

# ELECTROCALORIC RESPONSE OF STRESS-FREE RELAXOR FERROELECTRICS BY EXPERIMENTAL AND ANALYTICAL TECHNIQUES

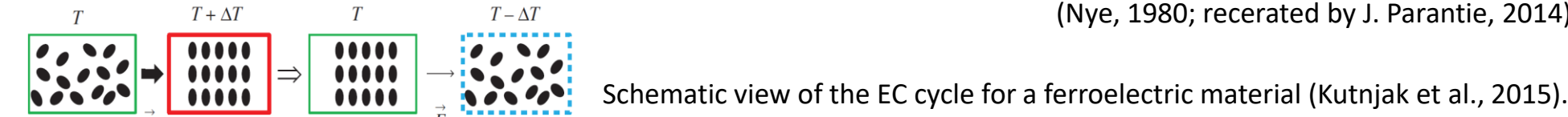
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## MOTIVATION

Electronic circuits and devices working in extreme environments require compact, efficient and environmentally friendly systems and materials for on-chip or on-board micro-cooling applications and energy storage, as such systems can be expected to operate in a large temperature range. Conventional cooling (refrigeration) technologies use a gas as the coolant and pressure to induce a change in the state of the coolant. The refrigeration is obtained through the compression and expansion cycles of the gas where the entropy change in the gas each time the gas expands. Gas is the agent to remove heat from the medium via entropy transfer. Although this technology is the most commonly used one in conventional refrigeration and its coefficient of performance (COP = inputpower/output cooling power) is high, the components are rather bulky and not suitable for miniaturization. Alternative cooling technologies include the thermoelectrics, magnetocalorics and electrocalorics. Such systems are often called “solid-state refrigeration”, and they utilize three principles: inducing a temperature change by running a current through a junction of two different materials, i.e. the thermoelectric effect (TEE); cooling through adiabatic demagnetization, which is the basis of the magnetocaloric effect (MCE), and cooling through adiabatic depolarization that is known as the electrocaloric effect (ECE).

Electrocaloric (EC) effect, which is the main subject of this work, is a coupling between electrical and thermal properties. EC effect is an electric field induced temperature and/or entropy change in an insulating material. With a similar analogy to magnetocalorics, adiabatic depolarization after the external electric field is removed results in cooling if the material was initially polarized with an electric field under adiabatic conditions. When electrical dipoles return to their disordered state during the adiabatic depolarization, the entropy of the system increases. Since it is much simpler to achieve high electrical fields compared to the magnetic fields, ECE allows the possibility for a variety of applications and miniaturization. The EC devices with potential COP values of 7-10 can possibly be developed for cooling applications in microrobotics and microelectronics such as microchips working in harsh environments that are faced in aviation and space exploration.

