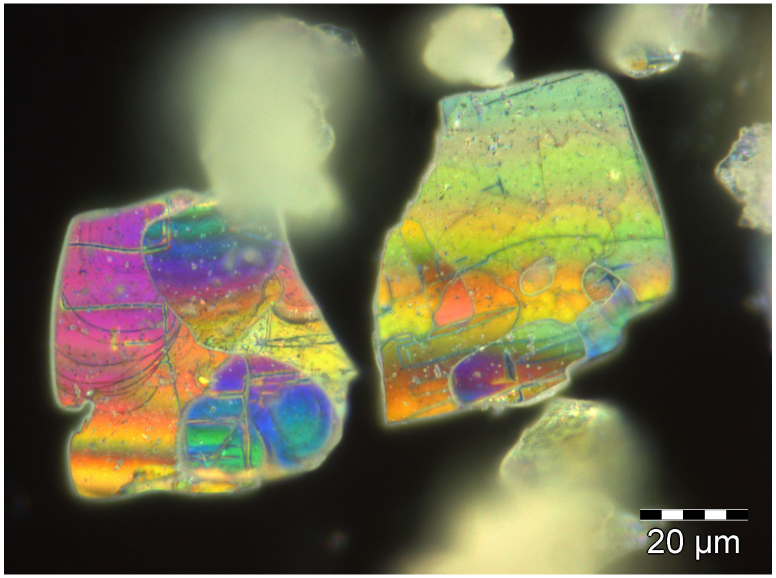
SAND2008-7914P

Texture for Industry: Leveraging 2454 Capabilities to Demonstrate Manufacturability of Textured Lead-free Ferroelectrics

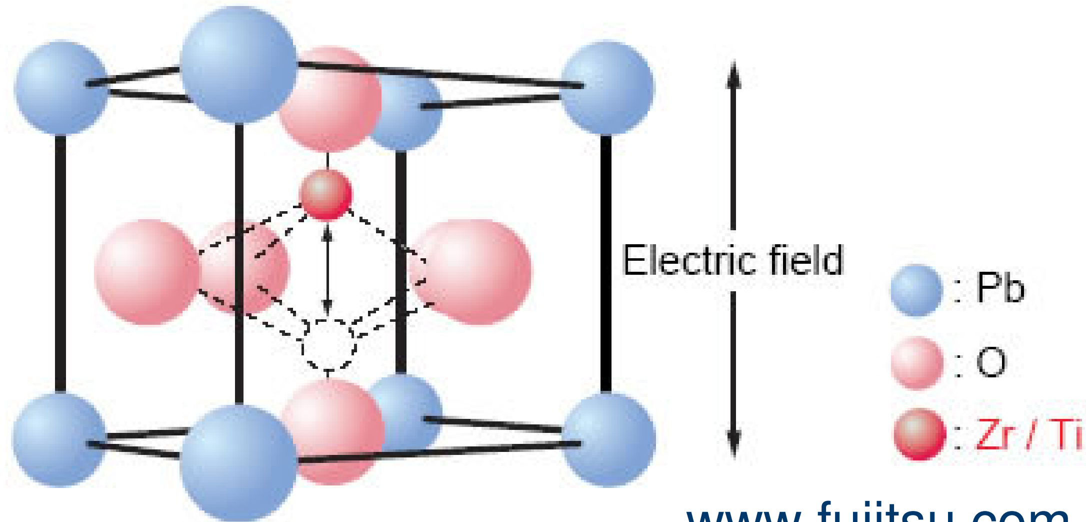


Michael R. Winter

Christopher B. DiAntonio **Tom Chavez**

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Ferroelectrics exhibit spontaneous, re-orientable polarization



www.fujitsu.com

direct piezoelectric effect - strain generates electric charge

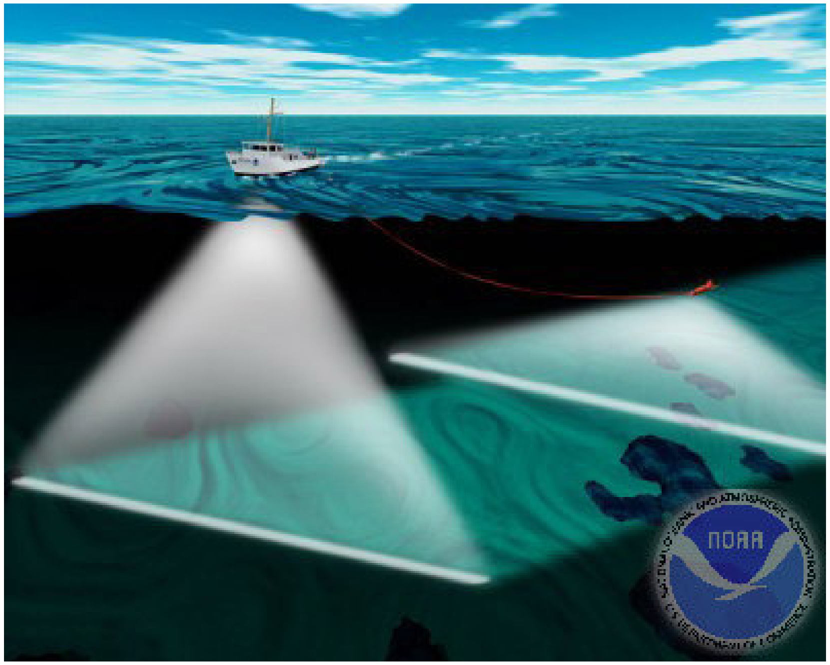
converse piezoelectric effect - electric field generates strain

pyroelectrics - heat generates electric charge

electro-optics - electric field changes optical properties

Lead-based ferroelectrics are used in a variety of applications

Sonar

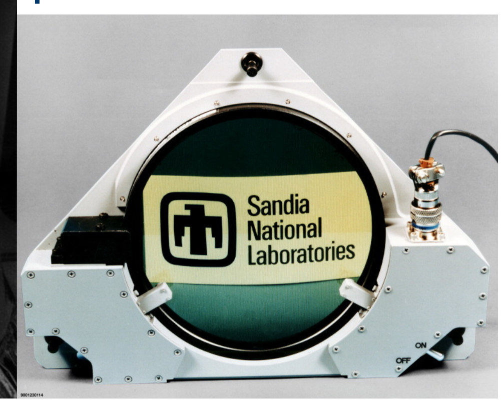


www.noaa.gov

Ultrasound

www.wikipedia.org

Thermal flash protection



optical waveguides and displays

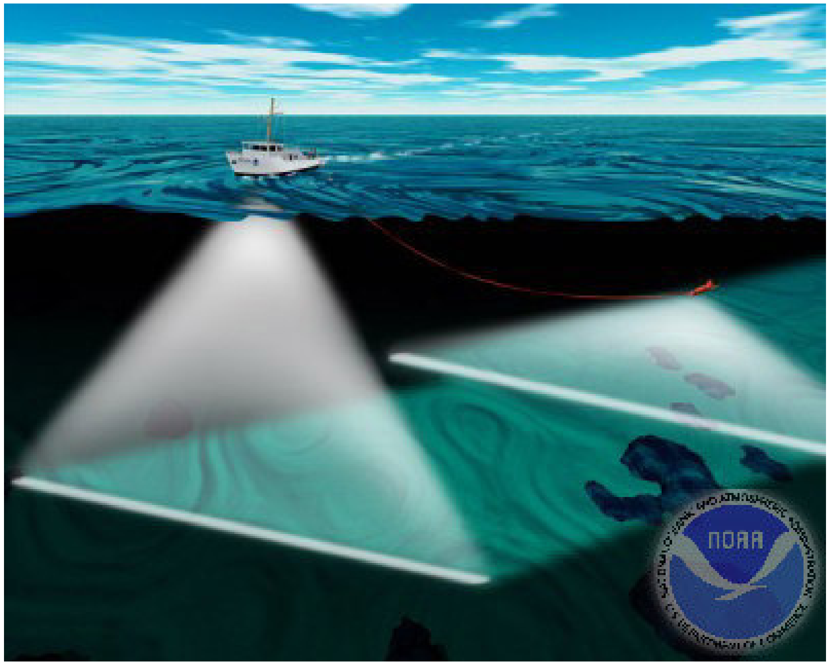
actuators

heat sensors

ferroelectric RAM

Relevant properties are application dependent

Sonar



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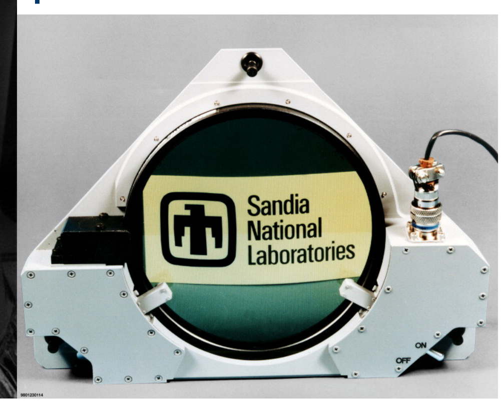
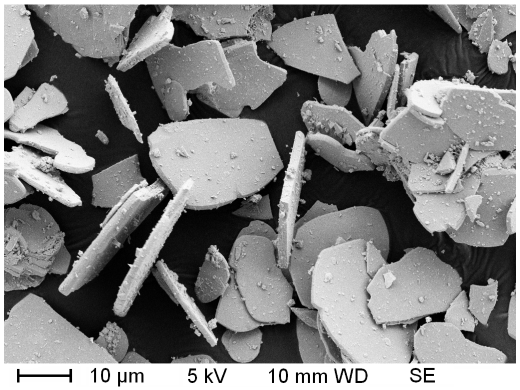
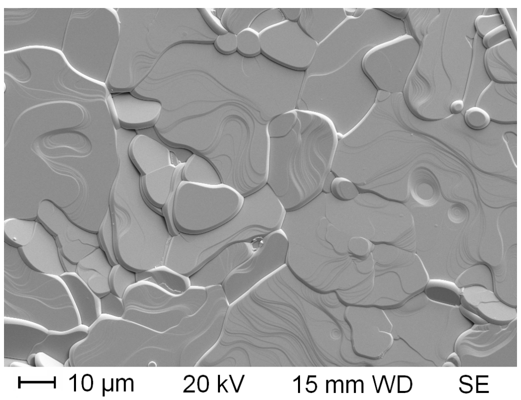


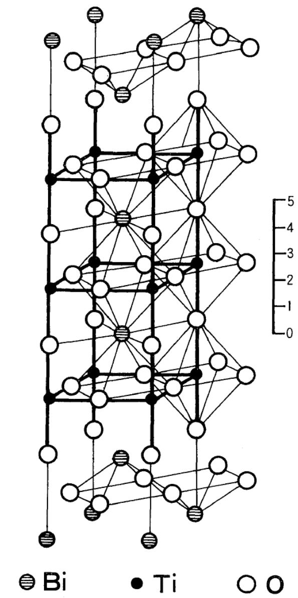
frequency	charge storage
temperature	coercive field
lifetime	piezoelectric response

This presentation focuses on improving the dielectric properties of lead-free materials textured by screen printing



