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Journal of the European Ceramic Society 25 (2005) 2393–2396

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Pressure-induced low symmetry phases in Ti-rich lead zirconate titanate $PbZr_{0.20}Ti_{0.80}O_3$

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Abstract

The titanium-rich PZT solid solution $PbZr_{0.20}Ti_{0.80}O_3$ was studied under high pressure by X-ray diffraction and Raman spectroscopy. A series of low-symmetry phases were observed, including monoclinic (space groups *Cm* and *Cc*) and triclinic forms (space groups $F1$ and $F\bar{1}$) in $PbZr_{0.20}Ti_{0.80}O_3$. High pressure Raman spectra obtained are consistent with a monoclinic (*Cc*)–triclinic ($F1$) phase transition involving a soft mode at 9 GPa, in agreement with the change in compressibility detected by X-ray diffraction. The strong Raman spectra observed in the paraelectric phase can also be explained by the triclinic $F\bar{1}$ symmetry.

Keywords: PZT; Perovskites; X-ray methods

1. Introduction

Due to their exceptional piezoelectric performances, compounds based on the lead zirconate titanate perovskite solid solution $PbZr_{1-x}Ti_xO_3$ (PZT) represent one of the most important class of piezoelectric materials, involved in various systems such as piezoceramics (piezoelectric transducers and actuators) and thin films (MEMS system or high-frequency components). Main compositions (with x close to 0.48) lie on what is termed the morphotropic phase boundary (MPB)[1] between the Zr-rich ferroelectric rhombohedral (*R3m*) and Ti-rich tetragonal (*P4mm*) phases. Up to now, the high piezoelectric coupling constants of these materials were attributed to the simultaneous presence of trigonal and tetragonal domains near the MPB. However, the recent discovery of a monoclinic phase (*Cm*)[2] in this region of the phase diagram provides a new explanation for the high electromechanical response, based on a polarization rotation mechanism[3,4] in which the polar axis is oriented between the directions corresponding to the tetragonal and rhombohedral forms. Additionally, a second monoclinic phase (*Cc*) with a double unit cell has been observed at low temperature[5] for $PbZr_{0.52}Ti_{0.48}O_3$.

PZT ceramics and thin films, which exhibit high dielectric and piezoelectric performance are sensitive to the level of stress induced by both external elastic and electric fields. It is thus very important to understand the effect of hydrostatic pressure on the nature and stability of the various structures in the phase diagram of this material. Tetragonal $PbTiO_3$ undergoes a classic second-order transition to a paraelectric cubic phase at high pressure.[6] Ti-rich PZT are of special interest as they cover the compositional range between pure $PbTiO_3$ and the morphotropic composition $PbZr_{0.52}Ti_{0.48}O_3$. Our previous studies on $PbZr_{1-x}Ti_xO_3$ ($0.50 \leq x \leq 0.80$) at moderate pressures ($\leq$2.5 GPa), showed that high pressure stabilizes the ferroelectric monoclinic phases responsible for the high piezoelectric properties of the MPB composition.[7] High-pressure neutron diffraction data for $x = 0.48$, showed that pressure induces polarization rotation and octahedral tilting leading to monoclinic (*Cc*) and triclinic phases ($F1$ and $F\bar{1}$).[8] This present study extends the structural investigation of PZT to higher pressures (up to 20 GPa), in Ti-rich compositions ($x = 0.80$ here) using X-ray diffraction and Raman spectroscopy. The results obtained allow us to (i) determine

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doi:10.1016/j.jeurceramsoc.2005.03.068

the phase transition sequence in this material and (ii) propose an extended pressure–composition phase diagram.

2. Experimental

The $PbZr_{1-x}Ti_xO_3$ solid solution ($x = 0.80$) was prepared by the conventional solid state reaction from high-purity (>99.9%) oxides via a two-stage calcination process.[9,10] Angle-dispersive X-ray diffraction data at high pressure were obtained using a diamond anvil cell (DAC).[9] Powdered ruby or NaCl were added as pressure calibrants. A 21:4:1 (volume ratio) methanol:ethanol:H_2O mixture was used as a pressure-transmitting medium. X-ray diffraction patterns were obtained on an imaging plate using molybdenum radiation from a microfocus tube. Pressures were measured based on the shifts of the ruby R_1 and R_2 fluorescence lines[11] or estimated using the Decker equation of state of NaCl.[12] Cell parameters were obtained by full profile refinement using the software Fullprof.[13] Pressure –volume data were fitted to Birch–Murnaghan equation of state (with $B'_0 = 4$). Raman experiments were performed in modified back-scattering geometry[6,10] using a Jobin Yvon Model U 1000 double monochromator and a liquid-nitrogen cooled CCD. The 647.1 nm line of a krypton ion laser was used for excitation. Samples were loaded in a membrane-type DAC along with a ruby crystal as a pressure calibrant and argon as a pressure-transmitting medium.

