Pressure-Induced Phase Transition in PLZT: A Neutron Diffraction and Dielectric Study

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Abstract. Zr-rich, La-doped lead zirconate titanate ceramic samples with composition near Pb0.99La0.01(Zr0.91Ti0.09)O3 (hereafter PLZT) were studied by time-of-flight neutron diffraction and dielectric measurements at 295 K and 1 bar and at 250 K versus increasing and decreasing pressure to 0.55 GPa. The diffraction data at 295 K show that the sample has the rhombohedral ferroelectric R3c structure (FR(LT)) and remains in that phase upon cooling to 250 K. As pressure is increased at 250 K, a transition is observed above 0.3 GPa to essentially the antiferroelectric CaTiO3 orthorhombic Pnma (AO) phase. There appear two other peaks in the neutron spectra, suggesting a possible incommensurate cell for this AO. After the initial drop of the FR(LT) content, the transformation remains incomplete to 0.55 GPa with ~10% of the sample retaining the FR(LT) low pressure phase. On pressure release, 91% of the FR(LT) phase is recovered with the remainder remaining in the AO phase. Isothermal dielectric data at 250 K suggest a structural transition with an onset near 0.37 GPa for increasing pressure, consistent with the diffraction results.

1. Introduction

Lead lanthanum zirconate titanate ceramics have had a long history for their optical properties.[1] These ceramics are doped members of the perovskites PbZrO3 and PbTiO3 which form the solid solution series PbZr1-xTexO3 over the entire composition range. The undoped solid solutions, commonly called PZTs, are rich in the variety of ferroelectric and nonferroelectric transitions that can be induced in them by variations in composition, temperature, electric field, or pressure (stress).[2] They also exhibit large spontaneous polarizations and piezoelectric coefficients. These factors along with their availability in high-quality ceramic form are responsible for their widespread technological usage in applications based on piezoelectric and ferroelectric properties.[2,3]

These perovskites are paraelectric (PE) and in the ideal cubic perovskite structure at high-temperature (T). On cooling, this phase transforms either to a rhombohedral ferroelectric (FE) phase or to an orthorhombic (Pbam) antiferroelectric (AFE), AO. The rhombohedral ferroelectric region usually is divided into two phases: a high-T phase of symmetry R3m (FR(HT)) and a low-T phase of symmetry R3c (FR(LT)), which has a unit cell double that of the R3m phase. For certain PZT compositions this phase is induced by pressure (P).

Doping with other metals such as Nb enhances various processing parameters as well as electrical and dielectric properties, particularly the various phases the materials undergo on either increasing P or decreasing T. One such ceramic of composition Pb0.99(Zr0.95Ti0.05)0.98Nb0.02O3, known as PZT95/5-2Nb was the subject of our recent study on the P and T induced changes of its crystal structure and dielectric properties.[4] The positions in the phase diagram of the FR(HT)-FR(LT) and FR(LT)-AO transition and the triple point are shifted dramatically from that of pure PZT. Most, if not all, of these phase transitions are known to be associated with lattice dynamical instabilities, or soft phonon modes. Small ionic displacements accompany such transitions, and hence they are often called displacive transitions.

With significant La doping, ceramics of high optical clarity with electrical controlled transmission are possible.[1] PLZT ceramics with a composition near Pb0.9(La0.09(Zr0.63Ti0.35)O3 are transparent with low optical loss for wavelengths from 400 to 6500 nm.[5] Many aspects of the various P and T-induced transitions in the PLZTs, including the details of the atomic displacement and changes in lattice parameters involved, remain unresolved. This paper reports the structure and dielectric
behaviour of our PLZT, Pb_{0.99}La_{0.01}(Zr_{0.91}Ti_{0.09})O_{3}, primarily at 250 K, and compares it with results previously determined on PZT95/5-2Nb.[4]

2. Experimental Details

2.1. Sample preparation.
Oxide powders were precipitated from liquid solutions containing the appropriate quantities of Zr, Ti, Pb, and La ions, with 3.75% PbO excess to account for the partial evaporation of Pb during calcining and the subsequent sintering process. The powders were filtered and dried, and then calcined at about 1175 K for 16 hours. The powder was mixed with organic binders (2 wt% acrylic binder solution) to facilitate pressing, dried, pressed into billets and fired to remove the organic additives. The billets were sintered at about 1625 K for 6 hours in the presence of calcined powder of composition similar to that of the compact in a double-crucible configuration in order to minimize Pb loss to form the final ceramic.