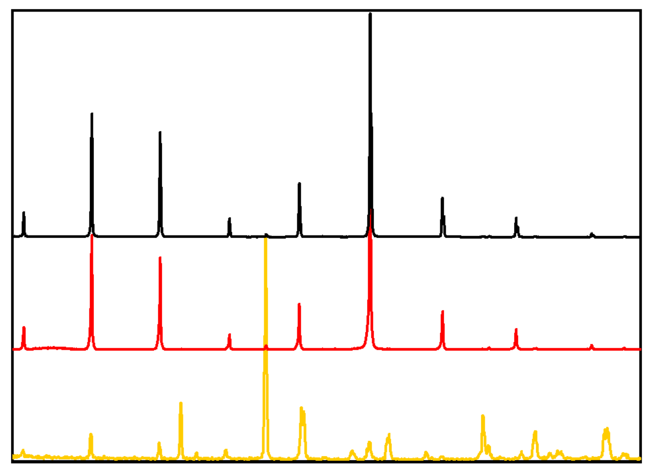


Lead-free dielectrics

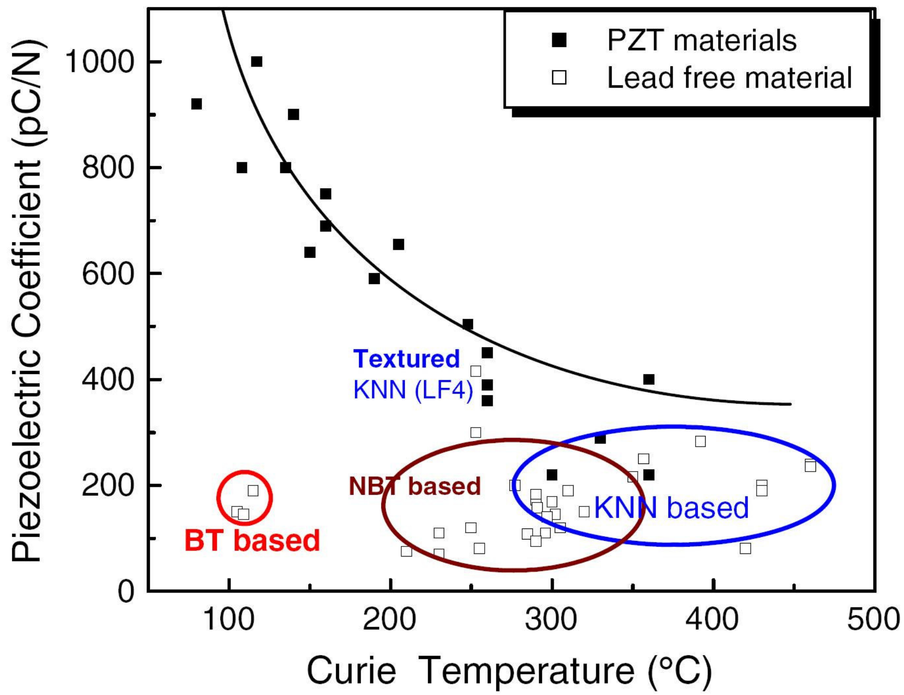


Scalable industrial techniques

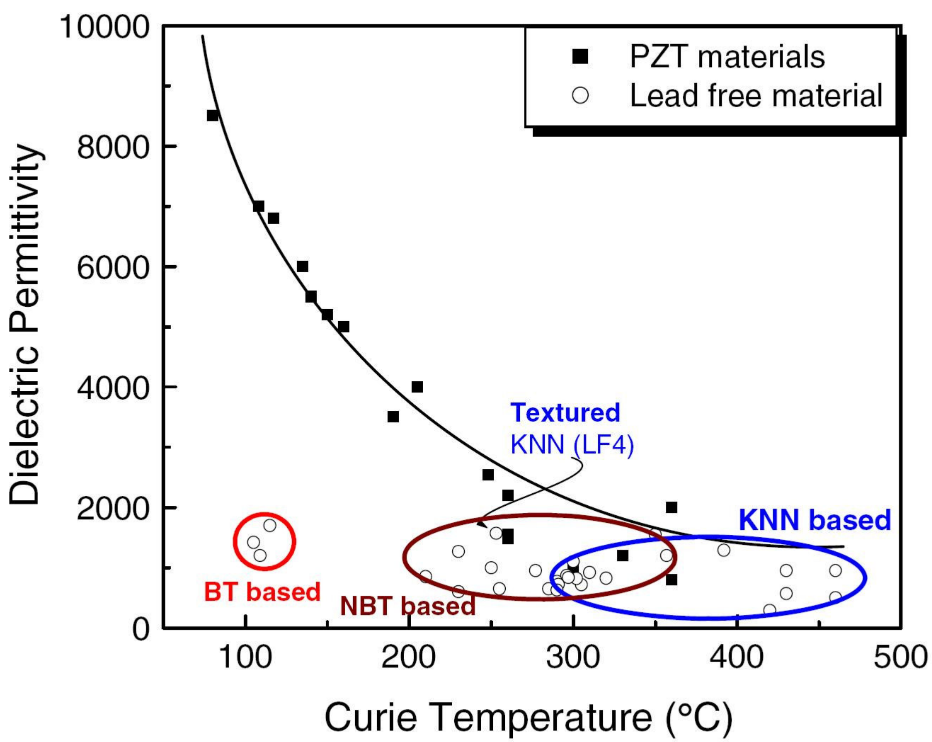
Near single crystal texture

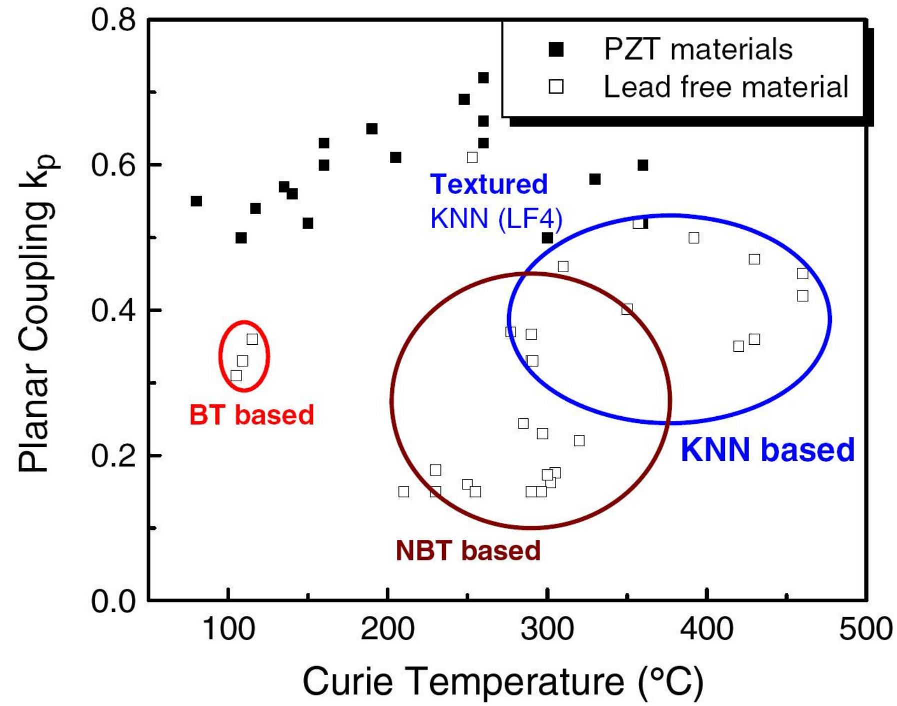


Lead Zirconium Titanate
vs
Lead-free

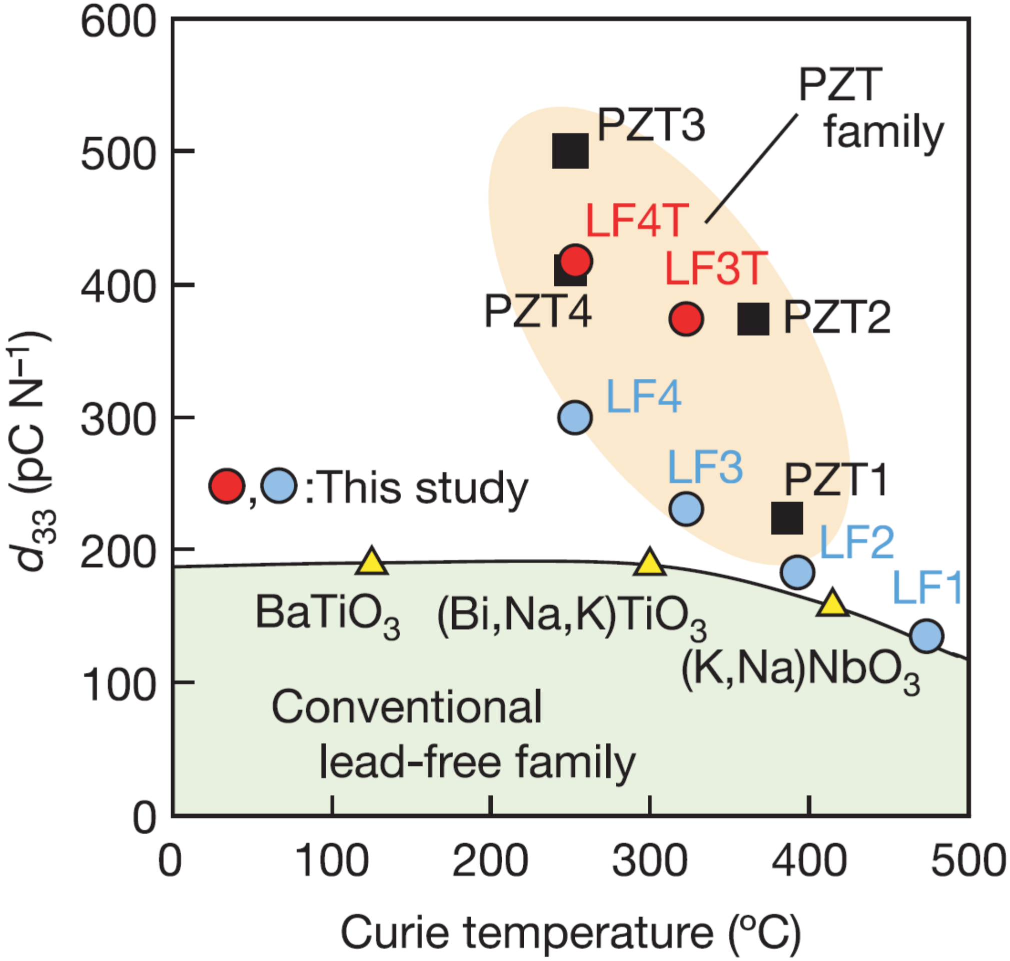


T.R. Shrout, J Electroceram (2007)





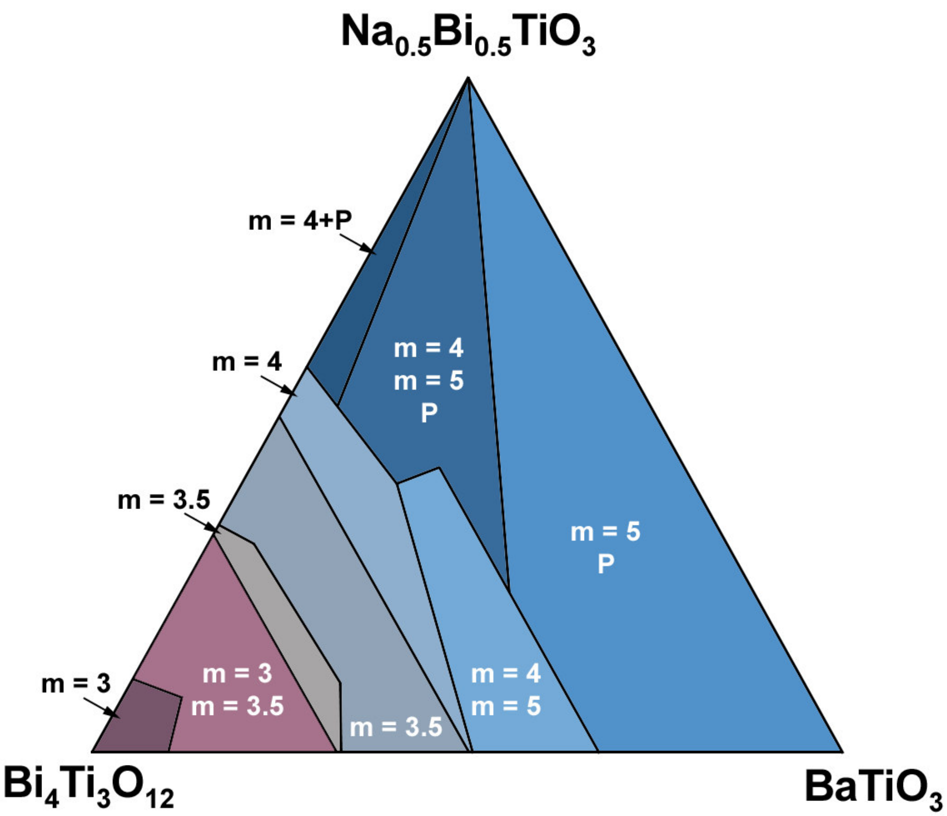
The motivation is to develop replacements for current lead-based systems that are rapidly scalable to industry



