## Finite-Temperature Properties of Antiferroelectric PbZrO<sub>3</sub>

B. K. Mani and I. Ponomareva

Department of Physics, University of South Florida, Tampa, Florida 33620, USA e-mail: bmani@usf.edu

The antiferroelectric PbZrO<sub>3</sub> exhibits several characteristic properties, such as the electric-field induced phase transition from antiferroelectric (AFE) to ferroelectric (FE) phase, large electrostriction coefficients, and giant electrocaloric effects. Thanks to these attractive functionalities, there is an increased interest for the use of this material in the several key technological applications [1, 2]. Below  $T_c = 505$  K PbZrO<sub>3</sub> develops an antiferroelectric orthorhombic distorted structure with an associated space group *Pbam*.

Several density functional theory (DFT) studies investigated the structural and electronic properties of  $PbZrO_3$  [3–5]. However, most of these studies are limited to zero temperature. As a result, some finite temperature properties such as temperature evolution of AFE and antiferrodistortive (AFD) order parameters, lattice distortion, and double hysteresis loops are less understood. Furthermore, the possible existence of an intermediate FE phase between high temperature paraelectric and low temperature AFE phases is under debate.



FIG. 1: Dependence of the AFE order parameter (a), the AFD order parameter (b), and the lattice distortion 1 - c/a (c) on the temperature. Experimental data (are rescaled to match the T<sub>c</sub>) in the panel (c) are from the Refs. [6–8].

We develop a first-principles-based effective Hamiltonian for PbZrO<sub>3</sub> that allows computation of properties at finite temperatures. The degrees of freedom for the Hamiltonian are the local modes that are proportional to the dipole moment of a unit cell, the AFD local modes that are responsible for the oxygen octahedron rotation, and the strain variables which describe local structural deformations [9, 10]. The parameters in the effective Hamiltonian are derived from the local density approximation based DFT calculations. Next, we use this effective Hamiltonian in Monte Carlo (MC) simulations to investigate the properties of PbZrO<sub>3</sub> in a wide range of temperatures. Simulations are done using 16x16x16 supercell with periodic boundary conditions applied along all three directions to simulate a bulk system. For each temperature we used 40,000 MC sweeps.

Our computations predict that, in agreement with both experiments and first-principles calculations, the ground state structure of  $PbZrO_3$  is an AFE orthorhombic structure with a tilting of the oxygen octahedron about the [110] axis. As evident from the Figs. 1(a)-(b),



FIG. 2: (a) The electric-field induced double hysteresis loops. (b) Dependence of the critical field on the temperature.

there is a single transition from a paraelectric cubic phase to an AFE orthorhombic phase at  $940\pm20$  K. The overestimation of  $T_c$  is attributed to the over binding of structure by DFT. We also find that, in agreement with the experimental findings, an application of electric field induces a AFE to FE transition through a double hysteresis loops (see Fig. 2(a)). Our study further shows that the critical field, required to induce such a transition, decreases with the temperature (see Fig. 2(b)). We will report our findings about the temperature evolution of the structural distortion and electric properties and discuss the possibilities of finding the intermediate ferroelectric phase.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under grant DE-SC0005245. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

- [1] H. Liu and B. Dkhil, J. Kristallog **226**, 163 (2011).
- [2] X. Tan, C. Ma, J. Fredrick, S. Beckman, and K. G. Webber, J. Am. Ceram. Soc. 94, 4091 (2011).
- [3] D. J. Singh, Phys. Rev. B. **52**, 12559 (1995).
- [4] R. Kagimura and D. J. Singh, Phys. Rev. B. 77, 104113 (2008).
- [5] M. D. Johannes and D. J. Singh, Phys. Rev. B. 71, 212101 (2005).
- [6] H. Fujishita and S. Tanaka, Ferroelectrics 258, 37 (2001).
- [7] R. W. Whatmore and A. M. Glazer, J. Phys. C 12, 1505 (1979).
- [8] E. Sawaguchi, J. Phys. Soc. Jpn. 7, 110 (1952).
- [9] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. B 52, 6301 (1995).
- [10] D. Vanderbilt and W. Zhong, Ferroelectrics **206**, 181 (1998).