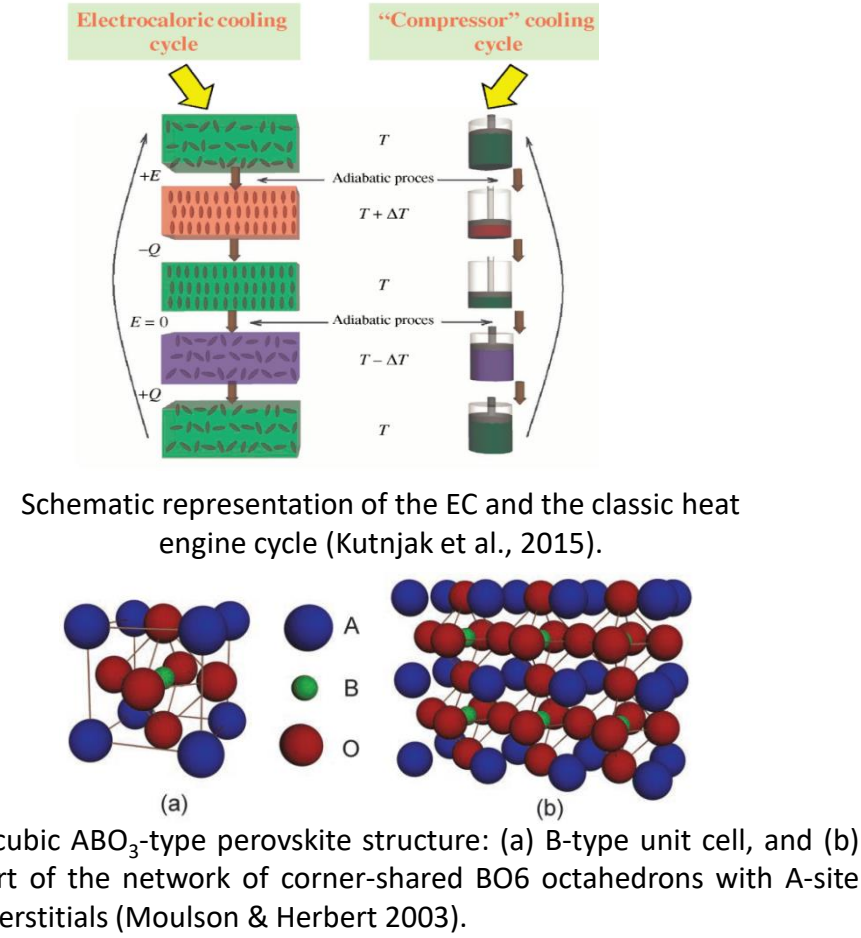


## OBJECTIVE

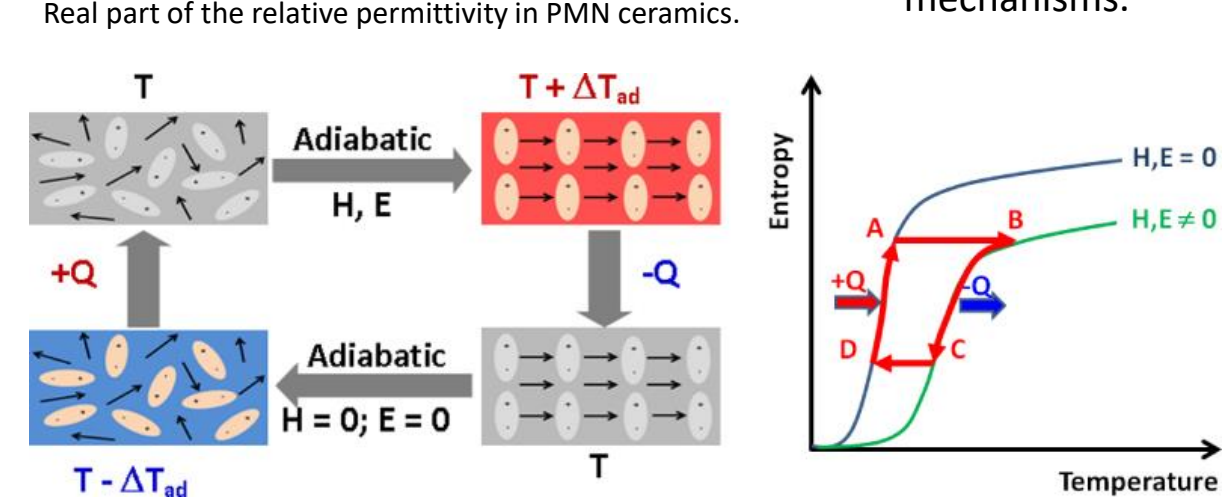
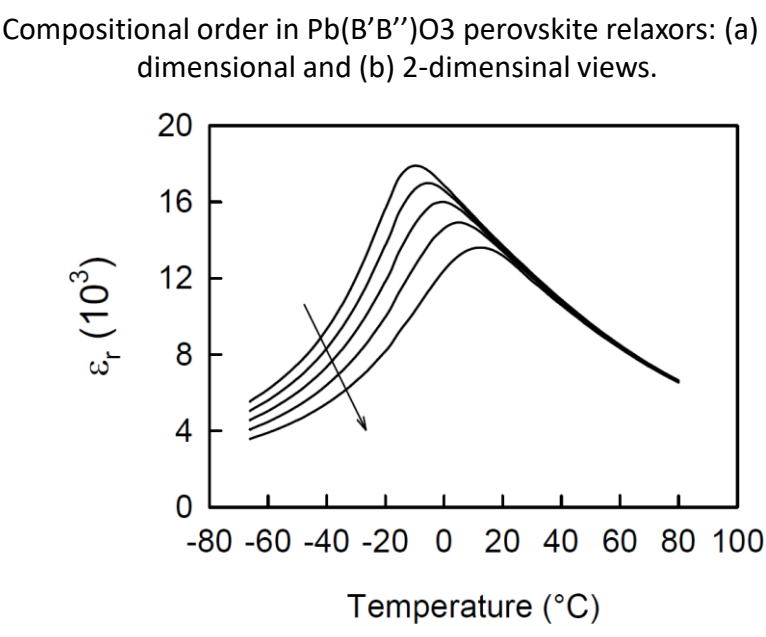
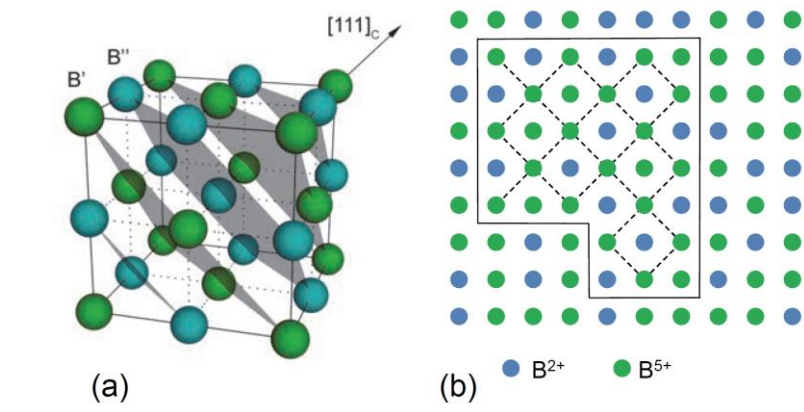
The research study that we propose on the investigation of the effect of crystallographic anisotropy and defects on the electrocaloric response of stress-free relaxor ferroelectric plates is in essence oriented towards developing a basic understanding of this phenomenon. Electronic circuits and devices working in these extreme environments require compact, light-weight, efficient and environmentally friendly systems, materials for on-chip, or on-board micro-cooling or even energy storage applications where precise control of local temperatures might be required in a large operational temperature range. Thus, increasing the ECE effect through the development and engineering of a crystallographic texture in relaxor ferroelectric materials in plate form may provide a viable future alternative.