Y. Saito, Nature (2004)

When textured, materials in the alkali niobate-based perovskite system have improved dielectric properties

Several compositions in the ternary are potential lead-free dielectrics

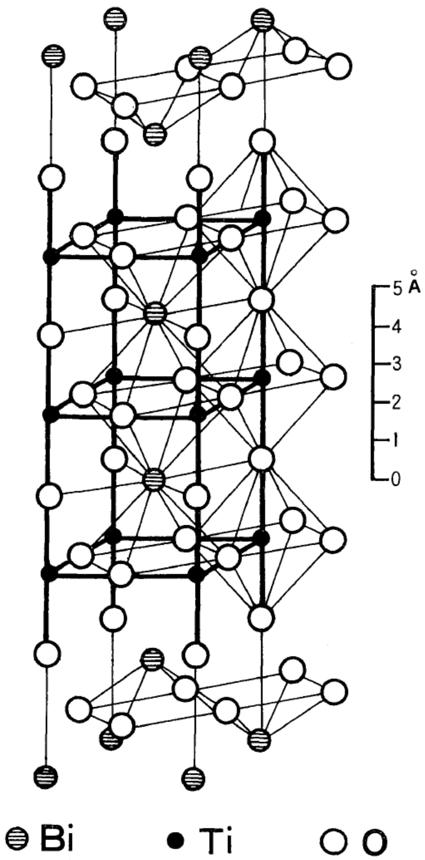


A. Sanson, JACS (2005)

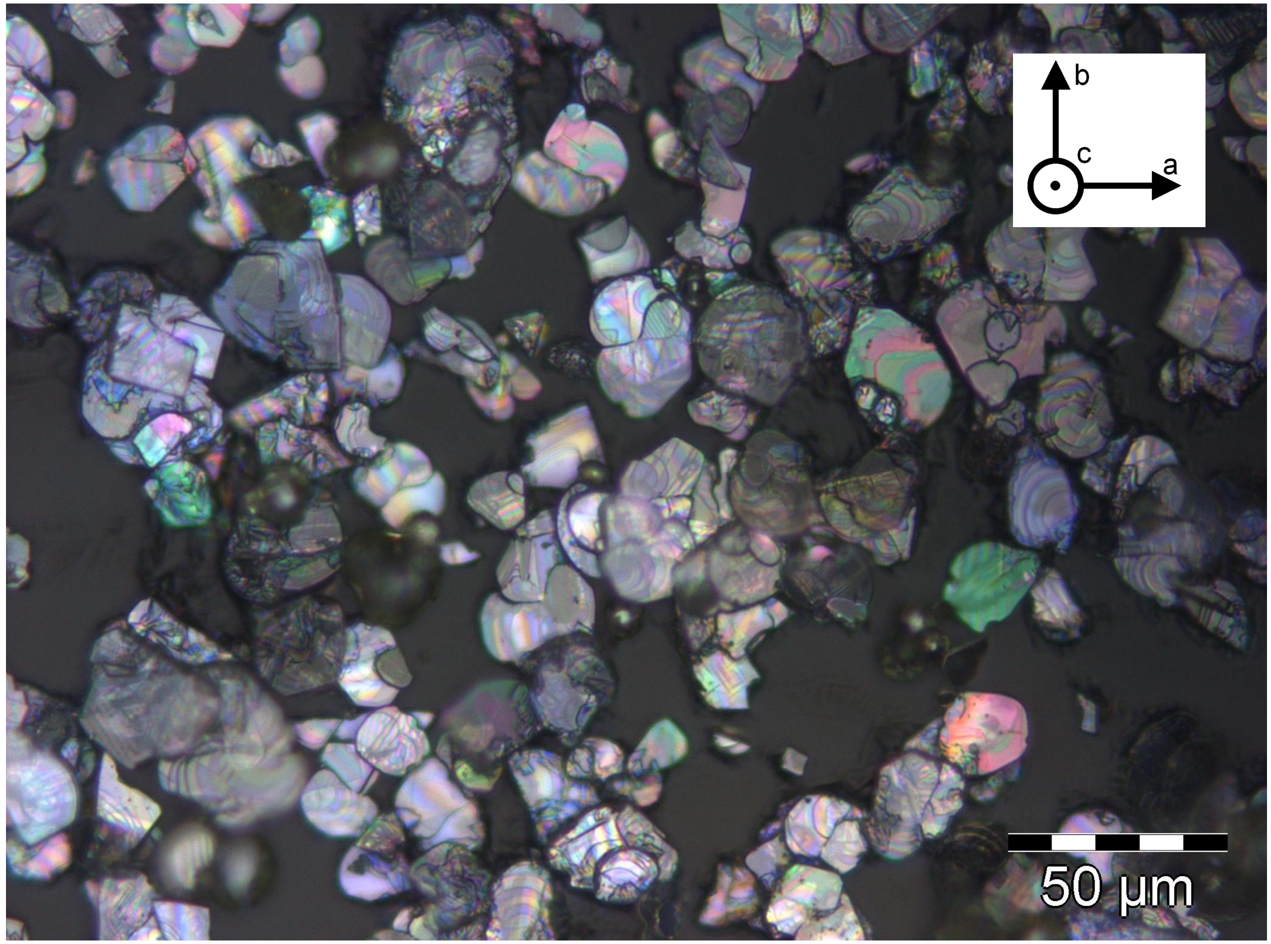
$Bi_4Ti_3O_{12}$	$Na_{0.5}Bi_{0.5}TiO_3$	$BaTiO_3$
100%	0%	0%
0%	100%	0%
0%	0%	100%
33%	33%	33%
50%	50%	0%
8.6%	43.3%	48.1%

Materials in the $Bi_4Ti_3O_{12}$ - $Na_{0.5}Bi_{0.5}TiO_3$ - $BaTiO_3$ ternary have a variety of layer structures for different compositions

Layer-structure materials are excellent candidates for crystallographic texturing



T. Takenaka, JJAP (1980)



High aspect ratio (~100:1) seeds of $Bi_4Ti_3O_{12}$ and $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ can be grown through molten salt synthesis

Union Process attrition mill to decrease matrix particle size

High energy milling of slurries and dry powders to sub-micron particle size

Up to 500 cc per run

Adjustable milling speed

Accommodates media from 1 mm to 2 mm

Horiba particle size analyzer to determine particle size distribution of matrix powder

Analyze particle size and distribution of powders

Wet and dry analysis possible

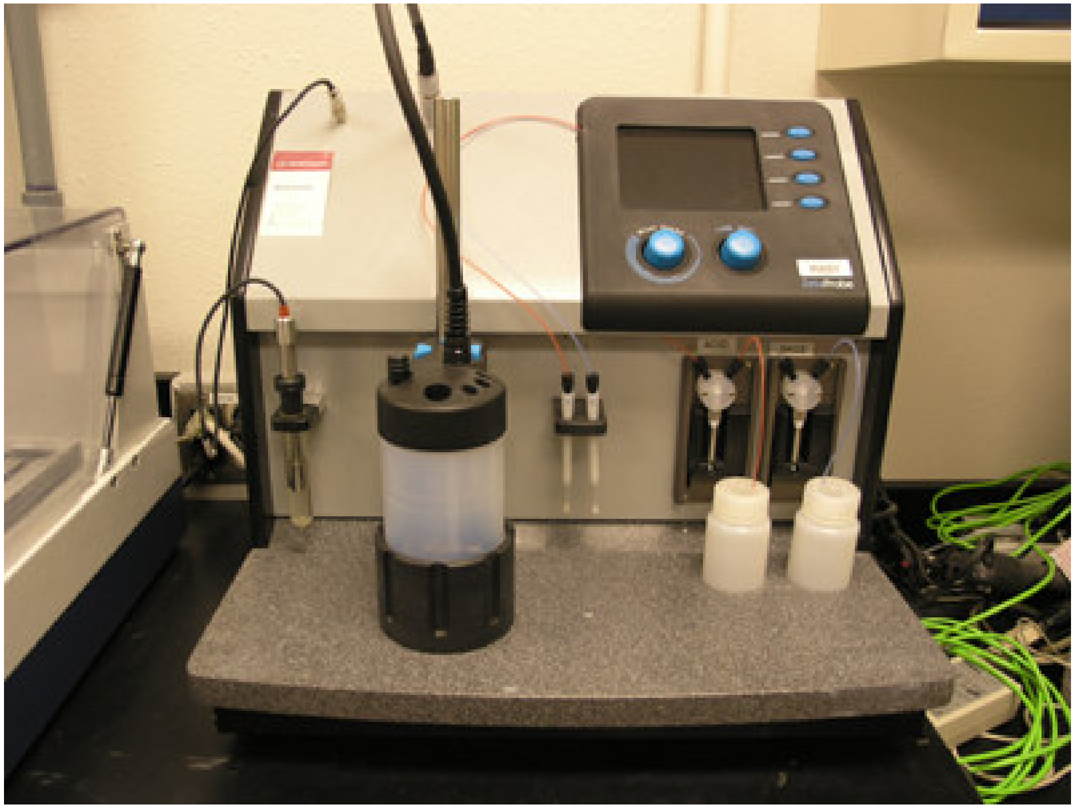
Variety of statistical information on particle size distribution

Micromeritics surface area analysis to determine matrix powder surface area

- Measures specific surface area of powders

- Up to 3 samples analyzed simultaneously
- Degas up to 6 samples in preparation simultaneously at up to 300ºC under nitrogen purge

Colloidal Dynamics zeta-probe to determine matrix powder surface charge



Analysis of zeta potential under a variety of pH, solvent and surfactant conditions

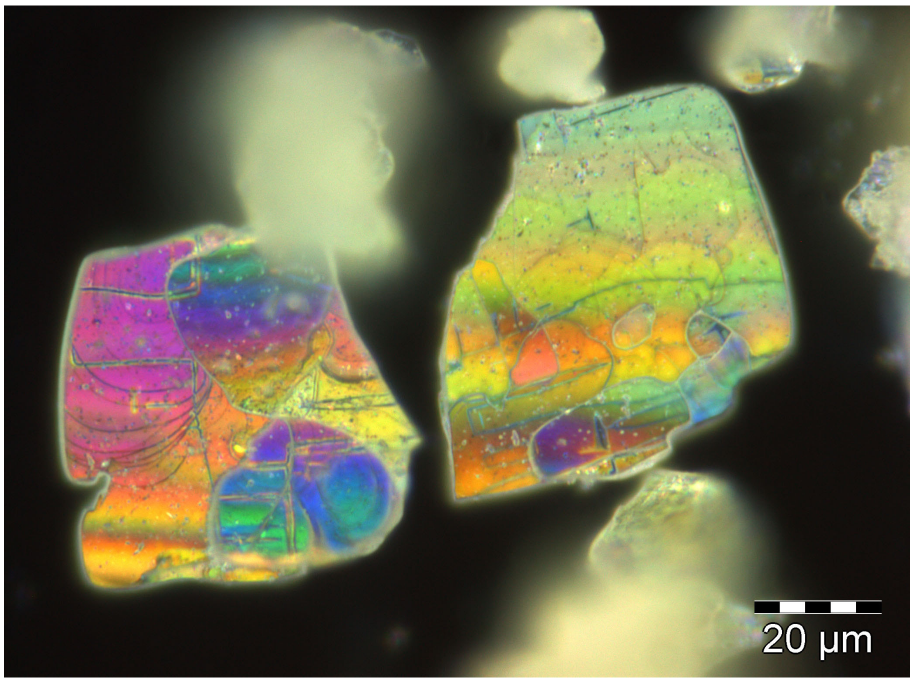
Zeta potential as a function of pH, surfactant addition

