Modeling the Electrocaloric Effect in Lead Magnesium Niobate (PMN)

Vanessa McHale

August 30, 2016

Abstract

We use a shell-based model to simulate PMN at various temperatures and electric fields, enabling us to calculate the electrocaloric effect in the material. We find a field-induced phase transition that greatly increases the electrocaloric effect at certain points. We investigate the effects of epitaxial strain on the electrocaloric effect and the phase transition temperature. We run the tests with both $\langle 001 \rangle$ and $\langle 111 \rangle$ fields. We compare our results to relevant experimental work. We find that the transition between the ferroelectric and relaxor phase leads to a large electrocaloric effect. Our results show that an electrocaloric refrigerator could be practical if the required fields could be generated.

Refrigeration is an issue of huge importance and economic value. Refrigerators based on the electrocaloric effect have a great potential since they are reversible and thus are able to approach maximum efficiency. Solid-state refrigerators also have the advantage that they do not release hydrofluorocarbons into the atmostphere and are thus more environmentally friendly[2][3]. Unfortunately, a suitable material has yet to be identified. Here, we present a material that can produce a large enough temperature change to work not only in chip-level applications but also in food storage.

We used molecular dynamics (via DLPOLY 2.20) to conduct our simulations. Runs were as long as necessary to see that equilibriums had been reached. Runs were often continued from a similar state. Timesteps were in half picoseconds. Typical runs lasted about 30000 timesteps or 15 nanoseconds. All data are averages over this time period. We used the Hoover thermostat in an NσT ensemble.

The jumps between about .6 C/m^2 and .3 C/m^2 represent a phase transition from the ferroelectric to the relaxor phase. Importantly, the tem-

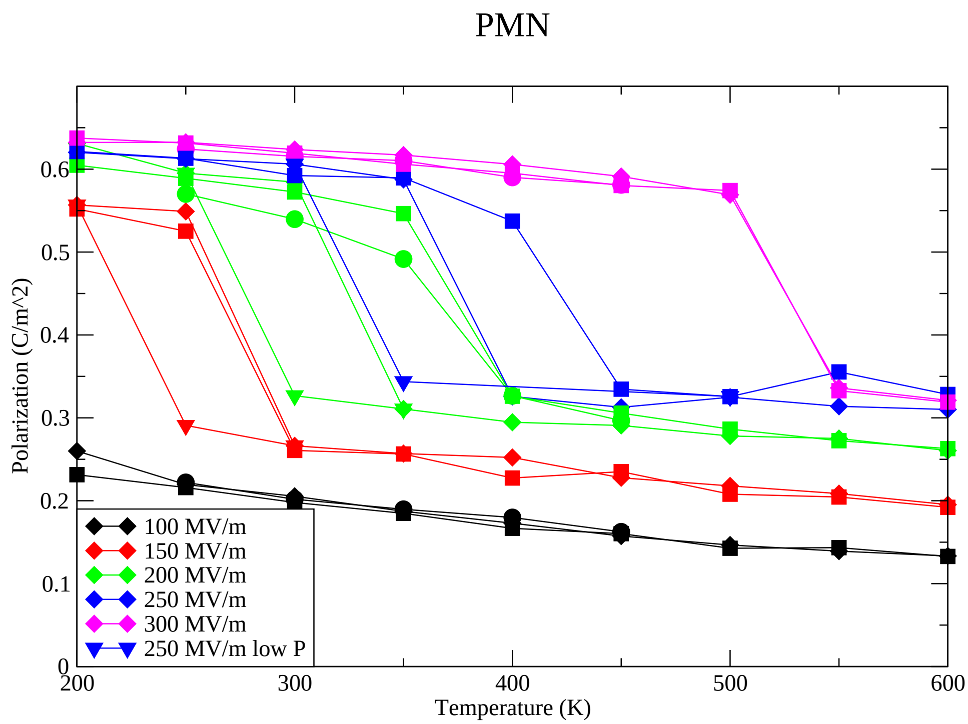

Figure 1: Polarization as a Function of Temperature

perature at which the phase transition occurs is a dependent on the field applied. Since electrocaloric cooling depends on cooling by lowering the field, and since the temperature at which the phase tranistion occurs decreases with field, we can keep the material between phases and take advantage of the extremely high $\frac{\partial P}{\partial T}$ this confers. We should also note that the materials exhibits hysteresis. The temperature at which the phase transition occurs varies based on whether it was taken from a high or a low polarization configuration.

