

The Influence of Lead Stoichiometry on the Phase Behavior of PZT 95/5

by E. L. Venturini, Pin Yang, and G. A. Samara

Motivation—The ferroelectric (FE) ceramic $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ or PZT 95/5 is the energy-storage element in explosively-driven power supplies. In the power supply, a shock wave drives the PZT 95/5 through a phase transition from the polarized FE state with bound electrical charge to an antiferroelectric (AFE) state with no bound charge. We are investigating the effects of temperature and varying Pb concentration on this FE/AFE transition using dielectric measurements under hydrostatic pressure. Pb volatility is a serious issue during the high-temperature processing of this ceramic, and a detailed knowledge of Pb stoichiometry effects on the physical properties is necessary.

Accomplishment—PZT 95/5 has five distinct structural phases in a pressure-temperature (P-T) phase diagram. The paraelectric, cubic phase is stable above ~ 500 K for pressures between 1 bar and several kbar. During cooling at 1 bar, the material transforms to a high-temperature, rhombohedral FE structure near 500 K, designated $\text{F}_{\text{R(HT)}}$. Upon further cooling, a lower temperature, rhombohedral FE structure appears near 320 K, designated $\text{F}_{\text{R(LT)}}$. With increasing pressure at temperatures below 320 K, the $\text{F}_{\text{R(LT)}}$ phase transforms to an orthorhombic AFE structure designated A_0 . At higher temperatures and pressures above ~ 3 kbar, the stable AFE phase has a tetragonal structure designated A_T . The $\text{F}_{\text{R(LT)}} \rightarrow \text{A}_0$ transformation is the basis for the power supply and, hence, changes with lead stoichiometry are of great interest.

Fig. 1 compares the real dielectric constant $\epsilon'(\text{P})$ at 300 K, normalized to its value at 1 bar, versus increasing P for four PZT 95/5 ceramic disks with different Pb concentrations. The sharp drop in ϵ' marks the $\text{F}_{\text{R(LT)}} \rightarrow \text{A}_0$ transformation P

(which is accompanied by charge release in the device) for a particular Pb content. The sharpness of the transition reflects the high quality of the chem prep ceramic samples. The data show a huge decrease in the transformation P with increasing Pb concentration.

The FE/AFE boundary can be determined from isothermal $\epsilon'(\text{P})$ data as shown in Fig. 1 or from $\epsilon'(\text{T})$ and loss $\epsilon''(\text{T})$ data versus decreasing T at constant P . Fig. 2 shows the FE/AFE boundary on a P-T partial phase diagram for the four PZT 95/5 ceramics. Increasing Pb content results in a substantial decrease in the FE/AFE transition pressure between 220 and 320 K. The solid symbols in Fig. 2 reflect transitions determined from $\epsilon''(\text{T})$ data, while the corresponding open symbols indicate $\epsilon'(\text{P})$ measurements. The lines in Fig. 2 are a guide to the eye.

There is substantial P and T hysteresis in the FE/AFE transition (not shown). A phase boundary for the reverse $\text{A}_0 \rightarrow \text{F}_{\text{R(LT)}}$ transition was determined from ϵ' versus increasing T at constant P and ϵ' versus decreasing P at constant T . Although not as dramatic, increasing Pb content shifts this reverse transition to lower P and higher T .

Significance—Detailed characterization and understanding of the properties of chem prep PZT 95/5 are necessary for improved design and reliable performance in applications. Clearly, the strong dependence of the FE/AFE transition pressure on Pb content imposes severe constraints on the processing protocol where Pb volatility must be compensated. Further, these studies augment a data base to test the numerical modeling. Our results will be important for calibrating and improving the simulations.