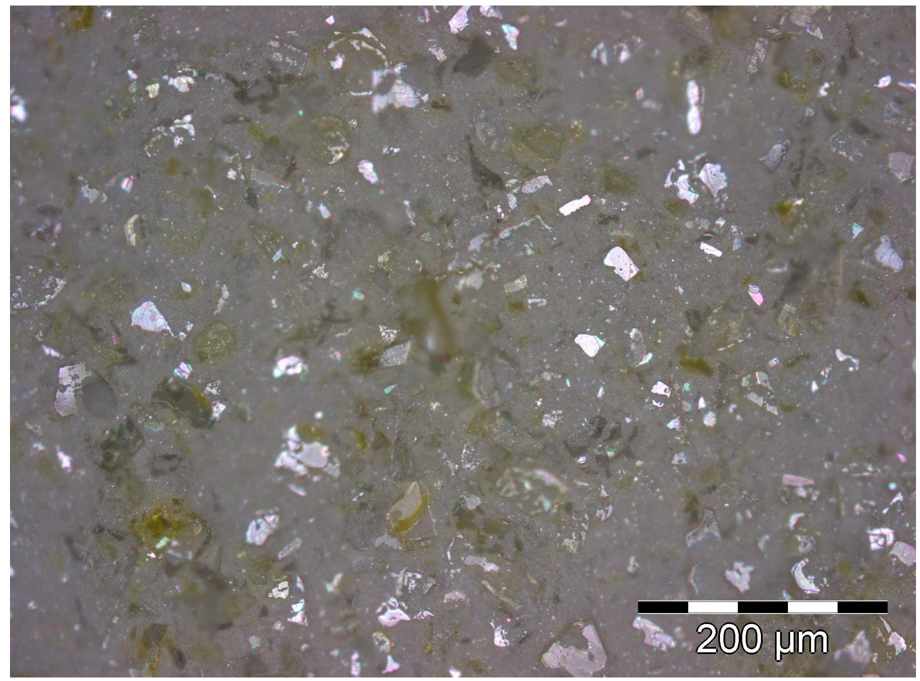
Both aqueous and solvent compatible

Variety of solids loading

Screen printing ink formulation is controlled to achieve the correct ink rheology and robust test samples

10 weight percent seeds + equi-axed powder + vehicle





Ratio of seeds to equi-axed powder is optimized to obtain fully dense, textured samples

Thinky ARE-250 centrifugal mixer to initially homogenize ink

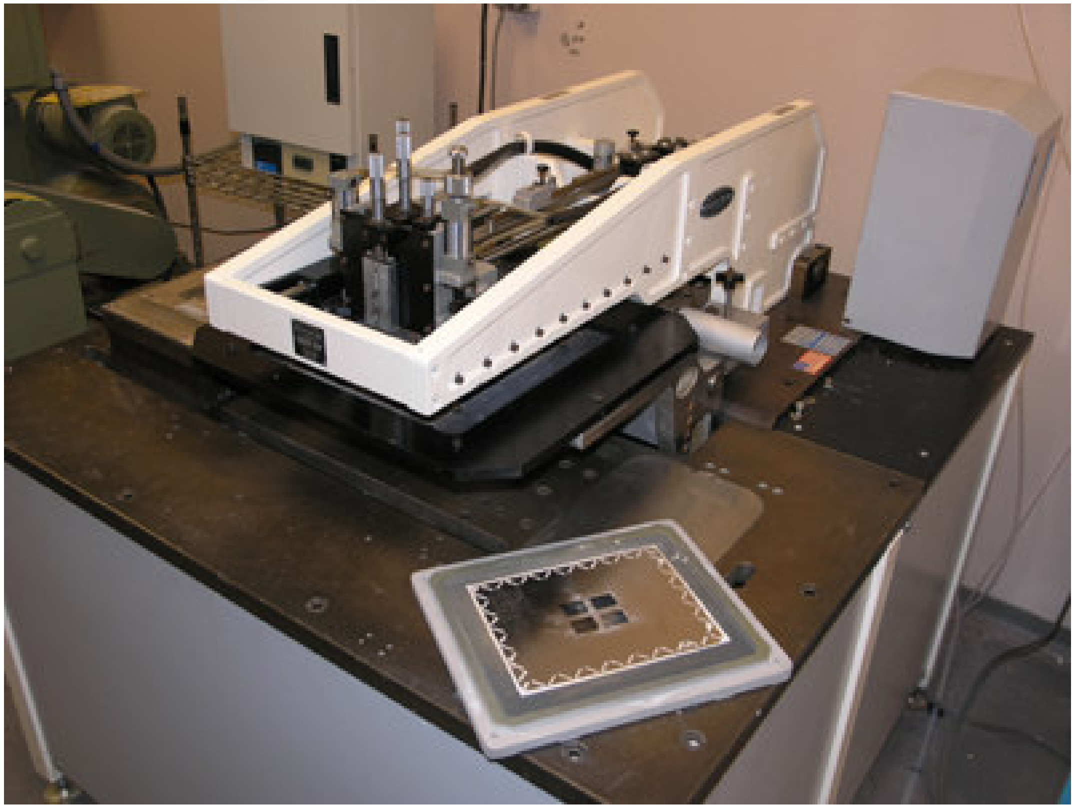
- Homogenous mixing of slurries and pastes
- Up to 2000 rpm
- Several programmable cycles for simultaneous mixing and de-airing
- Up to 210 g per run

Exakt 80E 3-roll mill to fully homogenize ink

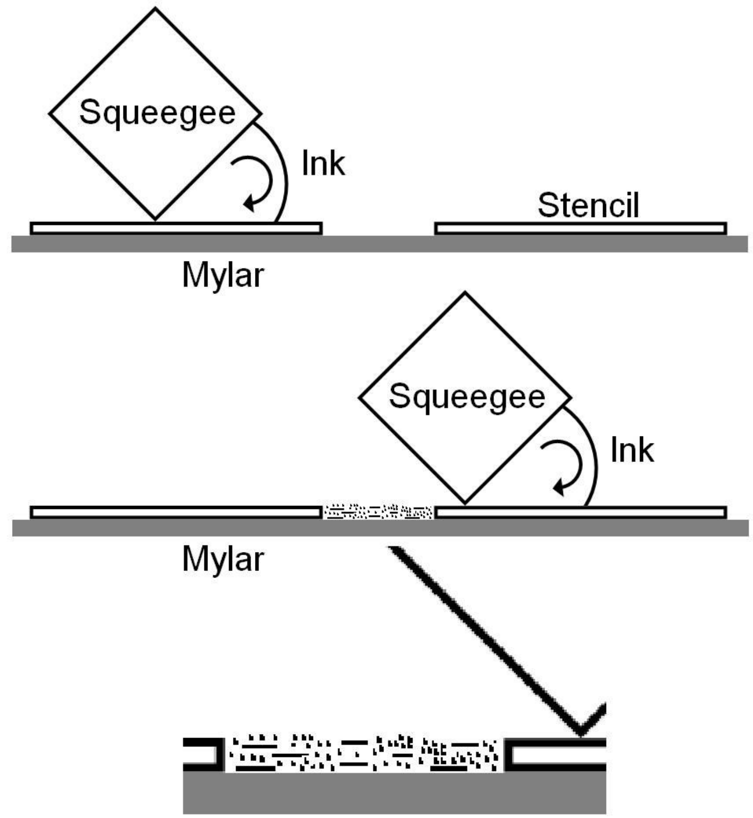
- Homogenization of tape casting slips and screen printing inks
- Calendar green tape

- Multiple speeds
- Temperature controlled rollers (10ºC to 80ºC)
- Multiple gap widths
- Force-mode to disperse nanometric powders
- Data logging for milling conditions

Presco MSP-885 screen printer to fabricate textured green samples



Fabricate thick films of materials



4 inch wafer printing

x, y, z, and rotational control

Variety of squeegee hardness

Print speed and distance control

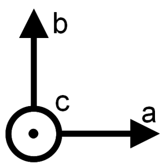
Both stencil and screens available

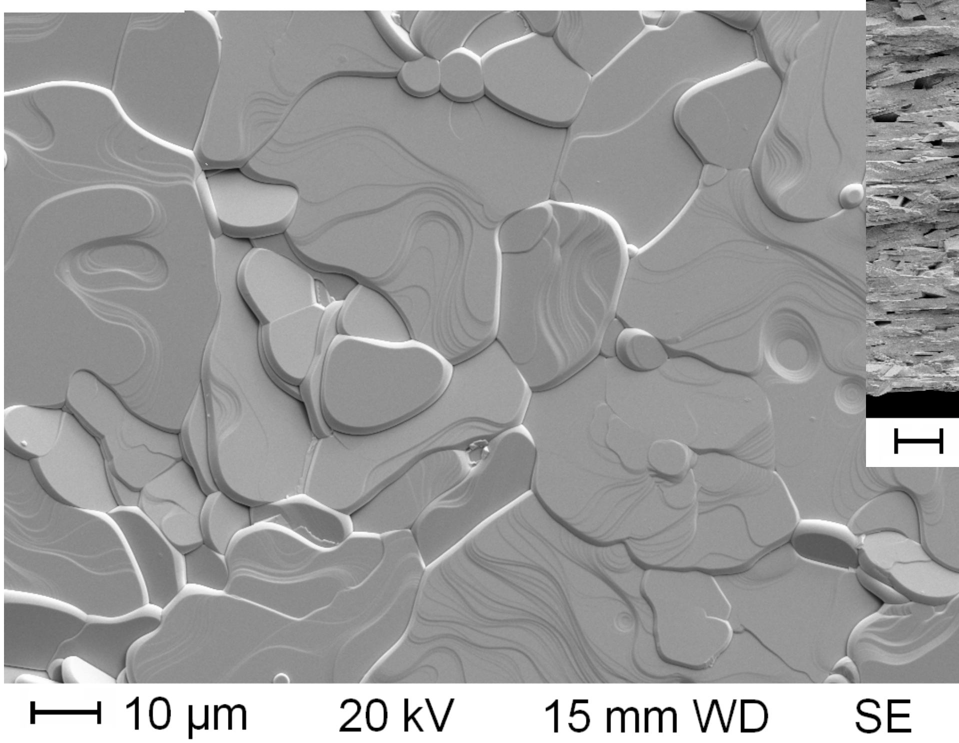
Furnaces and ovens to remove organics and sinter samples

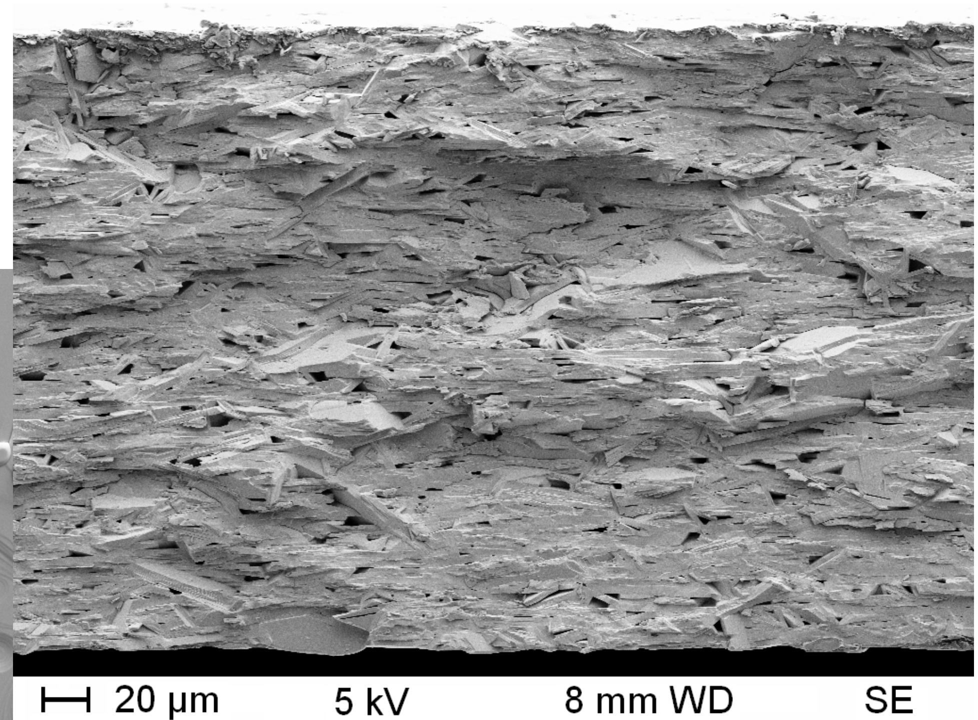
Sintering of samples
Removal of organics