The change in temperature is given by[1]:

$$\Delta T = -\int_{E_1}^{E_2} \frac{TV}{C_V} \left(\frac{\partial P}{\partial T}\right)_E dE$$

Where C_V is the specific heat at constant volume and is taken to be $3k_B$ per atom. The actual value of the specific heat is in reality smaller, so we can expect to see a higher ΔT in experiments. Volumes are automatically computed by DLPOLY.

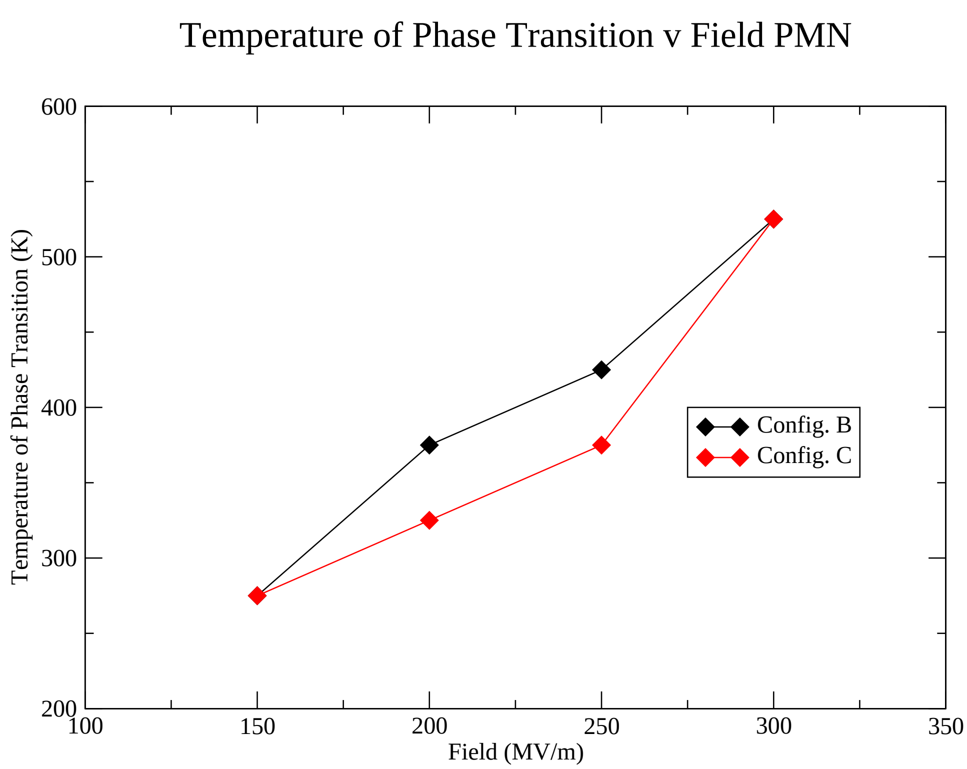

Figure 2: Phase Transition Temperature as a Function of Field

To find $\frac{\partial P}{\partial T}$ we simply took finite differences to approximate over a short interval. As an example at room temperature (300K), we go from a 150MV/m field to a 100MV/m field. We calculate $\frac{\partial P}{\partial T}$ as 0.005654 C/m^{2}K from the polarizations at 300K and 250K. We then find that ΔT is -28.22K. Since the temperature of phase transition decreases as the field decreases, we can lower the field such that the material is always near the phase transition and thus possesses a high $\frac{\partial P}{\partial T}$

For the effects of epitaxial strain we elongated the the cell vector in the X direction. The strain is the amount by which we elongate the X relative to a configuration stable at a given temperature with no field. The cell vectors in the X and Y directions were constant throughout the runs and only the Z-direction was allowed to vary. It was hoped that the epitaxial strain would enable smaller fields to produce larger $\frac{\partial P}{\partial T}$. Unfortunately, none of the strains caused a smaller field to produce a phase transition at around room temperautre.