Sponsors for various phases of this work include: Nuclear Weapons/Science & Technology

Contact: Eugene L. Venturini; Nanostructure & Semiconductor Physics, Dept. 1112
Phone: (505) 844-7055, Fax: (505) 844-1197, E-mail: elventu@sandia.gov

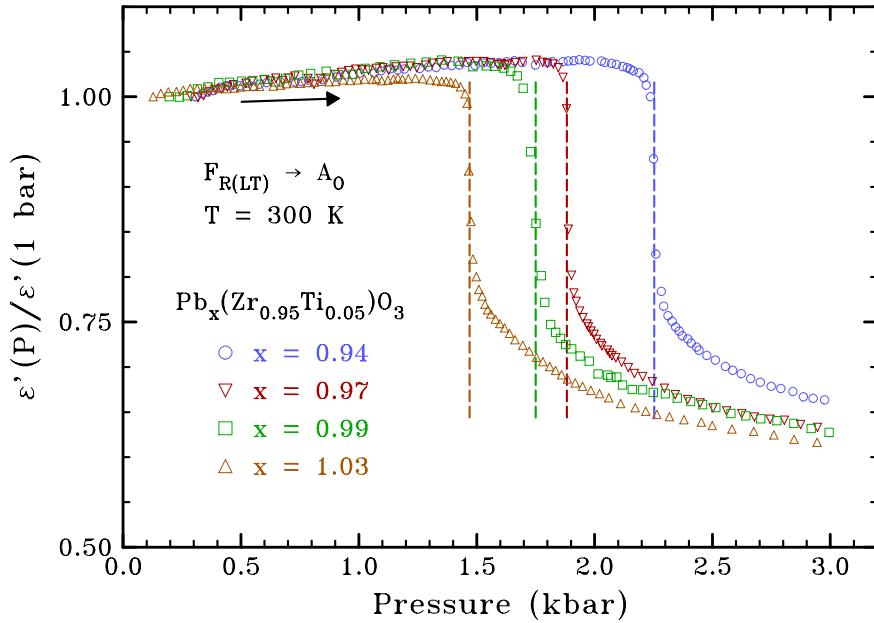


Figure 1. FE/AFE transition pressure at 300 K decreases with increasing Pb.

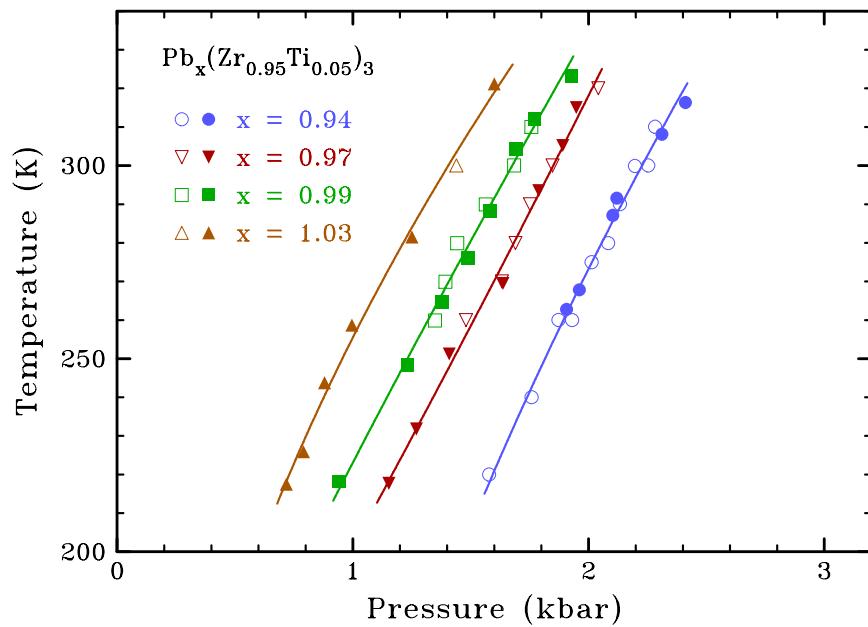


Figure 2. FE/AFE transition pressure decreases with increasing Pb over a range of temperatures.