Multiple furnaces reaching 1200ºC, 1500ºC, and 1700ºC
Several ovens for organic removal
Tube furnaces with controlled atmosphere

Upon sintering, seeds grow at the expense of the equi-axial powder matrix



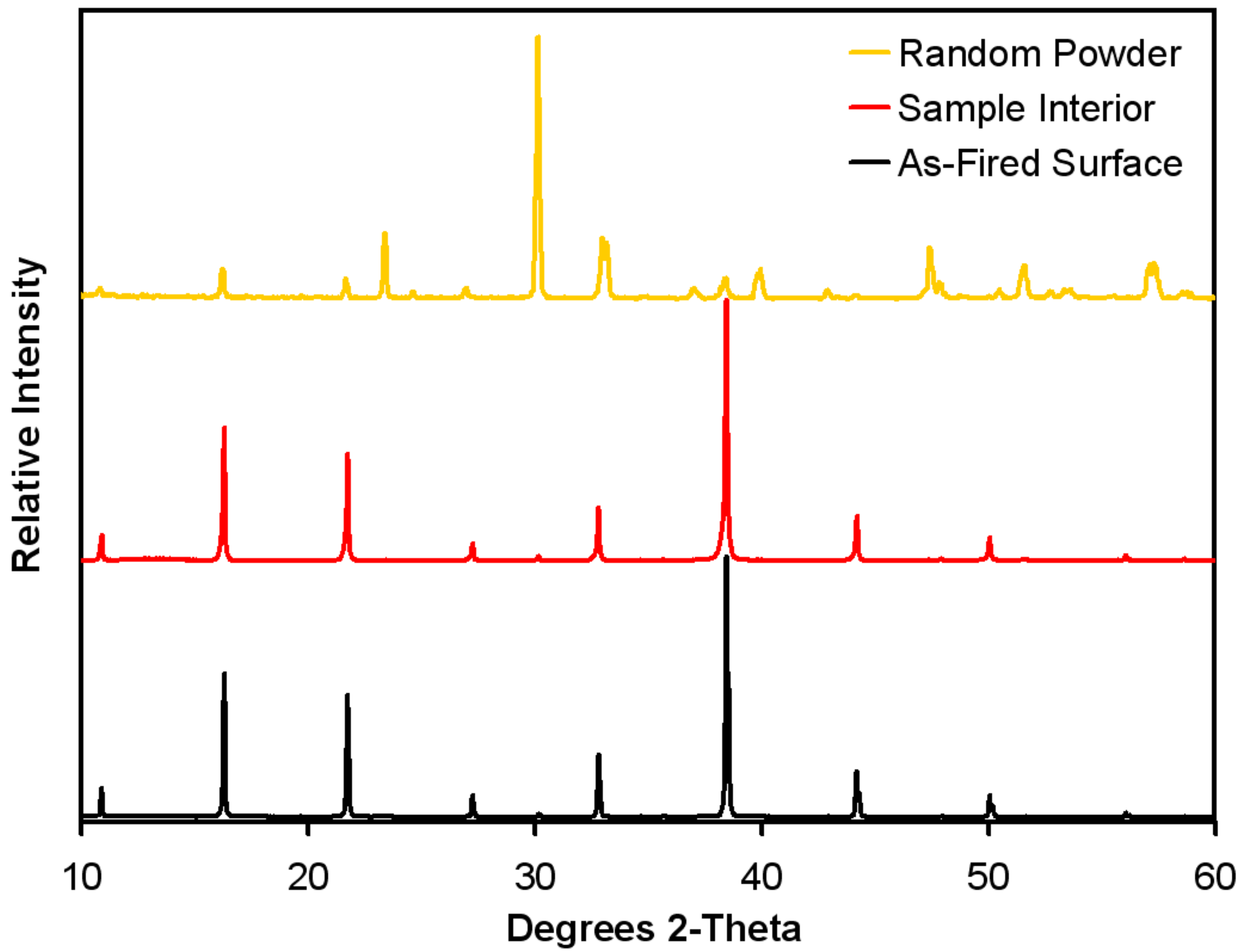




B McKenzie
Sandia Labs

10 weight percent seeds is sufficient to induce a large degree of texture in the sintered samples

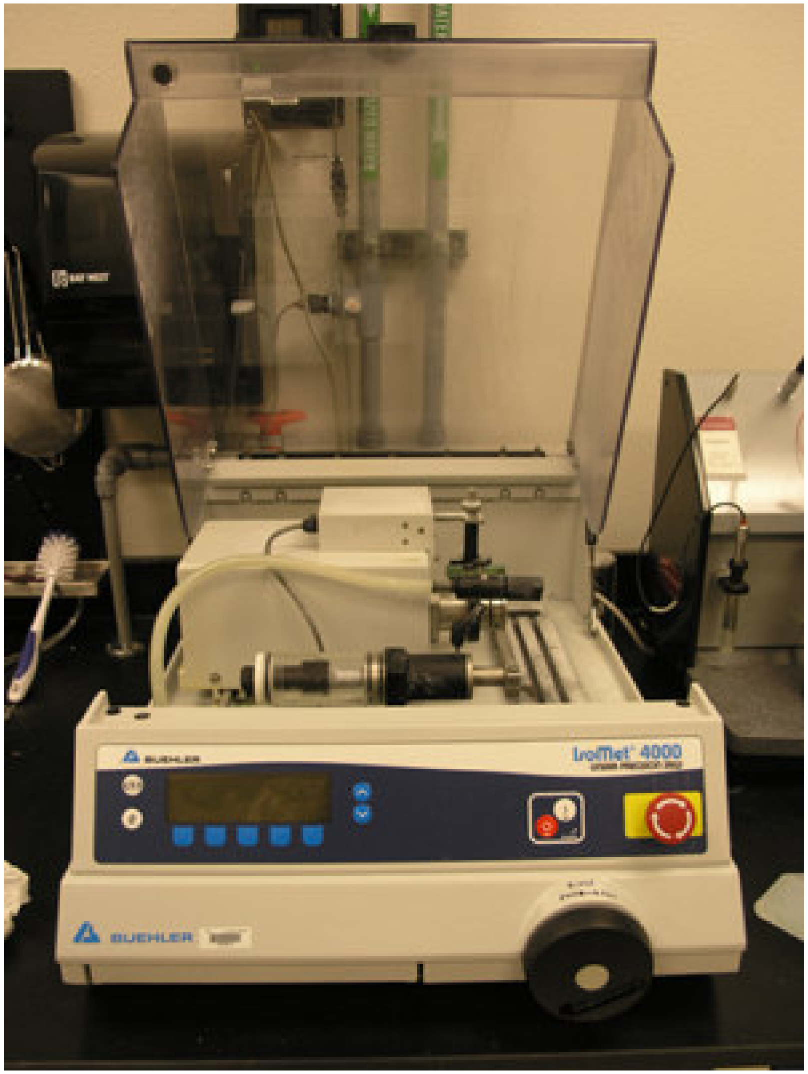
A high degree of texture is induced by printing



M Rodriguez
Sandia Labs

The Lotgering factor is 0.99 for the as-fired surface of the sintered screen printed sample and 0.98 for the sample interior

Buehler Isomet 4000 high speed saw to section samples



Cutting samples to precise dimensions

Up to 7" blade

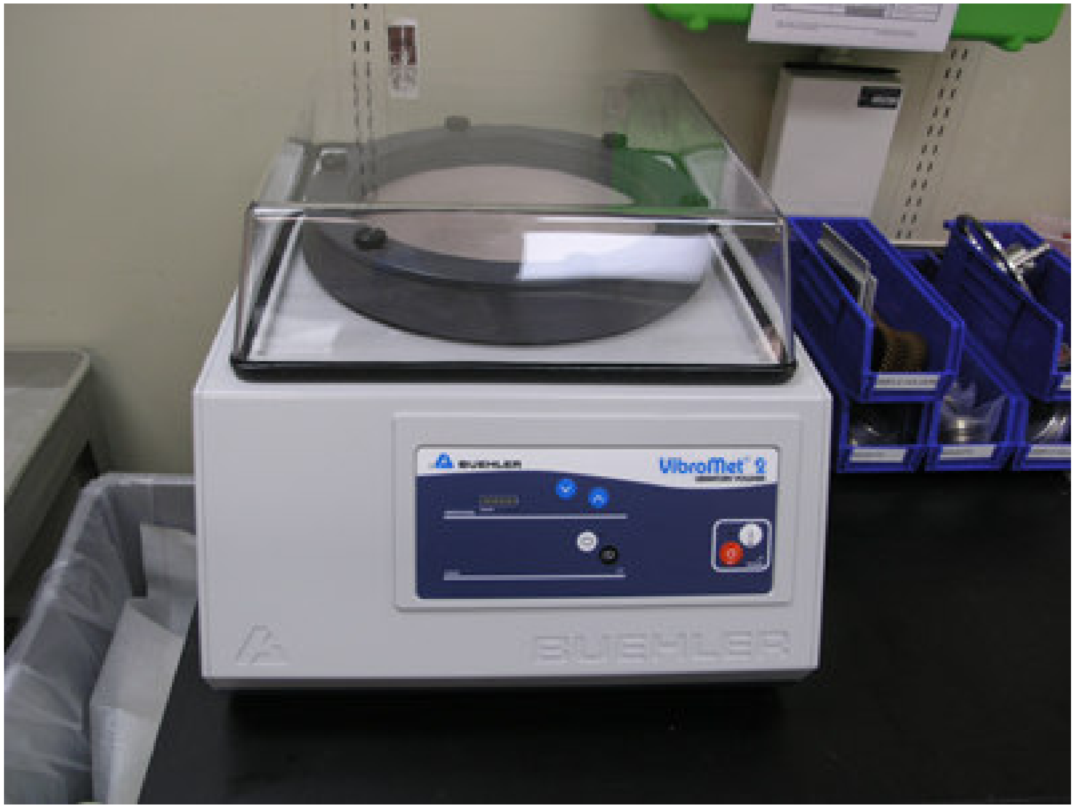
Variety of sample chucks

Wide range of feed rates and cutting speeds

Automatic dressing

Multiple programs

Buehler VibroMet 2 vibratory polisher to achieve sub-micron surface finish for analysis