2.2. Neutron powder diffraction measurements
Time-of-flight neutron powder diffraction data were collected on the Special Environment Powder Diffractometer (SEPD) [6] at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. Only limited diffraction data were collected as a function of hydrostatic P (0 - 0.55 GPa) at 250 K after initial measurements at ambient. Hydrostatic P was generated with a helium gas P cell, and cooling was achieved using a closed-cycle helium refrigerator. The ±90° detector bank data were analyzed using the Rietveld refinement method with the GSAS (EXPGUI) suite [7,8]. The composition was fixed to the nominal one Pb_{0.99}La_{0.01}(Zr_{0.91}Ti_{0.09})O_{3}. Neutron scattering lengths used were Pb: 9.405, Zr: 7.16, Ti: -3.438, La: 0.83, and O: 5.803 fm. In the course of refining the structure parameters above the phase transition, it was apparent that the transition involved a different high P orthorhombic phase than that of Pbam observed in our PZT95/5-2Nb study.[4] Various known structure types were attempted before the more satisfactory fit was obtained employing a cell similar to that of antiferroelectric CaTiO₃, of orthorhombic Pnma symmetry for the AO phase. In addition the possibility of an incommensurate cell was evident by two extra peaks, suggesting results similar to those of published HRTEM studies [9] on similar compositions. The latter were tentatively interpreted as a ferroelectric R3c to an incommensurate antiferroelectric phase.

2.3. Dielectric Measurements
The real (ε’') and imaginary (ε’’’ or dielectric loss tanδ = ε’’’/ε’') components of the dielectric response of our PLZT ceramic were measured versus T (250-400 K) and P (0-0.55 GPa) with an Agilent Model 4284A Precision LCR meter at frequencies from 10² to 10⁸ Hz. The dielectric sample was a thin plate, 0.3x0.3x0.08 cm³, with silver contacts fired on the broad faces. The P cell used helium gas as the P fluid and was placed inside a cryogenic dewar. The P was monitored by the change in resistance of a calibrated manganin coil, and the T was determined with a chromel/alumel thermocouple mounted adjacent to the sample holder. Typical AC voltages (<10 V/cm) generate a linear dielectric response and are insufficient to move any domain boundaries of the ferroelectric phases.

3. Results and Discussion

3.1. Neutron Diffraction
The diffraction study at 295 K and 1 bar shows that the sample is the rhombohedral ferroelectric R3c phase (F₁₋₂E₁) and remains in that phase upon cooling to 250 K. As P is increased at 250 K, a transition is observed just above 0.3 GPa to essentially an antiferroelectric CaTiO₃ orthorhombic Pnma (A0) phase, which because of the appearance of two other peaks in the spectra, may possibly be an incommensurate cell. Refined lattice and positional parameters and the weight fractions, f, for the
Table 1. Refined structural parameters for FR(LT) and AO phases in ceramic sample of PLZT at 250 K. For FR(LT), space group R3c (No. 161), with Pb (& La) at 6a (0,0,z), Zr/Ti at 6a (0,0,z), and O at 18b (x,y,z = 1/12). For AO, space group Pnma (No. 62), with Pb (& La) at 4c (x,1/4,z), Zr/Ti at 4b (0,0,1/2), O1 at 4c (x,1/4,z), and O2 at 8d (x,y,z). Numbers in parentheses are statistical standard deviations of the last significant digit; * denotes decreasing P from 0.552 GPa.

