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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 $Pb_{0.99}La_{0.01}(Zr_{0.91}Ti_{0.09})O_3$ (hereafter PLZT) were studied by time-of-flight neutron diffraction and dielectric measurements at 295 K and 1 bar and at 250K versus increasing and decreasing pressure to 5.5 kbar. The diffraction data at 295 K show that the sample has the rhombohedral ferroelectric *R3c* structure ($F_{R(LT)}$) and remains in that phase upon cooling to 250 K. As pressure is increased at 250 K, a transition is observed above 3 kbars to essentially the antiferroelectric $CaTiO_3$ orthorhombic *Pbnm* (A_O) phase. There appear two other peaks in the neutron spectra, suggesting a possible incommensurate cell for this A_O. After the initial drop of the $F_{R(LT)}$ content, the transformation remains incomplete to 5.5 kbars with ~10% of the sample retaining the $F_{R(LT)}$ low pressure phase. On pressure release, 91% of the $F_{R(LT)}$ phase is recovered with the remainder remaining in the A_O phase. Isothermal dielectric data at 250 K suggest a structural transition with an onset near 3.7 kbar for increasing pressure, consistent with the diffraction results.

INTRODUCTION

Lead lanthanum zirconate titanate ceramics have had a long history for their optical properties.[1] These ceramics are doped members of the perovskites $PbZrO_3$ and $PbTiO_3$ which form the solid solution series $PbZr_{1-x}Ti_xO_3$ 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), A_O. The rhombohedral ferroelectric region usually is divided into two phases: a high-temperature phase of symmetry *R3m* ($F_{R(HT)}$) and a low-temperature phase of symmetry *R3c* ($F_{R(LT)}$), which has a unit cell double that of the *R3m* phase. For certain PZT compositions this phase is induced by pressure.

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 pressure or decreasing temperature. One such ceramic of composition $Pb_{0.99}(Zr_{0.95}Ti_{0.05})_{0.98}Nb_{0.02}O_3$, known as PZT95/5-2Nb was the subject of our recent study on the pressure and temperature induced changes of its crystal structure and dielectric properties.[4] The positions in the phase diagram of the $F_{R(HT)}$-$F_{R(LT)}$ and $F_{R(LT)}$-A_O 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 $Pb_{0.91}La_{0.09}(Zr_{0.65}Ti_{0.35})O_3$ are transparent with low optical loss for wavelengths from 400 to 6500 nm.[5] Many aspects of the various pressure and temperature-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]

EXPERIMENTAL DETAILS

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. *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 pressure (0 - 5.5 kbar) at 250 K after initial measurements at ambient. Hydrostatic pressure was generated with a helium gas pressure 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 pressure 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 $CaTiO_3$, of orthorhombic *Pbnm* symmetry for the A_O 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.

3. *Dielectric Measurements*

The dielectric properties, ε' and tanδ = ε''/ε', of our PLZT ceramic were measured versus temperature (250-400K) and hydrostatic pressure (0-5.5 kbar) with an Agilent Model 4284A Precision LCR meter at frequencies from 10^2 to 10^6 Hz. The dielectric sample was a thin plate, $0.3 \times 0.3 \times 0.08$ cm^3, with silver contacts fired on the broad faces. The pressure cell used helium gas as the pressure fluid and was placed inside a cryogenic dewar. The pressure was monitored by the change in resistance of a calibrated manganin coil, and the temperature was determined with a chromel/alumel thermocouple mounted adjacent to the sample holder. Typical AC voltages (<10V/cm) generate a linear dielectric response and are insufficient to move any domain boundaries of the ferroelectric phases.