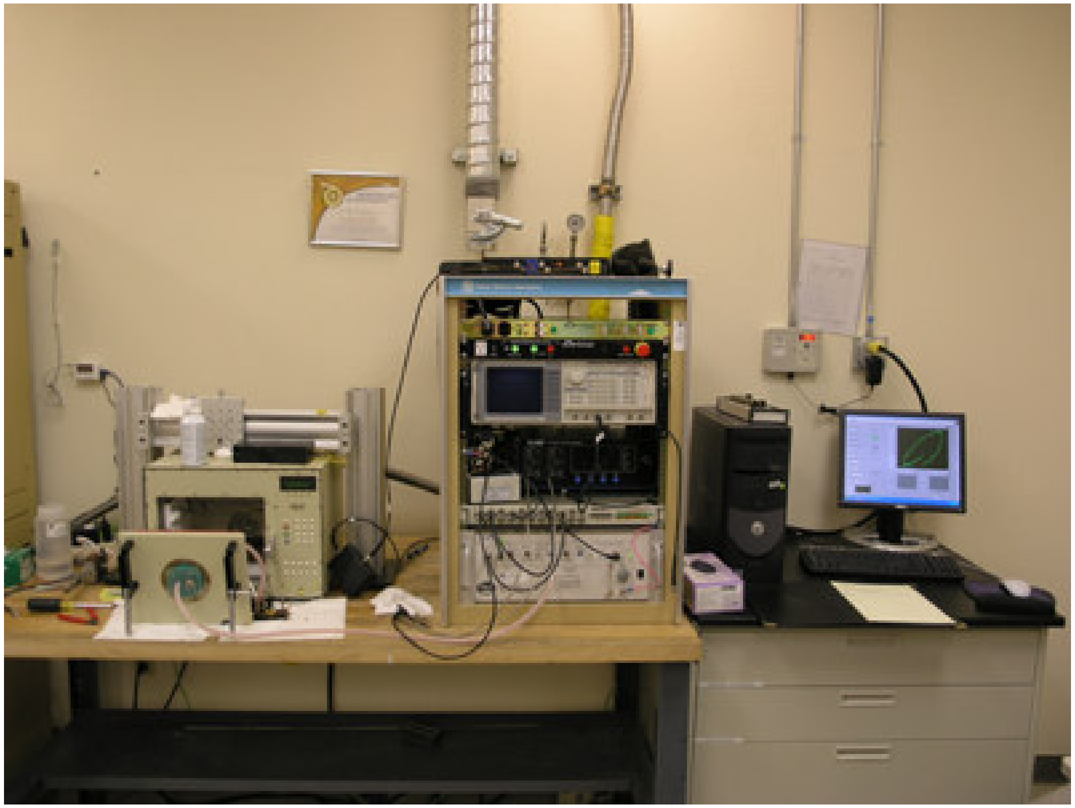


Final surface polishing for SEM, EBSD, etc analysis

Multiple speeds

Variety of finishing cloths and polishing pastes

Sandia looper to evaluate polarization behavior



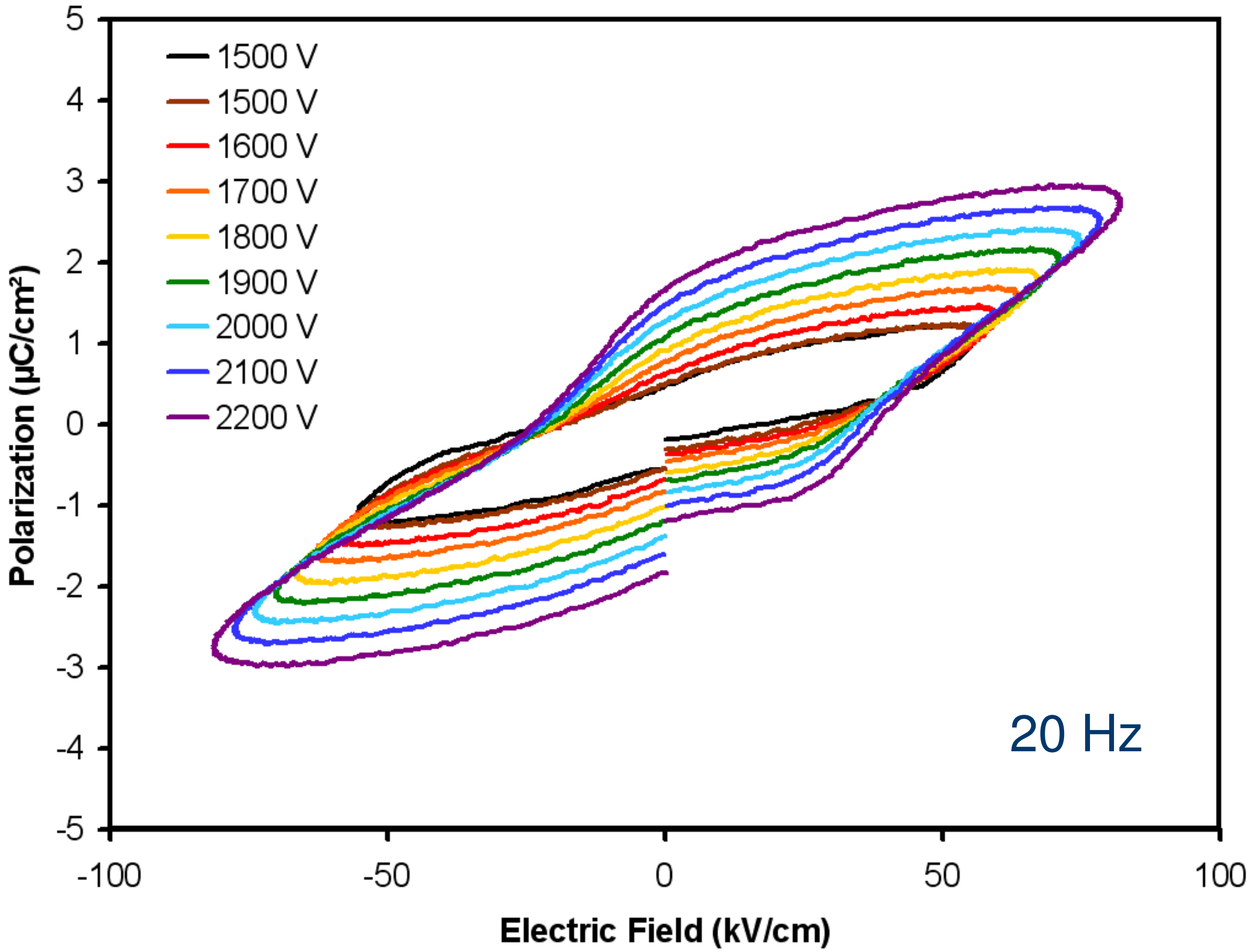
Polarization as a function of electric field

-100ºC to 250ºC measurement

Effectively DC to 20 Hz

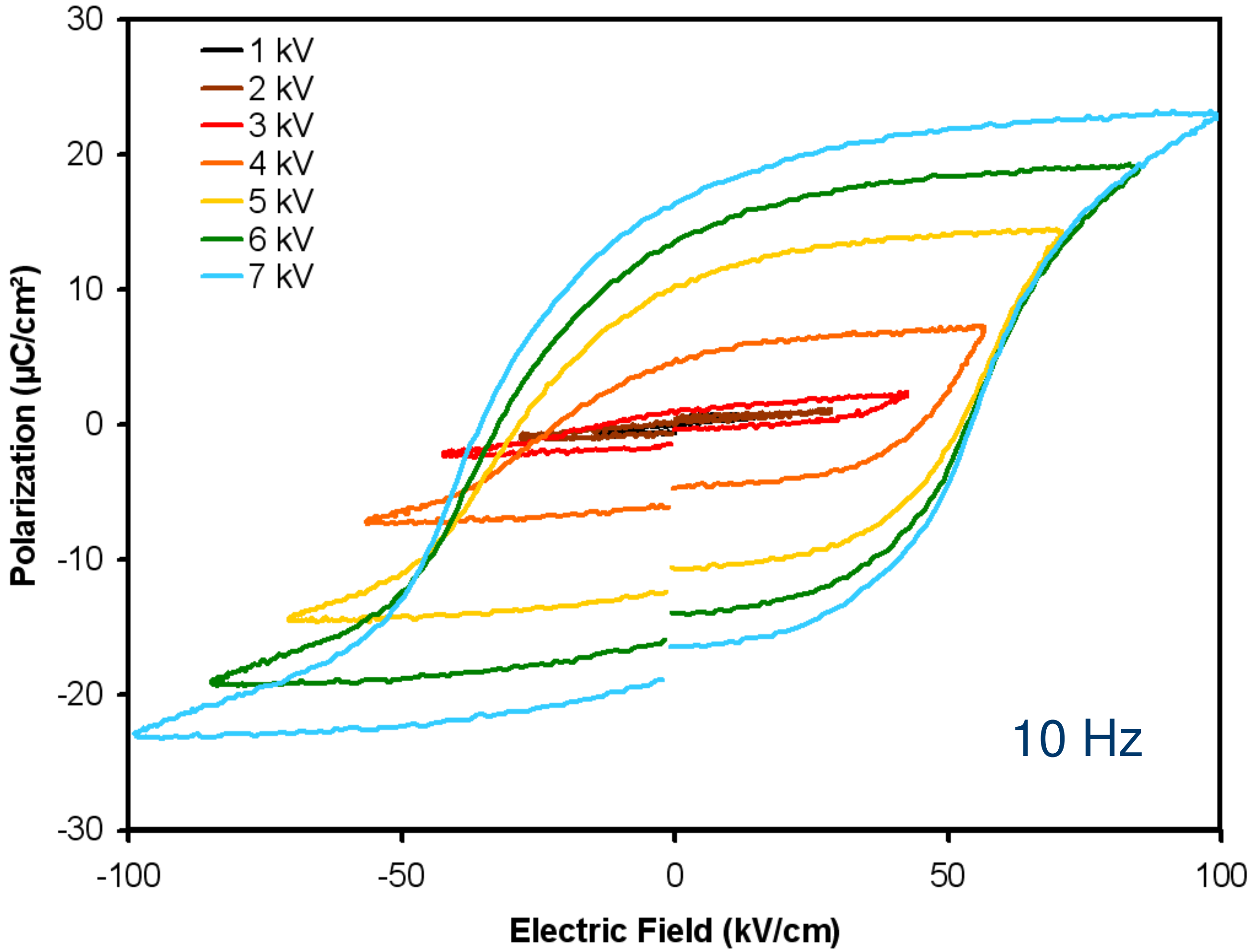
± 10,000 V drive voltage

Printed samples withstand high electric fields but show poor polarization along the c-axis



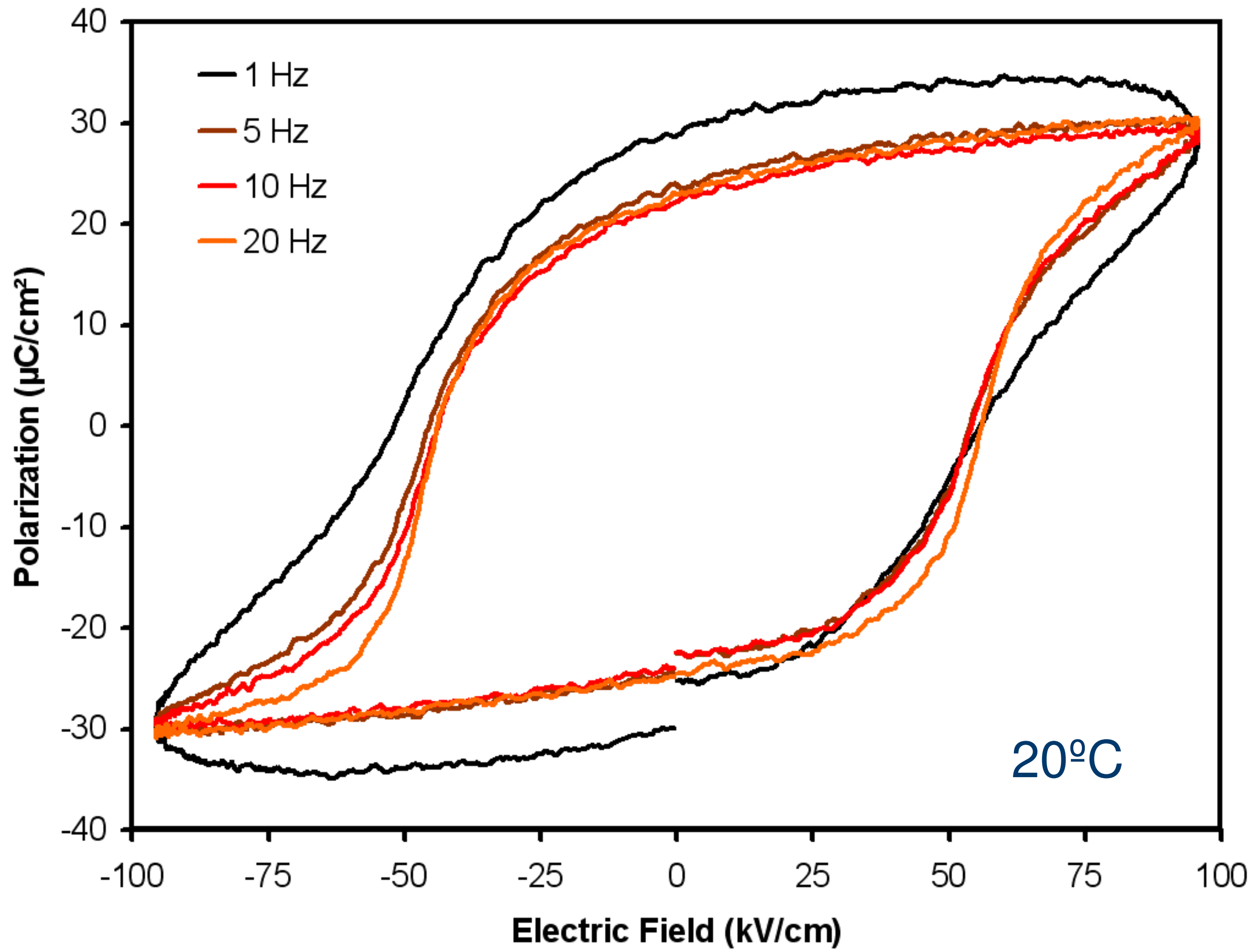
The P-E loops show some aging effects and do not maintain a consistent shape over larger drive voltages