While looking for the phase transition under a $\langle 111 \rangle$ field we did not

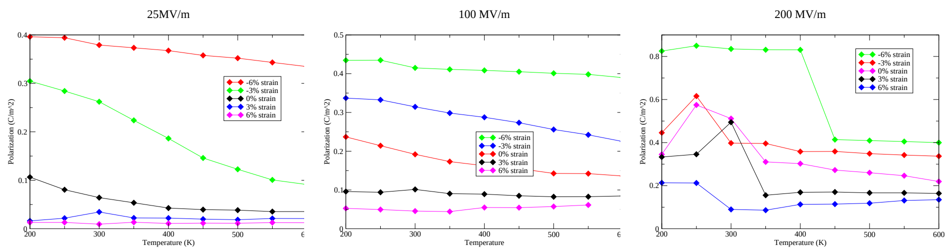

Figure 3: Polarization as a Function of Temperature in Strained PMN

find any transition where expected. Rather strangely, the magnitude of the polarization also decreased even when the applied field had the same magnitude. We looked for the phase transition at a lower field.

We can see that there may be a high and low polarization state. Though a transition is possible, though there is not sufficient evidence to conclude that there is one. Further, classical molecular dynamics is not guaranteed to be valid at temperatures much lower than 300K.

In summary, we present here models of the elctrocaloric effect. Using a $\langle 001 \rangle$ field we found that there is a field-dependent phase transition. Because $\frac{\partial P}{\partial T}$ increases dramatically with the phase transition, and since the phase transition temperature decreases with field, we can cool the material such that it is always between phases. This enables us to get a much larger electrocaloric effect out of the material.

Working with epitaxial strain, we found that there was no strain that could be applied to the material that would enable a phase transition at lower fields or create a larger $\frac{\partial P}{\partial T}$. When using a $\langle 111 \rangle$ field we surprisingly found no phase transition. Looking at lower fields showed something that may be a phase transition, but was not obviously one.

References

[1] Bret Neese, Baojin Chu, Sheng-Guo Lu, Yong Wang, E. Furman, and Q. M. Zhang *Large Electrocaloric Effect in Ferroelectric Polymers Near Room Temperature*

[2] Matthew G. Hilt, *A Solid-State Heat Pump Using Electrocaloric Ceramic Elements.* (Doctoral Dissertation)

[3] Yangbing Jia and Y. Sungtaek Ju, *A Solid-State Refrigerator Based on the Electrocaloric Effect.*

