

Modeling the Electrocaloric Effect in Lead Magnesium Niobate (PMN)

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Abstract

We use a shell-based model to simulate PMN ($\text{PbMg}_{(1/3)}\text{Nb}_{(2/3)}\text{O}_3$) 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 [001] and [111] 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. Since this transition is shown to be dependent on field, the large electrocaloric effect stemming from the transition can be maintained as the material cools. Our results show that an electrocaloric refrigerator could be practical if the required fields could be generated.

1 Introduction

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 the Carnot efficiency. Solid-state refrigerators also have the advantage that they do not release hydrofluorocarbons into the atmosphere and are thus more environmentally friendly[2][3]. Unfortunately, a suitable material has yet to be identified. Such a material must be able to produce the large electrocaloric effect at room temperature — previously the giant electrocaloric effect has been observed at the Curie temperature, i.e. the transition from the paraelectric to ferroelectric state[4]. The Curie temperature is higher than what would be desired for most applications. 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. The large temperature change is dependent on field and therefore can be executed at many temperatures.

2 Methods

We used molecular dynamics (via DLPOLY 2.20) to conduct our simulations. The shell model has been proven to make accurate predictions[4]. Runs were as long as necessary to see that equilibriums had been reached, typically about 30000 timesteps or 15 picoseconds (timesteps were in half femtoseconds). All data are averages over the time period after equilibration. Runs were continued from a lower temperature state, which represents a heating of the material. Initial runs were equilibrated over a longer time period, typically 80000 steps.

Our sample included 8640 atoms. Some runs near the phase transition were cooled to investigate the effects of hysteresis. We used the Hoover thermostat in an $N\sigma T$ ensemble.

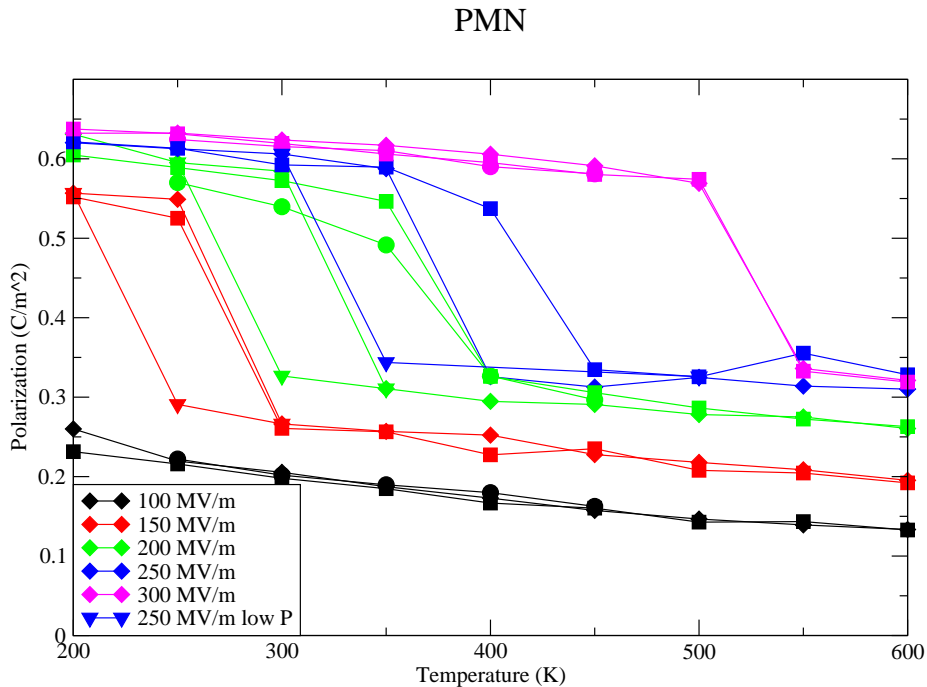


Figure 1: Polarization as a Function of Temperature

3 Results

The jumps between about $.6 \text{ C/m}^2$ and $.3 \text{ C/m}^2$ represent a phase transition from the ferroelectric to the relaxor phase. Importantly, the temperature 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 transition 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.