Samples withstand high electric fields and show excellent polarization and high coercive fields in the a-b plane



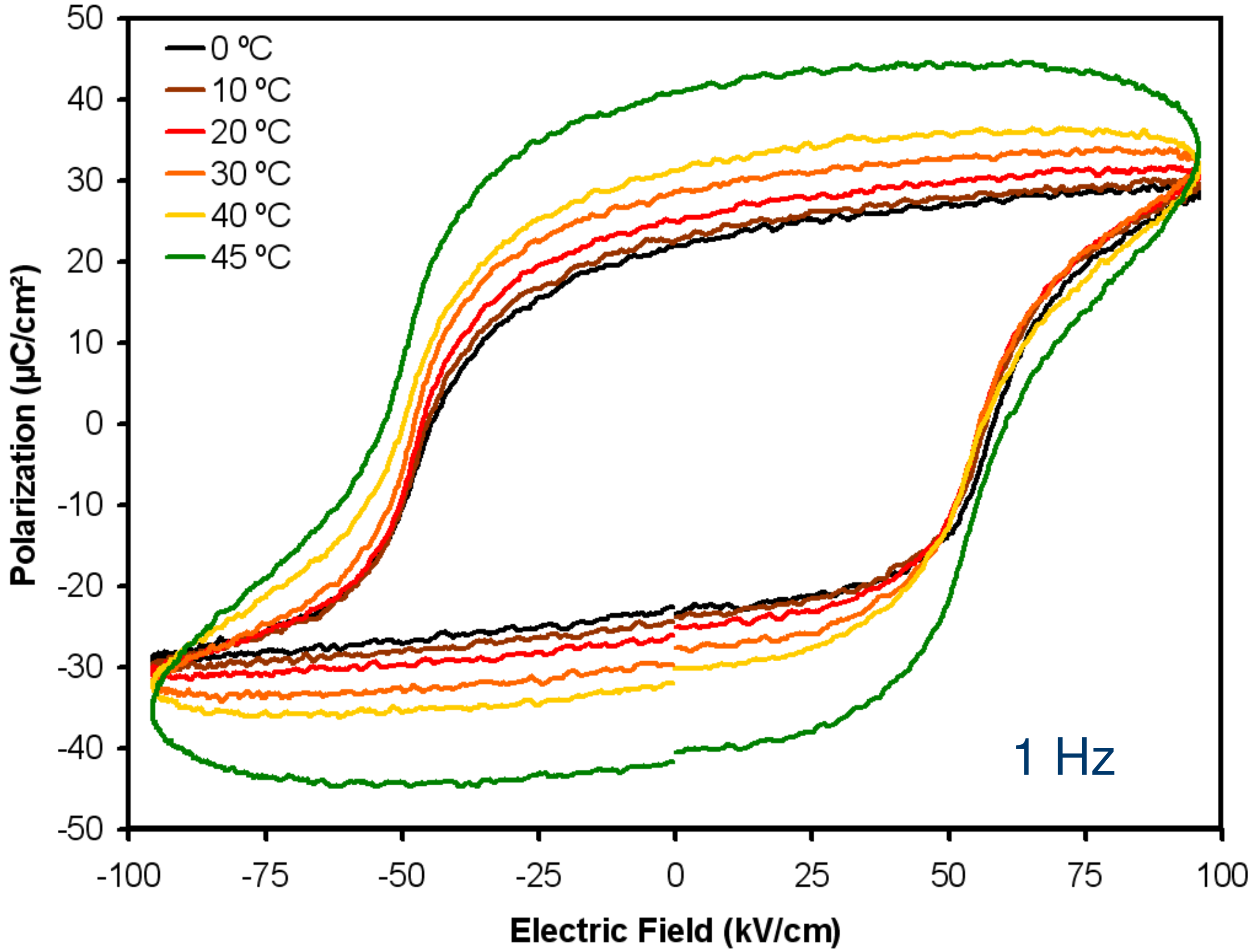
The P-E loops are not centered about the origin and show a degree of pinching at negative electric fields

The polarization loop decays at low frequency



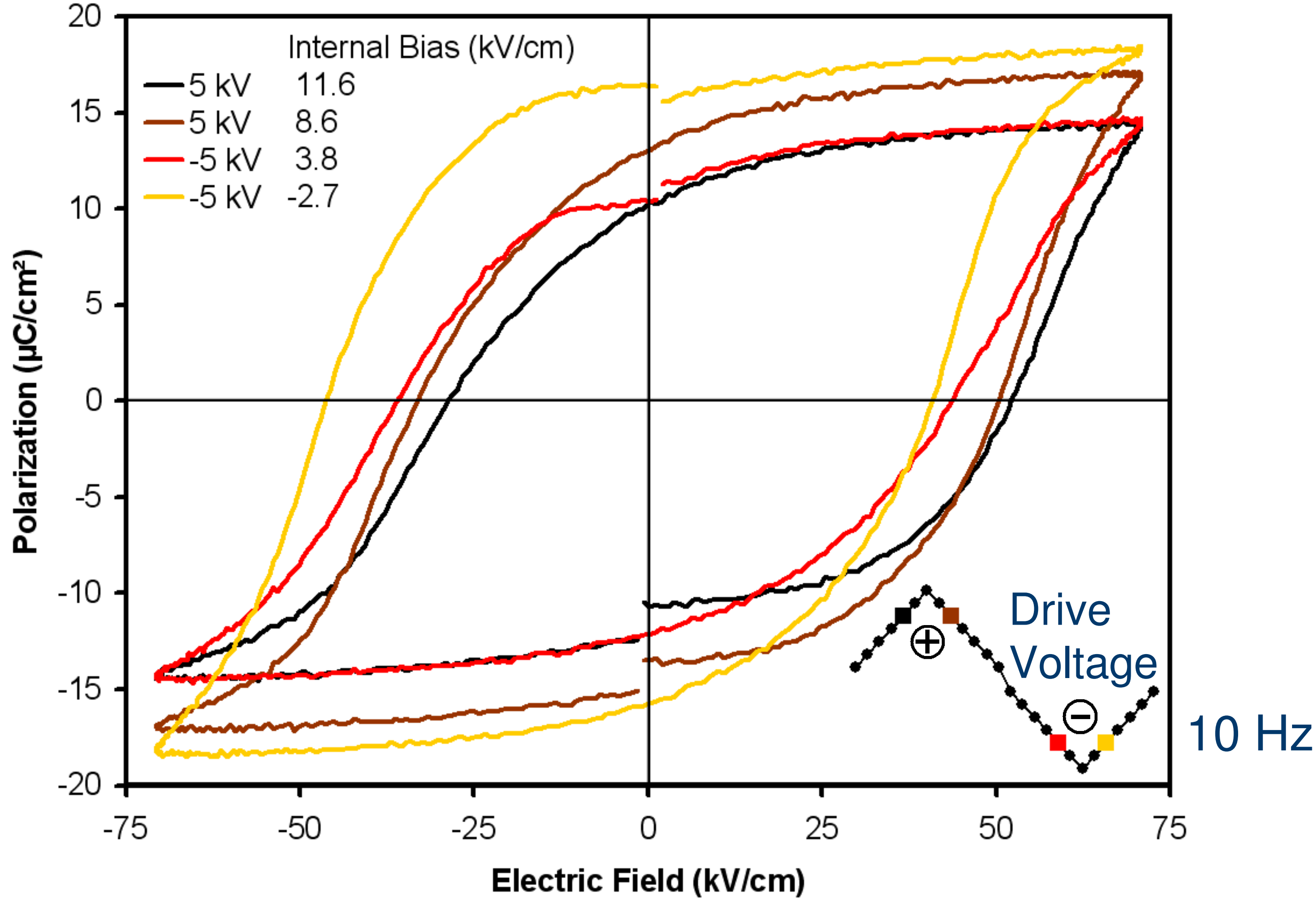
Some aging is present at lower frequencies and the loop begins to open, indicating conduction mechanisms

The polarization loop begins to decay just above room temperature



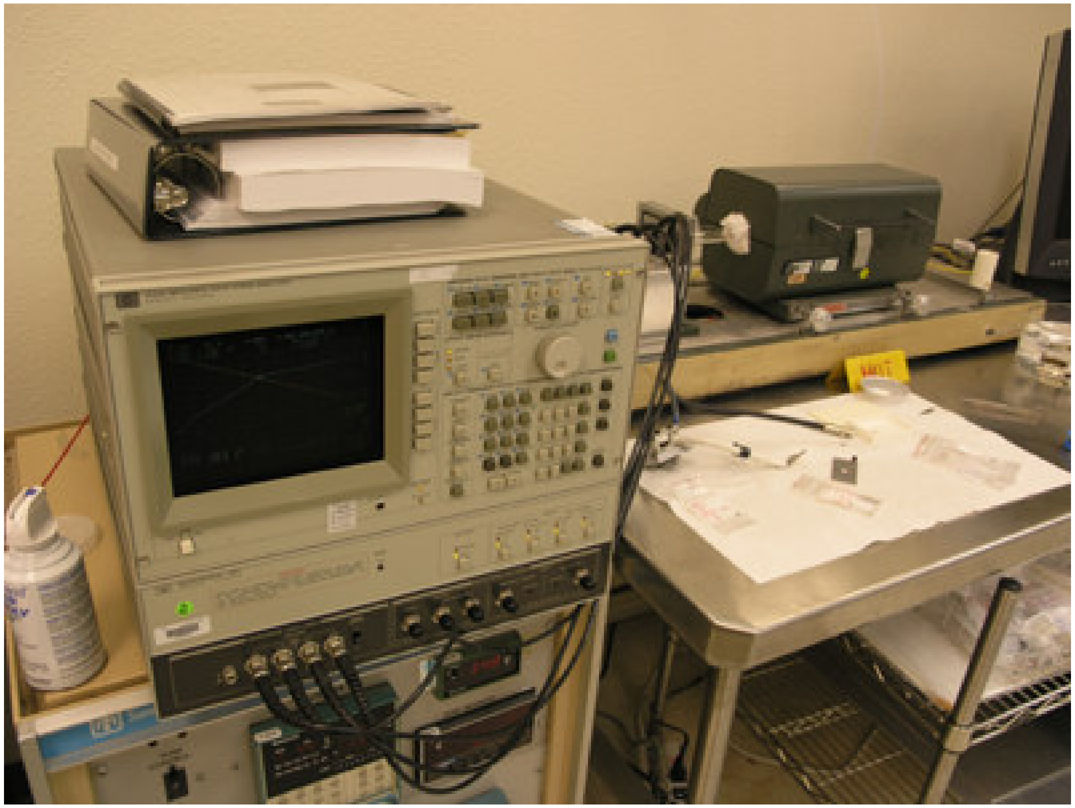
The opening of the loop indicates loss through conduction mechanisms