## PROBLEMS

- Ferroelectrics display large EC effect, especially in thin film form, in a temperature window around the paraelectric-ferroelectric transition temperature and can be driven with much lower electric fields, however, as it will be discussed in the following sections, the cooling volume and the stressed state of the films limits the applicability in this form.
- The polycrystalline bulk ferroelectrics, on the other hand, would be a viable alternative to thin films, but their EC effect would be much lower and the driving electric fields would be much higher.
- The single crystals, display higher EC effect (Moya et al., 2013) compared to their polycrystalline counterparts, indicating the drastic effect of anisotropy on ECE, but they are more difficult and expensive to synthesize.
- Additionally, the temperature window that the large ECE is observed is rather narrow (< 5K) in normal ferroelectrics, whereas it is rather broad (5-50 K) in relaxor ferroelectrics with diffuse phase transition.



## APPROACH of THE STUDY



From: M. M. Vapson, J. Phys. D. 46, 34 (2013)

A schematic representation of an electrocaloric cooling cycle: The entropy changes during the cycle.

When an external E is applied to the material at T, the temperature of an active EC element is adiabatically increased (stage transition A→B) to T+ΔT. This additional heat can be dissipated in a heat sink, which causes the active element to decrease its temperature back to T (B→C). Then, the removal of the applied E further decreases the temperature to T-ΔT within the active isolated material. Now, some heat energy can be extracted from a desired heat source which increases the temperature of the active EC element to T and completes the cooling cycle. (Scott 2011).

## ANALYTICAL VIEW

The change in Gibbs free energy density, dG, of a dielectric material is expressed as a function of temperature T, entropy S, stress X, strain x, electric field E, and dielectric polarization P and can be written as :

$$dG = -SdT - x_i X_i - P_j dE_j \quad \text{Change in Gibbs free energy in differential form}$$

$$S = - \left( \frac{\partial G}{\partial T} \right)_{X,P} \quad x_i = - \left( \frac{\partial G}{\partial X_i} \right)_{T,P} \quad P_j = - \left( \frac{\partial G}{\partial E_j} \right)_{T,X} \quad \text{Relation of stress, strain and polarization parameters to Gibbs energy via the coefficient relations}$$