RESULTS AND DISCUSSION

1. *Neutron Diffraction*

The diffraction study at 295K and 1 bar shows that the sample is the rhombohedral ferroelectric *R3c* phase ($F_{R(LT)}$) and remains in that phase upon cooling to 250 K. As pressure is increased at 250 K, a transition is observed just above 3 kbars to essentially an antiferroelectric $CaTiO_3$ orthorhombic *Pbnm* (A_O) 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 $F_{R(LT)}$ and A_O phases at 250 K before the transition and at maximum pressure as well as the corresponding results on pressure decrease are given in Table 1. Figure 1 shows the $F_{R(LT)}$ - A_O 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 $F_{R(LT)}$ phase as a function of pressure 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 5.5 kbar and that there is sufficient hysteresis as pressure is decreased that the majority of the A_O phase transforms below 3 kbar back to the $F_{R(LT)}$ phase. (On increasing pressure, a "back" smooth curve interpolation would yields ~3.5 kbars for the phase transition onset.) This is in contrast to the much sharper transition observed in our previous PZT95/5-2Nb study. Furthermore, the present high pressure phase is a different high pressure orthorhombic phase than that of Pbam observed in PZT95/5-2Nb. Just as in the latter case after the initial drop of the $F_{R(LT)}$ content, the transformation remains incomplete to 5.5 kbars with ~10% of the sample remains in the $F_{R(LT)}$ low pressure phase. On pressure release, 91% of the $F_{R(LT)}$ phase is recovered with the remainder remaining in the A_O phase, an amount larger than in PZT95/5-2Nb.[4] (These data points also fit a smooth curve toward ambient pressure.) There is a similar large hysteresis in the phase recovery.

The value of the *a* and *c* cell parameters (hexagonal basis) of the $F_{R(LT)}$ phase are given in Figures 2. Solid lines through filled circles are used for 250 K data with increasing pressure; dashed lines through filled circles with dot for decreasing pressure. 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 $F_{R(LT)}$ and A_O phases. Solid heavy line goes through 250 K values (open triangles/plus signs for increasing/decreasing P) with possibly less curvature for the A_O phase than that of the dashed line through the corresponding temperature values (open circles/open triangles for increasing/decreasing P) for the $F_{R(LT)}$ phase. Note the smaller cell for the A_O phase compared to the $F_{R(LT)}$ phase. The 0.7% volume contraction at the $F_{R(LT)}$–to- A_O 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.

2. *Dielectric Properties*

The isothermal data in Figure 4 show the in-phase dielectric constant ε' at 250 K and 10 kHz versus increasing and subsequent decreasing pressure. Increasing P produces a gradual rise in ε', reaching a maximum near 3.7(1) kbar; a similar increase in ε' 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 pressure for the ε' maximum. Based on the neutron diffraction results in Figure 1, 3.7 kbar is identified as the onset of the A_O phase with increasing P. The decrease in ε' above 3.7 kbar continues to the highest pressure of 5.7 kbar where the neutron data show that over 10% by weight of the sample remains in the $F_{R(LT)}$ phase.

With decreasing P there is a gradual, continuous rise in ε' with no evidence for a maximum. Again, consistent with the neutron diffraction results in Fig. 1, these data reflect a continuous transformation of the A_O fraction of the sample back to the $F_{R(LT)}$ phase. However, part of the increase in ε' with decreasing P is attributed to the pressure dependence of ε' within the A_O phase. In contrast to an increase in ε' with increasing P in the ferroelectric $F_{R(LT)}$ phase, ε' 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 ε' at 10 kHz and 0.1 kbar in this isothermal experiment is ~242, while the final value at the same frequency and pressure 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 pressure 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 (the maximum temperature for the gas pressure cell) and the cooling to 250 K under ~0.1 kbar. 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 temperature. A second 400 K anneal at 0.1 kbar after the 250 K pressure experiment restored ε' to its original value of ~242 at 250 K.