The polarization depends on the electric field history



The P-E loops are not centered about the origin and the shape changes depending on the drive voltage previously experienced

High temperature Sandia weak-field relative permittivity



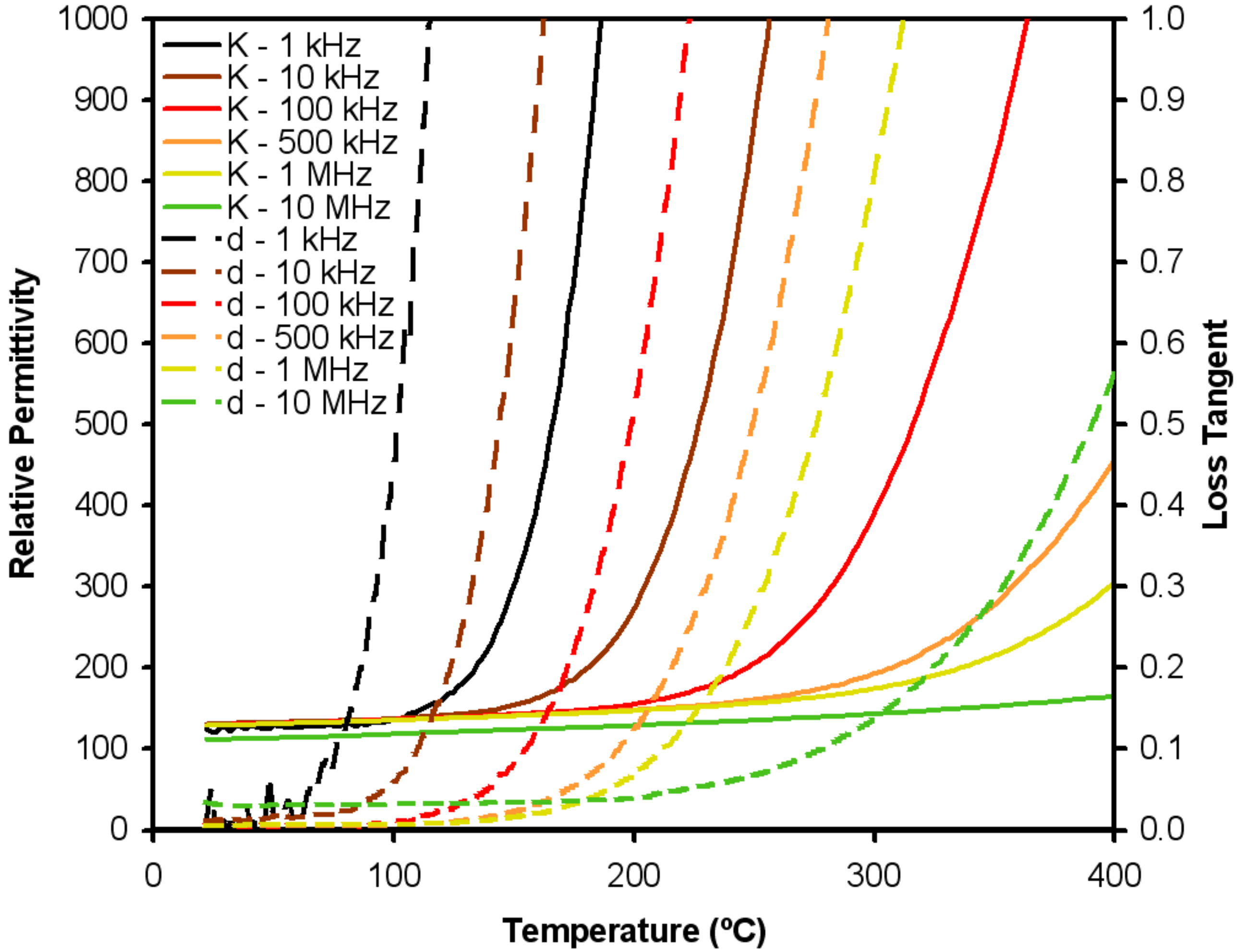
Relative permittivity characterization as a function of temperature and frequency

Room temperature to 800ºC measurement

40 Hz to 15 MHz

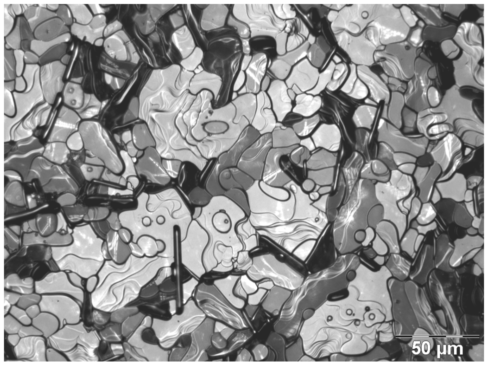
Programmable thermal profile

Higher frequencies show the best relative permittivity and lowest loss tangent



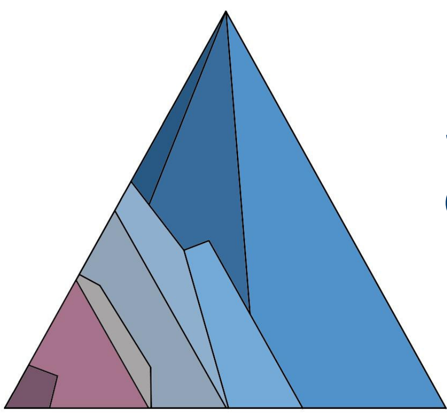
Previous work shows that the conduction mechanisms can be mitigated by doping with group V, VI, and other elements

Textured layer-structure, lead-free materials show considerable promise to replace lead-based dielectrics



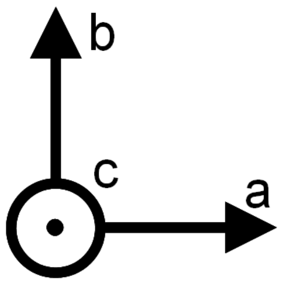
Screen printing has been shown to result in near single crystal texture

Textured materials show promise to achieve significant gains in dielectric properties

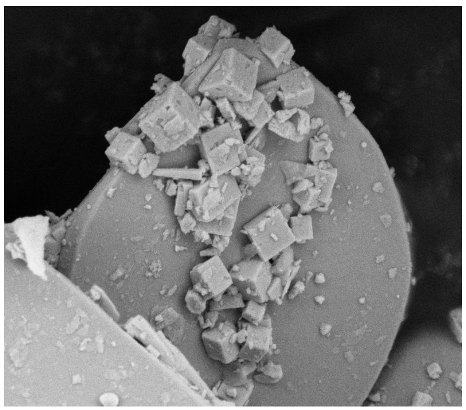


Several layer-structure materials have yet to be examined in the textured and untextured state

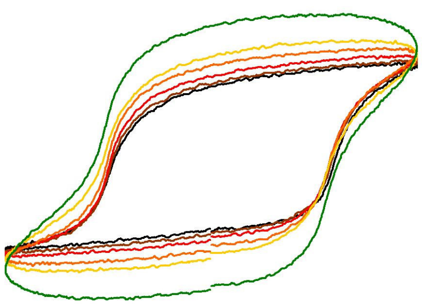
Textured ceramics: the big picture



Benefits of texturing are heavily influenced by material system characteristics



Anisotropic properties give rise to many unique opportunities



Crystalline texturing may also enhance “undesirable” properties – application dependent

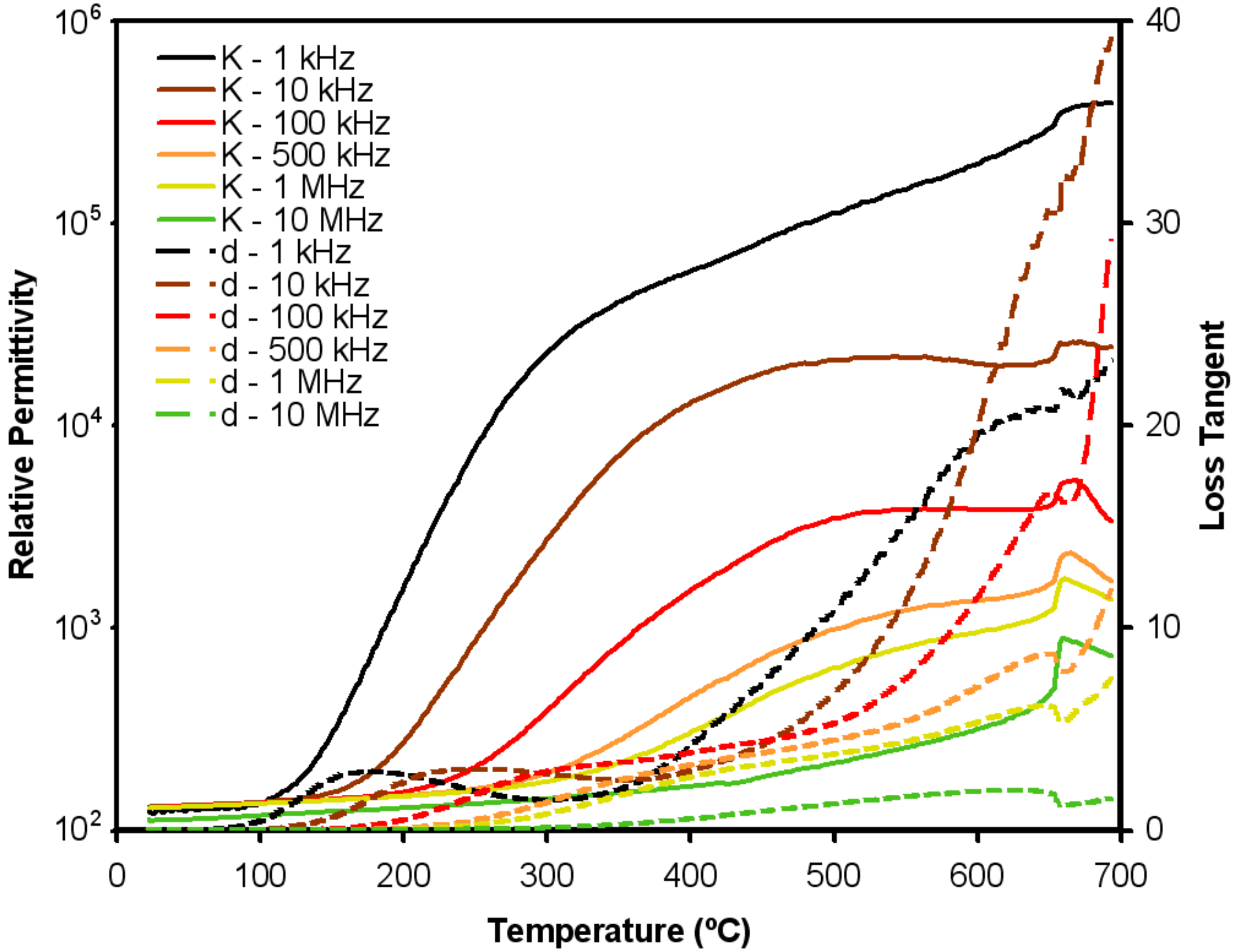
Questions?

Lotgering Factor is calculated from the powder diffraction pattern from 10 to 50 degrees 2-Theta

$$F = \frac{P - P_0}{1 - P_0}$$

$$P = \frac{\sum I\,(00l)}{\sum I\,(hkl)}, P_0 = \frac{\sum I_0\,(00l)}{\sum I_0\,(hkl)}$$

Textured samples show a small increase in relative permittivity but high loss in the a-b plane



The phase transition occurs at approximately 660ºC for this material