Title: Exploration of lead-free ferroelectric/piezoelectric ceramics from first-principles

Introduction:

In this project Beckman and Nishimatsu studied the lead-free perovskite compounds $KNbO_3$ (KNO) and $BaTiO_3$ (BTO). During the first part of the project the structural, elastic, and piezoelectric behavior of KNO was studied using ab initio first principles methods. For the first time in the literature, the full tensors were reported for all know phases. During the second part of the project the electrocaloric response of BTO was calculated using the FERAM software package developed by Nishimatsu. This is the first time that the electrocaloric response has been calculated using this type of theoretical method.

Body:

The elastic and dielectric properties of the four experimentally known phases of $KNbO_3$ (KNO) are investigated by first-principles methods and reported in Ref. [1]. The atomic structure and atomic pair distribution functions are reported and confirm the established hyphothesis that the covalent hybridized bonds between the Nb and O atoms are responsible for the ferroelectricity in KNO. In addition, the Born effective charge tensor is calculated to reveal the relation between Nb–O bonds hybridization and ferroelectric structural distortion. The dielectric, elastic, and piezoelectric properties of each phase are presented and compared to experimental measurements in the literature. The computed structures are found to match experiment to an accuracy of approximately 2%. Although there have been very few experimental studies of single crystal KNO, it is found that the elastic parameters computed for orthorhombic KNO agree with the measured values to better than 25%, which is within the anticipated exchange-correlation error; however, the computed piezoelectric coefficient differ from the experimental values by as much as 50%, which suggests that the disagreement may not be solely due to the theoretical approximations and in fact the experimental results should be readdressed.

The perovskite crystal $BaTiO_3$ (BTO) is modeled using the first-principles based effective Hamiltonian developed by Nishimatsu in the FERAM software package. These simulations are performed to estimate the pyroelectric response in the ferroelectric crystal. The electrocaloric temperature change, ΔT, is calculated for different temperatures and externally applied electric fields.

The electrocaloric effect (ECE), studied here, is important because it holds promise for application in future solid-state refrigeration technology. Domestic refrigeration for food storage is a major consumer of energy. The US Energy Information Administration (EIA) reported that in 2005 26.7% of household electricity is used in the kitchen and that of this 64% goes toward cooling food. These numbers suggest that 17.1% of US domestic electrical energy is used for food storage. It is approximated that the US has around 37 power plants dedicated to producing energy for domestic refrigeration.

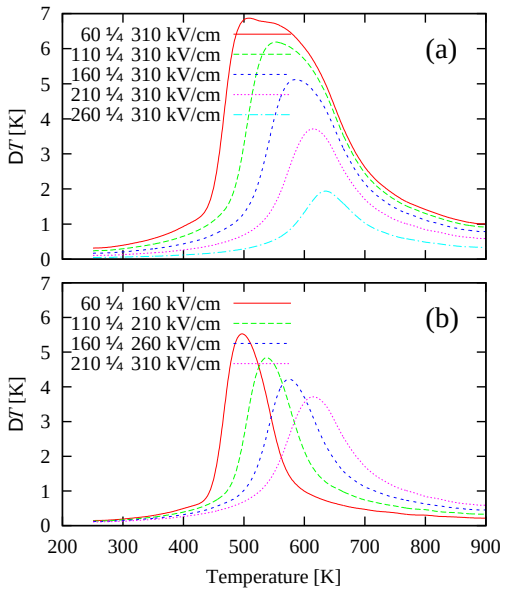

Fig. 1 The electrocaloric response of BTO as predicted by Beckman and Nishimatsu.

Refrigerators are relatively low efficiency devices that require a large mechanical condenser to compress a gas. Moving to solid-state cooling has the potential to dramatically increase the efficiency of refrigeration devices because it is based on changing the local structure (order) of atoms in a crystal by directly applying an electric field to the crystal. Because so much energy is used for refrigeration, even a modest increase in efficiency would result in a dramatic savings, for example increasing efficiency by 2.7% is enough to conserve one power plant worth of energy.

The results from this study predict that BTO is indeed a reasonable electrocaloric material and more importantly it is demonstrated that this computational approach can be used to predict the magnitude of the ECE in new material systems. The calculated electrocaloric temperature change is found to be as As shown in Fig. 1 is found that a ΔT as large as 5-6 K can be achieved for a relatively small electric field gradient, less than 100 kV/cm, if the applied fields have a small absolute magnitude. These results are counter to the current trend in research where

scientists and engineers are examining materials that require large field gradients. These results have been submitted for publication and are under review in Ref. [2].

References:

[1] L. F. Wan, T. Nishimatsu, and S. P. Beckman, "*The structural, dielectric, elastic, and piezoelectric properties of $KNbO_3$ from first-principles methods*," J. Appl. Phys. **111**, 104107 (2012).

[2] S. P. Beckman, L. F. Wan, Jordan A. Barr, and T. Nishimatsu, "Effective Hamiltonian Methods for Predicting the Electrocaloric Behavior of BaTiO$_{3}$," under review at Mater. Lett. (2012).

Key Words:

Perovskite, Ferroelectric, Electrocaloric Effect, Effective Hamiltonian, FERAM

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