3. Results and discussion

The tetragonal $PbZr_{0.20}Ti_{0.80}O_3$ composition, was studied under high pressure by X-ray diffraction and Raman scattering. Four phase transitions were successively observed based on the changes in the Raman spectra with increasing pressure, in the spectral regions noted 1, 2, 3, 4 and 5 (Fig. 1a). Upon initial compression, the Raman spectra of $PbZr_{0.20}Ti_{0.80}O_3$ (Fig. 1b) show a behavior similar to that observed for tetragonal $PbTiO_3$, which undergoes a second-order transition to a paraelectric,[6] cubic phase at high pressure, involving a soft mode. In particular, the softening of several modes (mode 3), including the low-frequency soft mode 2, is clearly observed as in $PbTiO_3$. An abrupt change in behavior occurs at close to 2.5 GPa with no further softening of these modes in the new phase, and the appearance of the mode 1. This mode 1 originates, in the case of a tetragonal–monoclinic (*Cm*) phase transition, from the loss of degeneracy of the E phonon (in $C_{4v}{}^1$ symmetry), leading to splitting into $A' + A''$ modes. In addition, region 5 which is dominated by vibrations of O^{2-} anions[14] (stretching and bending of BO_6 octahedra, with B = (Zr, Ti)) becomes more symmetric, which corresponds to a partial displacement of the B cations towards the center of the octahedra. A second transition was found to occur at close to 4 GPa from changes in the pressure-dependence of the various bands and from the appearance of mode 4 characteristic of the low-temperature monoclinic form (*Cc*) with a doubled unit cell.[10] These transitions were also detected by X-ray diffraction by a decrease in compressibility at 2.7 GPa in the case of the $F_T(Cm)$–$F_M(Cc)$ phase transition and a 0.4% volume change at 4 GPa for the $F_M(Cm)$–$F_M(Cc)$ phase transition. The $F_M(Cc)$ phase is more compressible as the compression mechanism is characterized by the rotation of octahedra.

The *Cc*–*F*1 phase transition observed for the morphotropic composition $PbZr_{0.52}Ti_{0.48}O_3$ by neutron diffraction[8] is also clearly seen for this Ti-rich sample (Fig. 1b and c) with the