CONCLUDING REMARKS

The pressure-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 pressure 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 15 kbar near room temperature (not shown) suggest two transitions with increasing pressure; based on published HRTEM studies[9] on similar compositions as a function of temperature (but pressure 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 pressure. Though we have some dielectric pressure data at 298 K which would be consistent with such a latter phase transition near 10 kbars, this would exceed the current pressure maximum of our neutron diffraction cell. Even though in general decreasing temperature acts as increased pressure, 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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Table 1. Refined structural parameters for $F_{R(LT)}$ and A_O phases in ceramic sample of PLZT at 250 K. For $F_{R(LT)}$, 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 A_O, space group *Pbnm* (No. 62), with Pb (& La) at 4c (x,1/4,z), Zr/Ti at 4a (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.

P, Kpsi	0	45.0	80.0	43.5*	0*
f(*R3c*)	1.0	1.0	0.13	0.13	0.92
R3c *a*, Å	5.83856(4)	5.8336(5)	5.8275(8)	5.84228(4)	5.8395(5)
R3c *c*, Å	14.4143(2)	14.375(4)	14.356(3)	14.416(2)	14.3970(2)
z(Pb)	0.2169(2)	0.2173(6)	0.2121(9)	0.2117(9)	0.2168(2)
z(Zr/Ti)	-.01352(6)	-.01493(9)	-.0149(9)	-.01550(9)	-.01331(3)
x(O)	0.1281(4)	0.1137(4)	0.107(3)	0.1131(3)	0.1275(3)
y(O)	0.3169(5)	0.3090(8)	0.293(3)	0.298(3)	0.3173(4)
f(*Pbnm*)	0.0	0.0	0.87	0.87	0.08
Pbnm *a*, Å			5.8451(6)	5.8412(6)	5.8565(8)
Pbnm *b*, Å			8.1804(3)	8.1860(3)	8.1909(9)
Pbnm *c*, Å			5.8540(7)	5.8565(7)	5.8649(7)
x(Pb)			0.0002(9)	0.0001(9)	0.010(7)
z(Pb)			-.0011(9)	-.0022(9)	0.012(9)
x(O1)			0.484(2)	0.483(2)	0.458(5)
z(O1)			0.0531(9)	0.053(4)	0.081(5)
x(O2)			0.253(9)	0.253(9)	0.254(7)
y(O2)			0.026(4)	0.026(4)	0.015(4)
z(O2)			-.263(3)	-.263(3)	-.243(6)