| P, GPa | f(R3c) | R3c a, Å | R3c c, Å | z(Pb) | z(Zr/Ti) | x(O) | y(O) | f(Pnma) | Pnma a, Å | Pnma b, Å | Pnma c, Å | x(Pb) | z(Pb) | x(O1) | z(O1) | x(O2) | y(O2) | z(O2) |
|--------|--------|----------|----------|-------|----------|------|------|---------|----------|----------|----------|-------|-------|-------|-------|-------|-------|-------|
| 0      | 1.0    | 5.83856(4)| 14.4143(2)| 0.2169(2) | -0.1352(6) | 0.1281(4) | 0.3169(5) | 0.0    | 5.8451(6) | 8.1804(3) | 5.8540(7) | 0.0002(9) | -0.0111(9) | 0.484(2) | 0.0531(9) | 0.253(9) | -0.263(3) |
| 0.310  | 1.0    | 5.8336(5) | 14.375(4) | 0.2173(6) | -0.1493(9) | 0.1137(4) | 0.3090(8) | 0.87   | 5.8412(6) | 8.1860(3) | 5.8565(7) | 0.0001(9) | -0.0022(9) | 0.483(2) | 0.053(4)  | 0.253(9)  | -0.263(3) |
| 0.552  | 0.13   | 5.8275(8) | 14.356(3) | 0.2121(9) | -0.149(9)   | 0.107(3)  | 0.293(3)  | 0.87   | 5.84228(4)| 8.1909(3)| 5.8649(7) | 0.01(7)  | 0.012(9)   | 0.458(5)  | 0.053(4)  | 0.253(9)  | -0.263(3) |
| 0.300* | 0.13   | 5.842(4)  | 14.416(2) | 0.2117(9) | -0.1550(9)  | 0.1131(3) | 0.298(3)  | 0.87   | 5.8395(5) | 8.1909(3)| 5.8649(7) | 0.01(7)  | 0.012(9)   | 0.458(5)  | 0.053(4)  | 0.253(9)  | -0.263(3) |
| 0*     | 0.92   | 5.8395(5)| 14.3970(2)| 0.2168(2) | -0.1331(3)  | 0.1275(3) | 0.3173(4) | 0.08   | 5.8395(5)| 8.1909(3)| 5.8649(7) | 0.01(7)  | 0.012(9)   | 0.458(5)  | 0.053(4)  | 0.253(9)  | -0.263(3) |

FR(LT) and AO phases at 250 K before the transition and at maximum P as well as the corresponding results on P decrease are given in Table 1. Figure 1 shows the FR(LT) - AO phase transition deduced from neutron diffraction data on a stack of ceramic disks cut from the same pellet as the thin disks used for the dielectric measurements. Plotted in Figure 1 is the weight fraction, f, of the FR(LT) phase as a function of P at 250 K as well as the initial ambient 298 K point. It is seen that the transition in the ceramic is not sharp and occurs over the range of ~3 to 0.55 GPa and that there is sufficient hysteresis as P is decreased that the majority of the AO phase transforms below 0.3 GPa back to the FR(LT) phase. (On increasing P, a “back” smooth curve interpolation would yields ~0.35GPa for the phase transition onset.) This is in contrast to the much sharper transition observed in our previous PZT95/5-2Nb study.
Figure 1. Weight fraction of FR(LT) phase as a function of increasing hydrostatic pressure at 250 K (filled circles). The open symbols with dot are for decreasing pressure. Ambient datum at 298 K (filled triangle). The remaining weight fraction is the A phase.

Furthermore, the present high P phase is a different high P orthorhombic phase than that of PbSn observed in PZT95/5-2Nb. Just as in the latter case after the initial drop of the FR(LT) content, the transformation remains incomplete to 0.55 GPa with ~10% of the sample remains in the FR(LT) low P phase. On P release, 91% of the FR(LT) phase is recovered with the remainder remaining in the Ao phase, an amount larger than in PZT95/5-2Nb.[4] (These data points also fit a smooth curve toward ambient P.) There is a similar large hysteresis in the phase recovery.

The value of the \( a \) and \( c \) cell parameters (hexagonal basis) of the FR(LT) phase are given in Figures 2.

Figure 2. Relative change in the \( a \) and \( c \) cell parameters (hexagonal basis) of the FR(LT) phase. Dashed lines through filled circles are used for 250 K data with increasing P; solid lines through circles with dot for decreasing P. The corresponding 295 K, ambient P data are filled triangles. Note that the \( a \) cell parameter is particularly non-linear, as though the ceramic sample might be “clamped” more along that direction than perpendicular to it (along the \( c \) direction). Such clamping was also an issue in our previous PZT95/5-2Nb study.

Figure 3 shows the reduced cell volume as a function of pressure for the FR(LT) and Ao phases. Dashed/solid lines go through 250 K values (solid circles/circles with dots for increasing/decreasing P).
Figure 3. Reduced cell volume as a function of pressure. For the $F_{R(LT)}$ phase, dashed line (solid circles) through 250 K values) for increasing $P$; solid line for decreasing $P$ values (circles with dots). For the $A_0$ phase, dotted wide line is through 250 K values (open diamonds/plus signs used for increasing/decreasing $P$). Ambient shown as a filled triangle. Note the smaller cell for the $A_0$ phase compared to the $F_{R(LT)}$ phase.

for the $F_{R(LT)}$ phase; for the $A_0$ phase, heavy dashed line is through the corresponding T values (open diamonds/plus signs for increasing/decreasing P). Note the smaller cell for the $A_0$ phase compared to the $F_{R(LT)}$ phase. The 0.7% volume contraction at the $F_{R(LT)}$ -to- $A_0$ transition is of the same order as the 1% contraction observed in PZT95/5-2Nb.[4] The ambient value for the reduced cell volume is shown as a filled triangle.