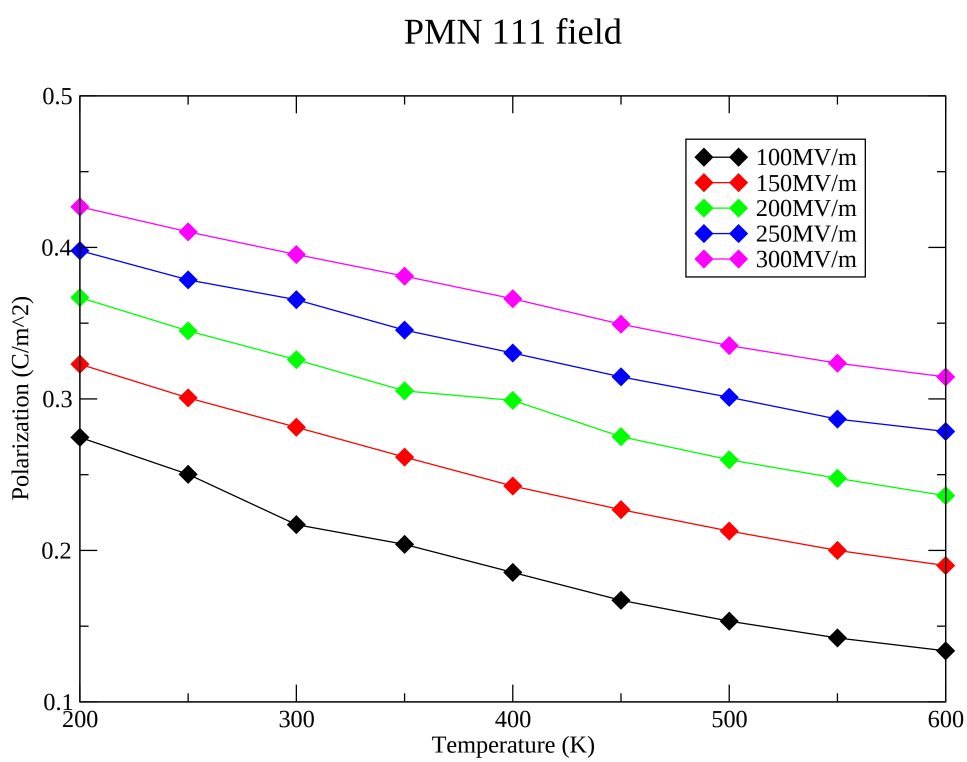

Figure 4: Polarization as a Function of Temperature under a $\langle 111 \rangle$ Field

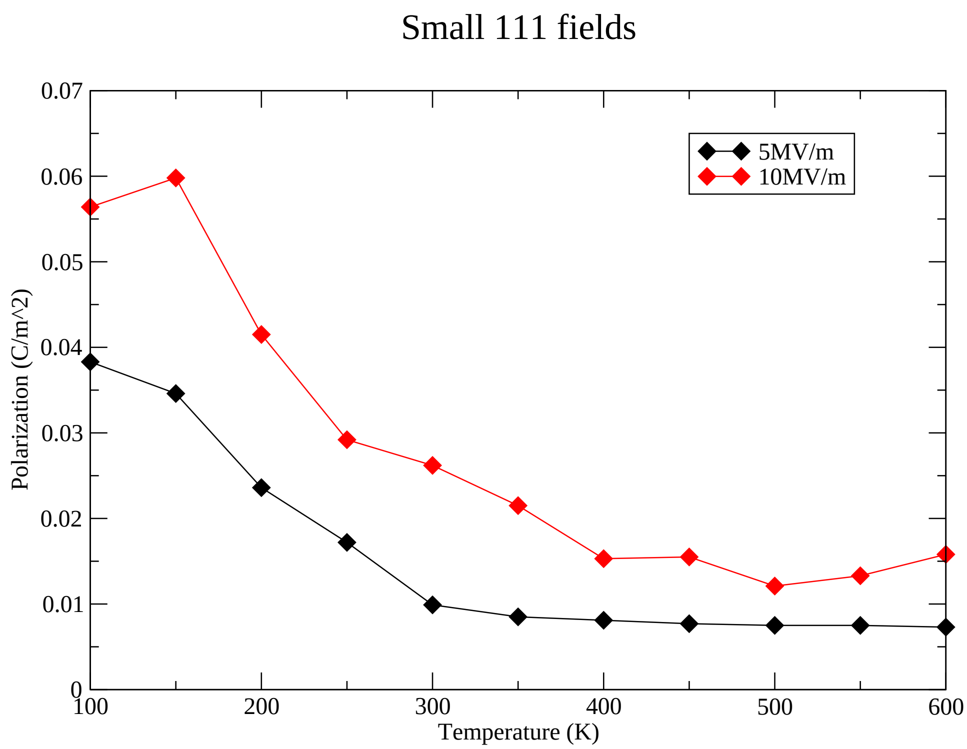

Figure 5: Polarization as a Function of Temperature at Low Fields