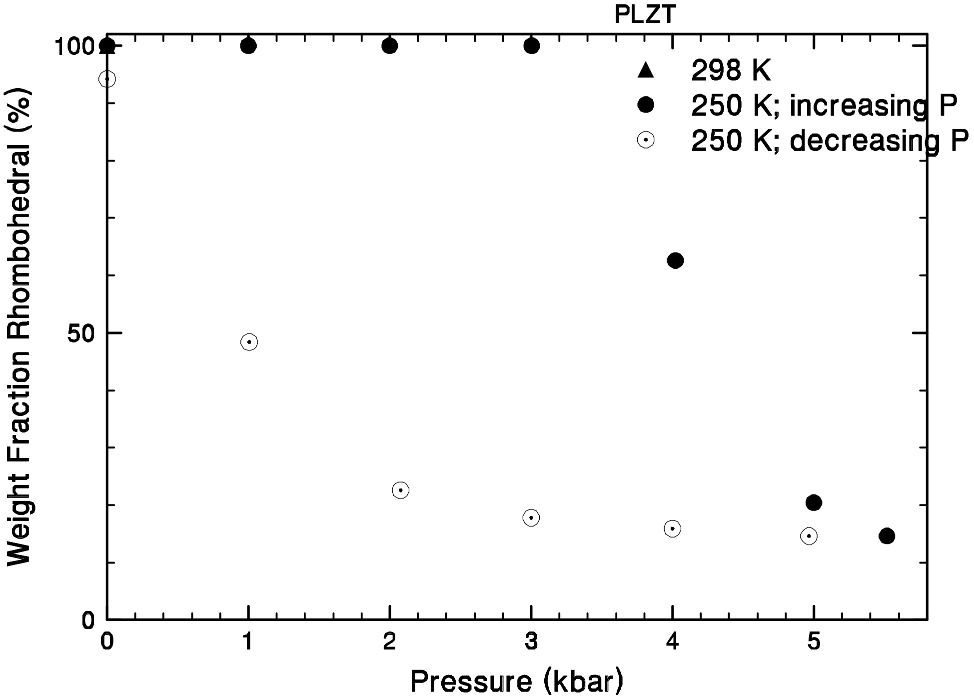

Figure 1. Weight fraction of $F_{R(LT)}$ phase as a function of increasing hydrostatic pressure at 250 K (filled circles) and at 298 K (filled triangle). These symbols are open with dot for decreasing pressure. The remaining weight fraction is the $A_{\mathbb{O}}$ phase.

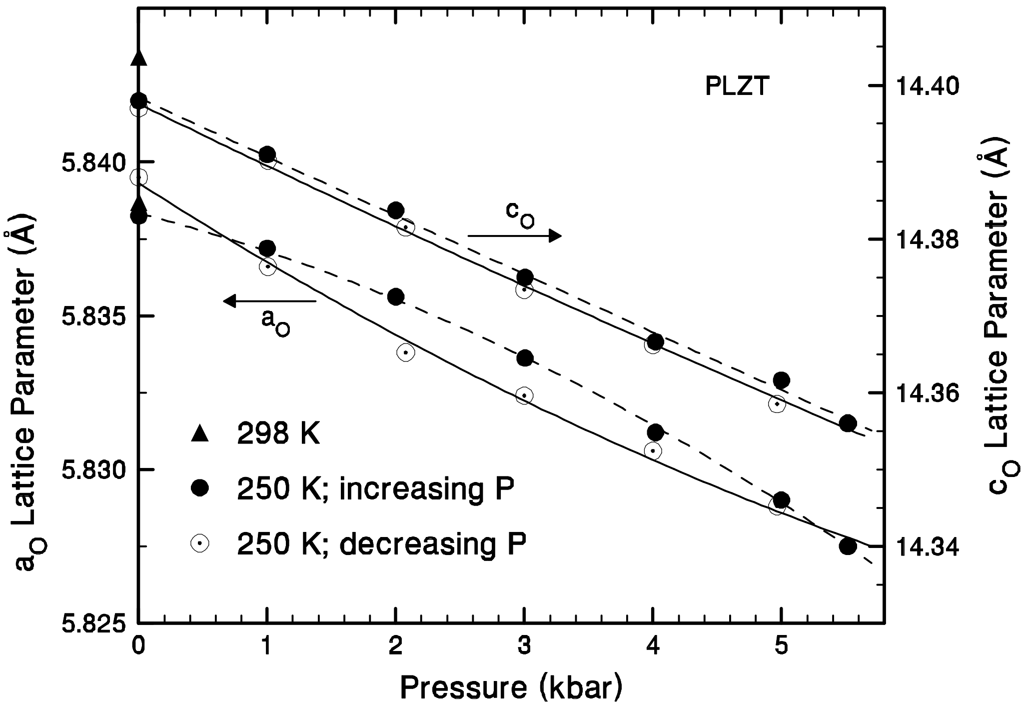

Figure 2. Relative change in the *a* and *c* cell parameters (hexagonal basis) of the $F_{R(LT)}$ phase. Solid lines through filled circles are used for 250 K data with increasing pressure; dashed lines through filled circles with dot for decreasing pressure. The corresponding 295 K, ambient P datum is a filled triangle.