3.2. Dielectric Properties
The isothermal data in Figure 4 show the in-phase dielectric constant $\varepsilon'$ at 250 K and 10 kHz versus increasing and subsequent decreasing P. Increasing $P$ produces a gradual rise in $\varepsilon'$, reaching a maximum near 0.37(1) GPa; a similar increase in $\varepsilon'$ with increasing $P$ is observed for PZT95/5-2Nb ceramic samples in the $F_{R(LT)}$ phase. Dielectric data at other frequencies form parallel curves with no dispersion in the P for the $\varepsilon'$ maximum. Based on the neutron diffraction results in Figure 1, 0.37 GPa is identified as the onset of the $A_0$ phase with increasing $P$. The decrease in $\varepsilon'$ above 0.37 GPa continues to the highest $P$ of 0.57 GPa where the neutron data show that over 10% by weight of the sample remains in the $F_{R(LT)}$ phase.

Figure 4. Dielectric constant $\varepsilon'$ for a PLZT ceramic sample at 250 K and 10 kHz versus increasing (solid circles) and decreasing (open circles) pressure.

With decreasing $P$ there is a gradual, continuous rise in $\varepsilon'$ with no evidence for a maximum. Again, consistent with the neutron diffraction results in Figure 1, these data reflect a continuous transformation of the $A_0$ fraction of the sample back to the $F_{R(LT)}$ phase. However, part of the increase in $\varepsilon'$ with
decreasing $P$ is attributed to the $P$ dependence of $\varepsilon'$ within the AO phase. In contrast to an increase in $\varepsilon'$ with increasing $P$ in the ferroelectric $F_{R(LT)}$ phase, $\varepsilon'$ is expected to show a decrease with increasing $P$ in the antiferroelectric $A_O$ phase based on dielectric data for PZT95/5-2Nb. Also note that the initial value of $\varepsilon'$ at 10 kHz and 0.01 GPa in this isothermal experiment is ~242, while the final value at the same frequency and $P$ is nearly 10% larger. This increase is attributed to a different ferroelectric domain structure in the recovered $F_{R(LT)}$ phase as well as residual internal strains (i.e., the clamping effect discussed above) following the $P$ excursion. Hence, it is not possible to separate these effects and estimate the fraction of $A_O$ phase from the dielectric data for either increasing or decreasing $P$.

Prior to the isothermal experiment at 250 K the dielectric sample was “annealed” by heating to 400 K (maximum $T$ for the gas pressure cell) and then cooling to 250 K under ~0.01 GPa. During heating the dielectric data indicated a transition from the $F_{R(LT)}$ to the $F_{R(HT)}$ phase at 248(2) $K$; during cooling the reverse transition occurred at 242(2) $K$. Similar thermal hysteresis is observed for PZT95/5-2Nb ceramic samples, where this transition occurs at lower $T$. A second 400 K anneal at 0.01 GPa after the 250 K $P$ experiment restored $\varepsilon'$ to its original value of ~242 at 250 K.

4. Concluding Remarks
The $P$-induced $F_{R(LT)}$-$A_O$ phase transition in PLZT has been shown to differ from that in PZT95/5-2Nb. Initial details of the ionic displacements accompanying the transformation have been determined. The present study shows the degree of incompleteness and irreversibility of the transformation, possibly resulting from strains experienced by the untransformed $F_{R(LT)}$ grains that exist as a minority phase in the high $P$ $A_O$ phase. However, these strains are not as large as that determined in our previous study of the PZT95/5-2Nb material due to the much smaller reduced volume difference between the $F_{R(LT)}$ and $A_O$ phases.

Isothermal dielectric data to 1.5 GPar near room $T$ (not shown) suggest two transitions with increasing $P$; based on published HRTEM studies[9] on similar compositions as a function of $T$ (but $P$ data are not available), these transitions are tentatively identified as ferroelectric $R3c$ to an incommensurate antiferroelectric phase, then to an orthorhombic antiferroelectric phase at higher $T$. Though we have some dielectric $P$ data at 298 K which would be consistent with such a latter phase transition near 1.0 GPa, this would exceed the current $P$ maximum of our neutron diffraction cell. Even though in general decreasing $T$ acts as increased $P$, at 250 K no evidence for this transition is seen to the current limits of either the neutron or dielectric data taken to date.

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