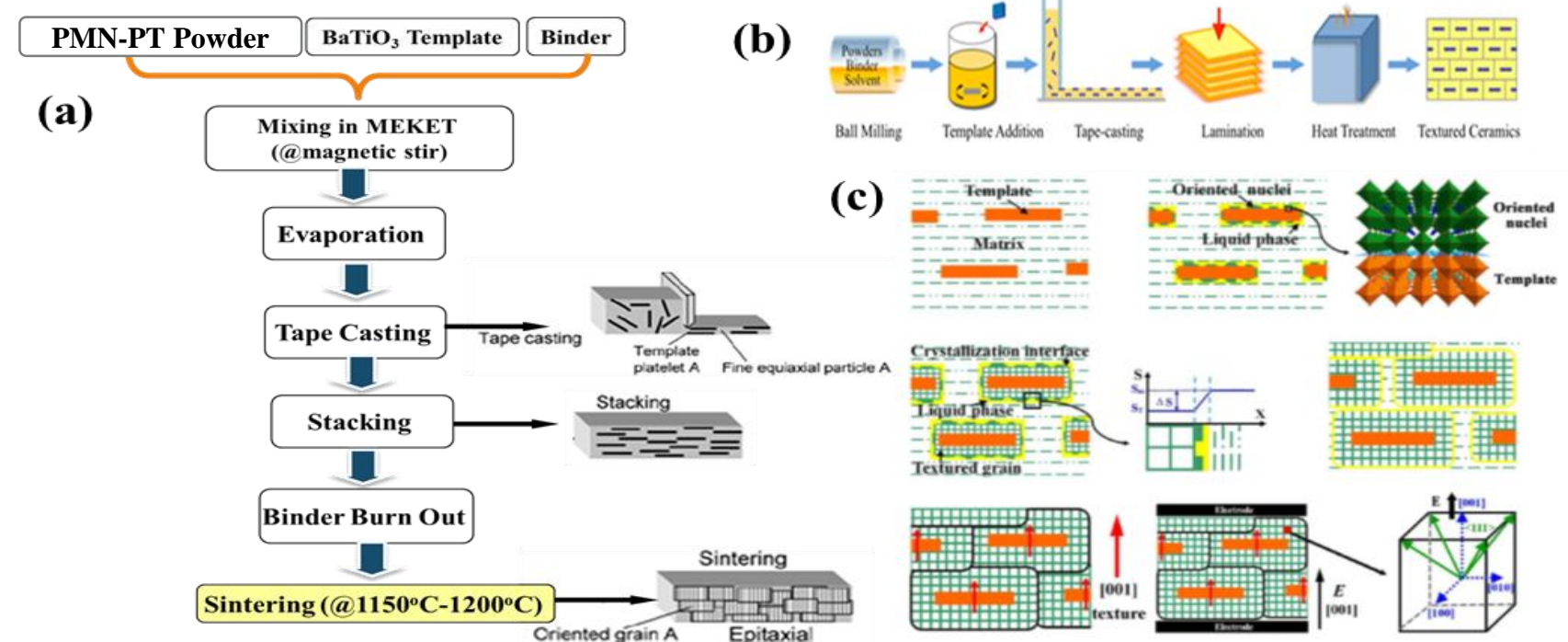
$$\left( \frac{\partial S}{\partial E_i} \right)_{T,X} = \left( \frac{\partial P_i}{\partial T} \right)_{E,X} \quad \text{Relation between S and P}$$

$$dS = \left( \frac{\partial S}{\partial E} \right)_T dE + \left( \frac{\partial S}{\partial T} \right)_E dT = 0 \quad \text{Pyroelectric coefficient at constant electric field: } p_E = \left( \frac{\partial P}{\partial T} \right)_E$$

Here,  $C_E = \rho c_E$  is the heat capacity per unit volume (in  $J/(K \cdot m^3)$ ),  $C_E = T \left( \frac{\partial S}{\partial T} \right)_E$

## EXPERIMENTAL PLAN

- PMN-PT powders will synthesized through solid state calcination method following the columbite precursor route to obtain phase-pure perovskite structure. PMN-PT ceramics will be produced using two different methods: dry pressing and tape casting.
- Dry pressing and sintering will be used to investigate the effect of composition and dopants on the Curie temperature and electrical properties.
- Textured ceramics with grains oriented along specific crystallographic directions will be fabricated using the combination of templated grain growth (TGG) and tape-casting methods.
- The TGG technique consists of the orientation of single crystal template particles in the matrix, followed by a high temperature annealing process that induces grain growth and densification.
- The single crystal template particles will be synthesized through a two-step molten salt synthesis method followed by a topochemical microcrystal conversion process.