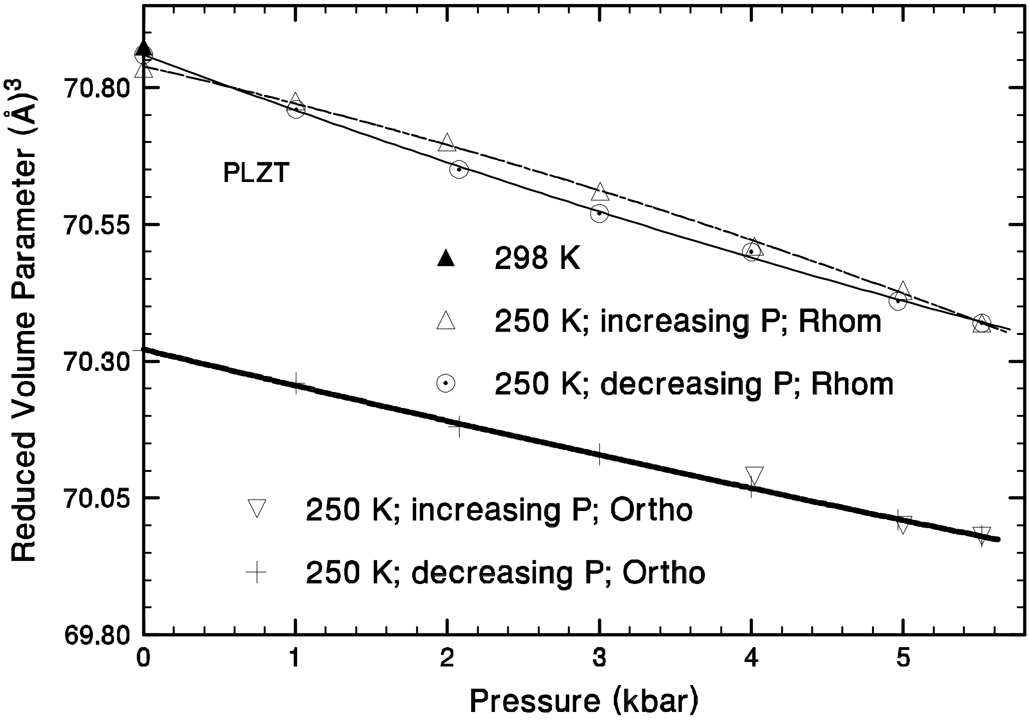

Figure 3. Reduced cell volume as a function of pressure. Solid line through 250 K values (open triangles/plus signs for increasing/decreasing P) for the A_O phase; dashed through 250 K values (open circles/open triangles for increasing/decreasing P) for the $F_{R(LT)}$ phase. Ambient shown as a filled triangle. Note the smaller cell for the A_O phase compared to the $F_{R(LT)}$ phase.

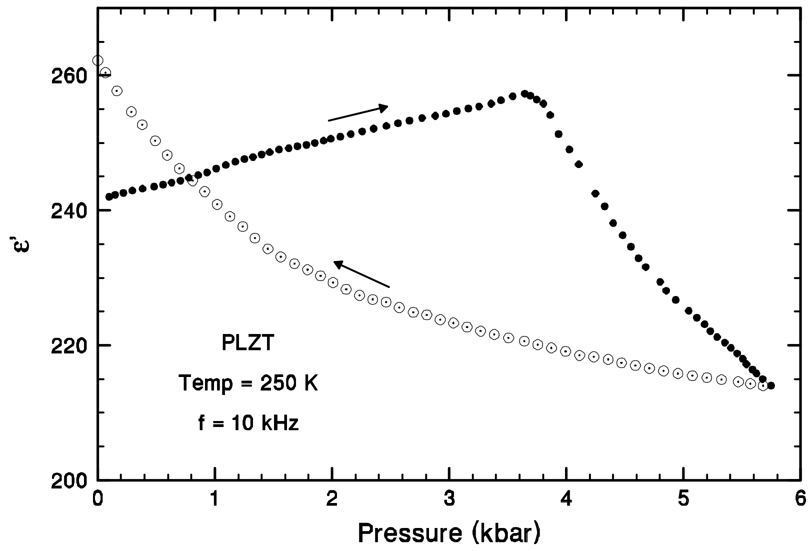

Figure 4. Dielectric constant ε' for a PLZT ceramic sample at 250 K and 10 kHz versus increasing (solid circles) and decreasing (open circles) pressure.