New Insights into the Structure and Properties of PZT from Mesoscopic to Atomic Scale

Zuo-Guang Ye, Nan Zhang, Yujaun Xie, and Alexei A. Bokov

Department of Chemistry and 4D LABS, Simon Fraser University,
Burnaby, British Columbia, V5A 1S6, Canada

Lead zirconate-titanate solid solution, $PbZr_{1-x}Ti_xO_3$ (PZT), has been studied extensively over the past decades for both industrial applications and fundamental research, but almost exclusively in the forms of ceramics and thin films because of the difficulties encountered in the growth of PZT single crystals. On the other hand, the mesoscopic domains, the microstructure and the atomistic mechanisms that cause the outstanding piezoelectric performance of this class of materials near the morphotropic phase boundary (MPB) remain poorly understood. Therefore, it is of particular interest to grow large single crystals of PZT, which are not only necessary for thorough characterization of the anisotropic properties of this prototype ferroelectric solid solution system, but are also expected to exhibit superior piezo- and ferroelectric performance over the PZT ceramics, and a higher depoling temperature (T_d) and higher coercive field (Ec) (than the relaxor-based PMN-PT and PZN-PT single crystals), which are required for a broader range of advanced applications. The objective of this work is to synthesize the PZT single crystals and to characterize their domain structures, phase transitions, local structure, and micro polar structures in order to provide a better understanding of the structure-property relations.

Recently, thanks to the capability to grow PZT single crystals and the availability of advanced characterization and analytical techniques, such as piezoresponse force microscopy (PFM), spherical aberration-corrected transmission electron microscopy, high-resolution neutron total scattering and diffuse scattering, and pair-distribution function analysis, we have gained new insights into the complex local structure, atomic scale polarization rotation, nano-scale domain structure, intricate phase transition and critical behaviour, and tri-critical points in PZT. These results have provided a better understanding of the relationship between micro-/nano-scopic structure and macroscopic functional properties for this important material, but also for the piezo-/ferroelectric materials in general.

In this paper, we present our successful growth of $PbZr_{1-x}Ti_xO_3$ single crystals with a wide composition range across the morphotropic phase boundary (MPB) ($0.20 \leq x \leq 0.65$) by a top-seeded solution growth (TSSG) technique. The systematic characterization of the grown PZT single crystals by a variety of techniques, such as dielectric and piezo-/ferroelectric measurements, polarized light microscopy, piezoresponse force microscopy and transmission electron microscopy, has allowed us to discover a series of new physical phenomena in this important family of piezo-materials.

The crystal growth conditions are optimized in terms of the chemical, thermodynamic and kinetic parameters. The growth temperature is found to be a key factor for controlling the composition of the grown crystals. PZT crystals with composition from $x = 0.42$ to $x = 0.47$ show characteristic ferroelectric-to-ferroelectric phase transitions due to the presence of a curved MPB. The crystals of MPB composition, $x = 0.46$, are found to exhibit the best properties, with a piezoelectric coefficient $d_{33} = 1223$ pC/N, an electromechanical coupling factor $k_{33} = 80\%$, a large coercive field $E_c = 7$ kV/cm and a high Curie temperature $T_C = 386$ ℃, potentially useful for high temperature and high power electromechanical transducer applications.

The studies of the mesoscopic domain structure [1], local polar domain structure and phase transition behaviour of PZT single crystals suggest that quenched random fields play an important role in the formation of nanodomain state in PZT, which is discussed in the framework of the behaviour and mechanisms of relaxor ferroelectrics [2].

Pair Distribution Function (PDF) analysis and Rietveld refinement have been carried out to study both the short- and long-range orders in the Zr-rich rhombohedral region of the PZT phase diagram. The nature of the monoclinic phase across the Zr-rich and morphotropic phase boundary area of PZT is clarified. Evidence is found that long-range average rhombohedral and both long- and short-range monoclinic regions coexist at all compositions. In addition, a boundary between one type of monoclinic (M_A) structure and another monoclinic (M_B) structure has been found. The general advantage of a particular monoclinic distortion (M_A) for high piezoactivity is discussed from a spatial structural model of susceptibility to stress and electric field, which is applicable across the wide field of perovskite materials science [3].

The atomic structure of PZT crystals with x=0.42 is imaged by means of high-resolution TEM. The accurate Pb displacements and their directions are successfully determined relative to the centre of the four B-cations, on the <110> monoclinic mirror plane. The orientation and distribution of local polarizations indicate a mixture of rhombohedral, tetragonal and monoclinic local symmetry, providing the atomistic evidence of the monoclinic phase.

The work was supported by the U.S. Office of Naval Research (Grant No. N00014-12-1-1045) and the Natural Science & Engineering Research Council of Canada (NSERC).

References:

[1] A. A. Bokov, X. Long, and Z.-G. Ye, *Phys. Rev. B*, **81**(17), 172103/1-4 (2010)..

[2] D. Phelan, C. Stock, J. A. Rodriguez-Rivera, S. Chi, J. Leão, X. Long, Y. Xie, A. A. Bokov, Z.-G. Ye, P. Ganesh, and P. M. Gehring, *Proc. Natl. Acad. Sci. U.S.A.*, **111**(5)， 1754 – 1759 (2014).

[3] N. Zhang, H. Yokota, A. M. Glazer, Z. Ren, D. A. Keen, D. S. Keeble, P. A. Thomas and Z.-G. Ye, *Nat. Commun.* **5**, Article #5231 [DOI: 10.1038/ncomms6231] (*2014*).