## Measurement of the Electrocaloric Response

### Indirect Determination from P-E Hysteresis

Polarization P(E, T) will be measured as a function of electric field and temperature and the electrocaloric response will be calculated using equation:

$$\Delta T_{EC} = - \int_{E_1}^{E_2} \frac{T(E)}{\rho c_E(T)} \left( \frac{\partial P}{\partial T} \right)_E dE$$

where,  $\Delta T_{EC} = T(E_2) - T(E_1)$  is the magnitude of the ECE, i.e. Electrocaloric temperature change under the change of an electric field from  $E_1$  to  $E_2$ ,  $\rho$  is the density of the material and  $c_E$  is the specific heat.

However, due to the difficulties in obtaining the derivative  $(\partial P / \partial T)_E$  in the vicinity of the discontinuous phase transitions, the ECE predictions of the indirect method in the relaxor ferroelectric PMN-PT materials will also be tested by the direct method, the so-called electrocaloric thermometry.

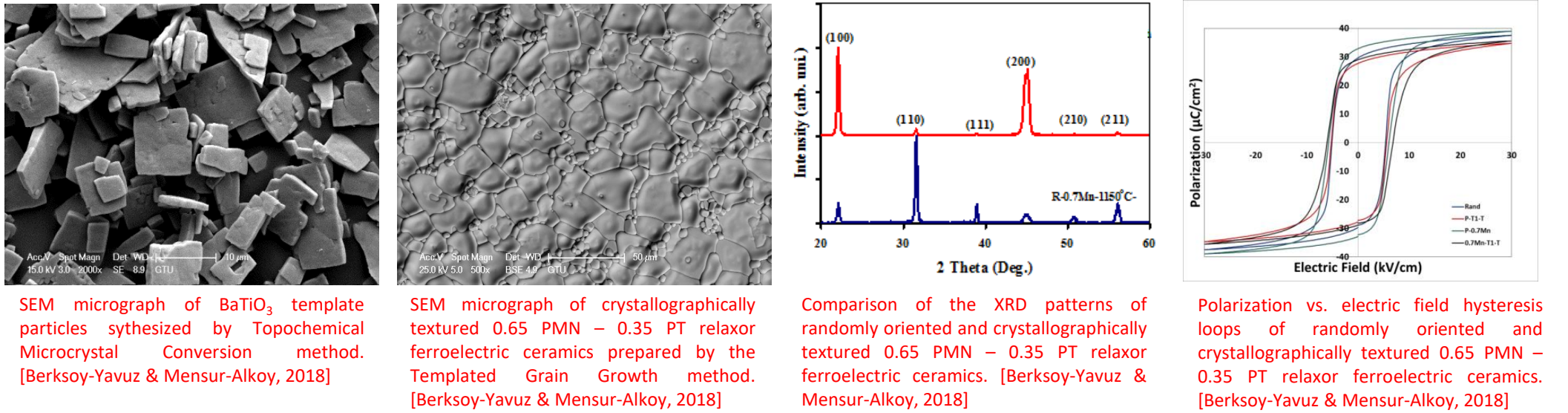
### Direct Measurement by Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a well-known technique to study the thermal behavior of materials with a good sensitivity in detecting enthalpy changes and requires relatively small samples. DSC is an ideal electrocaloric technique for the bulk samples measured at relatively high electric fields, resulting in a large change of the electrocaloric temperature.

In the electrocaloric experiments, the temperature will first be stabilized. Then the field will be applied and the heat flow will be measured as a function of time. From the measured heat flow, the EC entropy or EC temperature change can be calculated.

### Preliminary Studies

As a preliminary study for the project, the texture development in the PMN-PT system have been studied with an initial aim to optimize the synthesis conditions of single crystal BaTiO<sub>3</sub> template particles and the processing conditions of the templated grain growth process. The initial composition was the 0.65 PMN - 0.35 PT with a Curie temperature of ~160°C. Highly <001> textured bulk ceramics have successfully been prepared with a degree of orientation, as measured by the Lotgering factor  $f > 0.95$ .



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