Temperature of Phase Transition v Field PMN

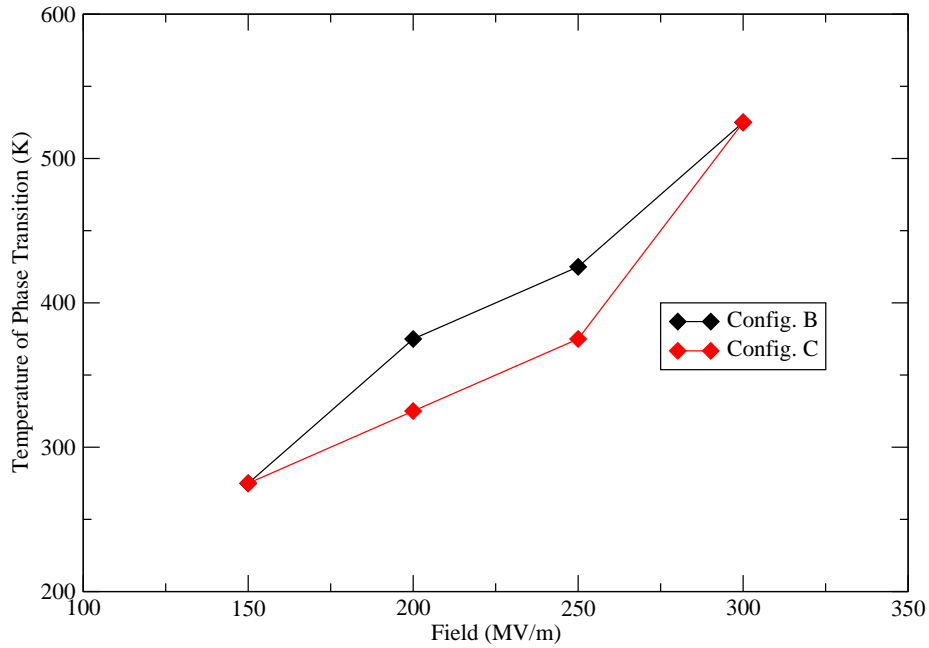


Figure 2: Phase Transition Temperature as a Function of Field

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.

To find $\frac{\partial P}{\partial T}$ we 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/m²K from the polarizations at 300K and 250K. We can then see that ΔT is -28.22K. This is capable of cooling from room temperature to freezing, enough for a refrigerator. 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 $\frac{\partial P}{\partial T}$

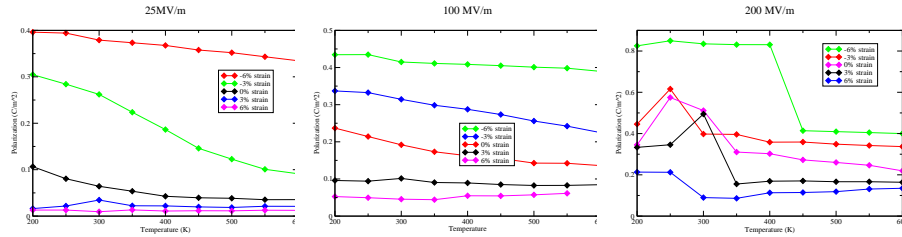


Figure 3: Polarization as a Function of Temperature in Strained PMN

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.

PMN 111 field

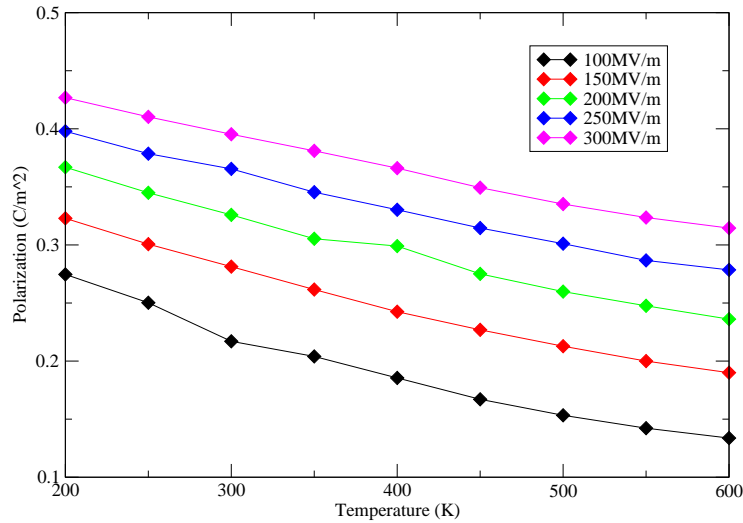


Figure 4: Polarization as a Function of Temperature under a $\langle 111 \rangle$ Field

While looking for the phase transition under a $\langle 111 \rangle$ field we did not find any transition where expected. We looked at the angled fields to determine whether the angle had an effect on the phase transition. It is expected that

the angle at which the field was applied affected the steepness of the transition; data that was collected pointed to this being true. 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.

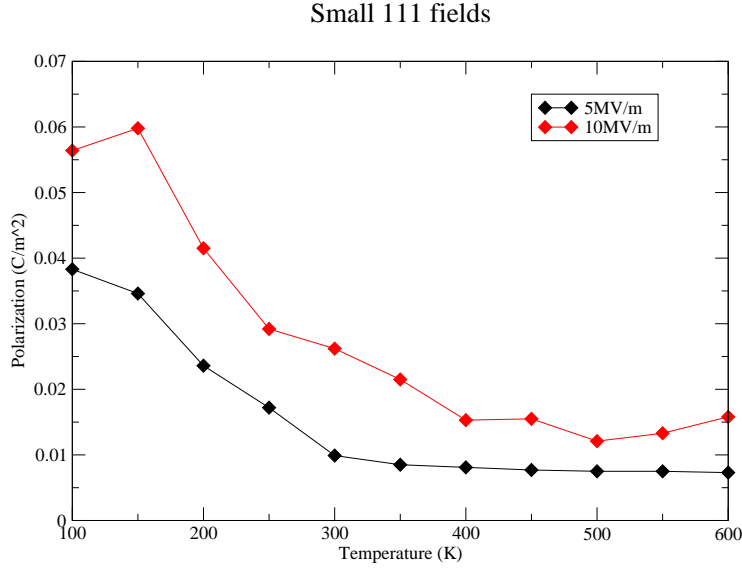


Figure 5: Polarization as a Function of Temperature at Low Fields

4 Discussion

We can see that there may be a high and low polarization state. Though a transition is possible, we did not see one. Classical molecular dynamics makes it difficult to investigate temperatures much lower than 300K.

In summary, we present here models of the electrocaloric 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*.
- [4] Maimon C. Rose and R. E. Cohen, *Giant Electrocaloric Effect around T_c* .