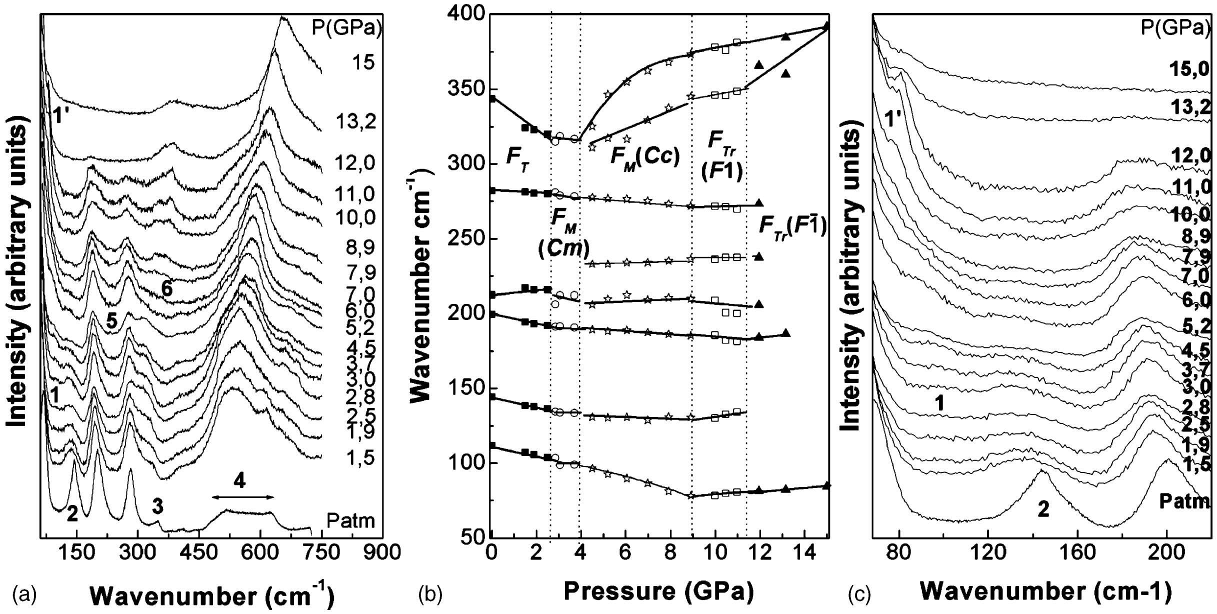

Fig. 1. (a) Raman spectra for the tetragonal F_T, monoclinic F_M (*Cm*), F_M (*Cc*), triclinic F_{Tr} (*F*1) and $P_{Tr}(F\bar{1})$ phases of $PbZr_{0.20}Ti_{0.80}O_3$ as a function of pressure. (b) Pressure dependence of the Raman modes and (c) F_M (*Cc*) → F_{Tr}(*F*1) phase transition with 1 → 1′.

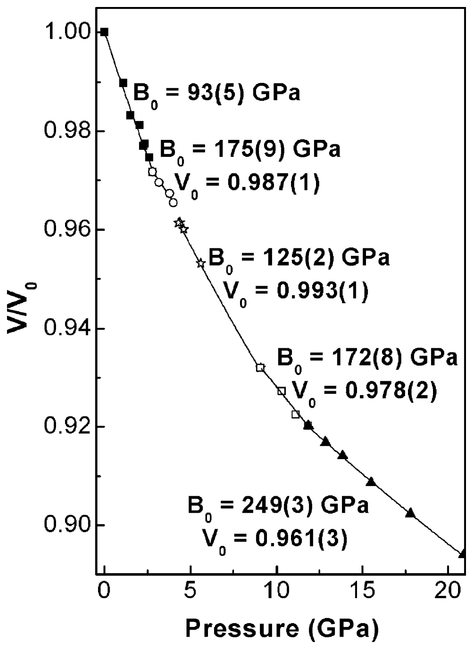

Fig. 2. Volume-change vs. pressure of $PbZr_{0.20}Ti_{0.80}O_3$ at 298 K. The B_0 values are calculated with the Birch–Murnaghan state equation ($B'_0 = 4$).

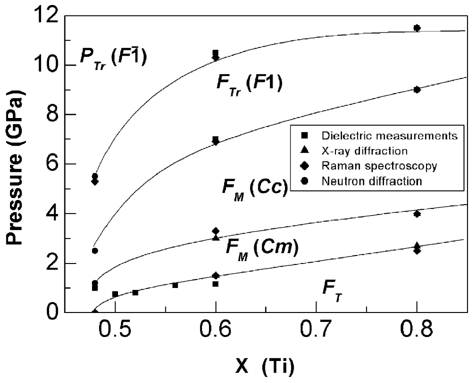

Fig. 3. Pressure–composition phase diagram of Ti-rich PZT.

softening of the mode 1, which is replaced by $1'$ at the transformation around 9 GPa. The transition to the paraelectric triclinic phase ($F\bar{1}$) is found to occur at about 11.5 GPa, with the disappearance of the mode 2. This paraelectric form is still characterized by a strong Raman spectrum allowed by group theory (in contradiction with the cubic form found in $PbTiO_3$). Both transitions were also detected by X-ray diffraction by a decrease in compressibility; at the same pressures (Fig. 2).

4. Concluding remarks

A series of low symmetry phases, including monoclinic (space groups Cm and Cc) and triclinic forms (space groups $F1$ and $F\bar{1}$) were observed in the present study of the titanium-rich PZT $PbZr_{0.20}Ti_{0.80}O_3$ under high pressure by X-ray diffraction and Raman spectroscopy.

A pressure composition phase diagram can now be proposed (Fig. 3) by combining the results of this study with those obtained by neutron diffraction and dielectric measurements on various compositions in the Ti-rich region[7,8]. This phase diagram is complex with four ferroelectric and one paraelectric one. This complexity could have been previously predicted due to the presence of preexistent rotational and ferroelectric lattice distortions (R_4^+ and Γ_4^-) in the $PbZrO_3$ and $PbTiO_3$ perovskite end-member. By stabilizing monoclinic phases, hydrostatic pressure can tune the MPB to include compositions that do not normally lie in the MPB. The high-pressure behavior of this system is characterized by two mechanisms: (1) a rotation and reduction of the spontaneous polarization and (2) octahedral tilting. Pressure, as in the case of temperature and electric fields, is found to induce polarization rotation.

Acknowledgement

We would like to acknowledge the European Union for funding the work at LENS under Contract No. RII3-CT-2003-506350.

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