The equation of state of $PbTiO_3$ up to 37 GPa: a synchrotron x-ray powder diffraction study

2002 J. Phys.: Condens. Matter 14 10601

(http://iopscience.iop.org/0953-8984/14/44/340)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 10601–10604 PII: S0953-8984(02)39631-0

The equation of state of $PbTiO_3$ up to 37 GPa: a synchrotron x-ray powder diffraction study

A Sani[1], **M Hanfland**[1] **and D Levy**[2]

[1] European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France
[2] Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino,
via Valperga Caluso 35, I-10125 Torino, Italy

E-mail: sani@esrf.fr

Received 1 June 2002
Published 25 October 2002

Abstract

High-pressure synchrotron x-ray powder diffraction patterns were collected using ID09 of ESRF (Grenoble, France) for a powder sample of $PbTiO_3$, placed in a diamond anvil cell. The patterns were collected at room temperature using nitrogen (up to 37 GPa) and methanol–ethanol solution (up to 7 GPa) as pressure-transmitting media. The bulk moduli were calculated for the first time using the Vinet equation of state and they were compared to those of isostructural compounds. The trend of the spontaneous polarization as a function of pressure confirms that the ferroelectric–paraelectric phase transition at 11.2 GPa possesses a second-order character.

1. Introduction

$PbTiO_3$ is one of the more interesting and most studied ferroelectric perovskites. Its structure under ambient conditions possesses a tetragonal distortion away from cubic symmetry (space group $P4mm$, $a = 3.899$ Å, $c = 4.143$ Å) and the cation shifts along the ferroelectric axis are markedly larger than those of other ferroelectric perovskites (e.g. $BaTiO_3$). These properties are responsible for the wide range of temperature stability of the ferroelectric phase: the ferroelectric–paraelectric (tetragonal–cubic) phase transition temperature (765 K) is higher than those of all other isostructural ferroelectrics. Above 765 K $PbTiO_3$ is cubic with space group $Pm3m$.

The stability of the room temperature ferroelectric phase and the nature of the temperature-driven phase transition have been extensively studied during the last few decades by several experimental techniques (see for instance [1] and references therein) and computational methods (see for instance [2]). There is poor consensus regarding the nature of this phase transition. For a long time it was considered as a textbook example of a purely displacive first-order phase transition, but recently EXAFS [1] and low-frequency Raman spectroscopy measurements [3] suggested the presence of non-negligible order–disorder behaviour.

Little is known about the behaviour of $PbTiO_3$ under pressure: the literature x-ray studies do not exceed 8 GPa [4, 5]. Inoue and Asada [6] report a tetragonal–cubic phase transition in Nb-doped $PbTiO_3$ at 5.8 GPa, while a second-order pressure-driven phase transition at 12.1 GPa was observed by the study of the soft modes by Raman spectroscopy [7].

In this study we report the first x-ray diffraction study of lead titanate up to 37 GPa, the aim of which was to get information on the value of the critical pressure and the character of the phase transition.

2. Experimental details

High pressure was achieved by means of a membrane-type diamond anvil cell. Data were collected in two different runs: one in the 0–6.7 GPa range using a 600 μm diameter culet diamond with methanol–ethanol (4:1) solution as the transmitting pressure medium, the second one from 1.4 to 37 GPa using a 300 μm diameter culet diamond and N_2 as the pressure medium. Some diffraction patterns were collected also in decompression, in order to check the reversibility of the phase transition. The measurement of the pressure was carried out by means of the fluorescence shift of a ruby pellet placed on one of the two anvils, using a non-linear hydrostatic pressure scale [8].

X-ray powder diffraction patterns were collected at ID09 of ESRF, at the wavelength of 0.431 04 Å during the first run and 0.414 36 Å during the second run. The x-rays from the U46 undulator were focused vertically with a Pt-coated Si mirror and horizontally by means of an asymmetrically cut bent Si(111) Laue monochromator [9] to a beam size of 30×30 μm^2.

The diffraction images collected on the MAR-345 with pixels of dimension 100 μm^2 were integrated by means of the software FIT2D [10] into one-dimensional diffraction patterns (figure 1).

The structural refinement of the integrated patterns was achieved by means of Rietveld method as implemented in the GSAS [11] software package. A correction for anomalous dispersion of the Pb atom was applied, using the values of -1.407 and 4.007 for f' and f'' respectively (tabulated data). A pseudo-Voigt profile function proved to be appropriate to fit the experimental pattern and no symmetry correction was applied.

3. Results and discussion

Figure 2 shows the dependence of the cell edges upon applied pressure for the two runs. The good agreement of the data collected with the two different pressure-transmitting media is evident.

The study of the evolution of the cell parameters with pressure allowed the location of the tetragonal–cubic phase transition at about 11.2 GPa, in agreement with the value of 12.1 GPa reported by Sanjurio *et al* [7]. No additional phase transitions, such as that recently observed in $KNbO_3$ at about 40 GPa [12], were detected in the pressure range explored. The transition is fully reversible and no hysteresis effect was detected (figure 3).

In the tetragonal phase the two cell parameters show different compressibilities: while the c-axis shows a contraction of 6.7%, the a-axis contracts by only 0.9%. The dependences of the cell edges on pressure are both clearly non-linear, in disagreement with the results obtained by Inoue and Asada [6] which indicate a linear contraction for both cell parameters. Indeed, the observed a-values are fitted by a second-order polynomial in p, while c is properly fitted by a third-order polynomial. $\mathrm{d}a/\mathrm{d}p$ and $\mathrm{d}c/\mathrm{d}p$ are always negative, in contrast with previously reported data which evidence an expansion of a at low pressures [4]. Comparing the behaviour

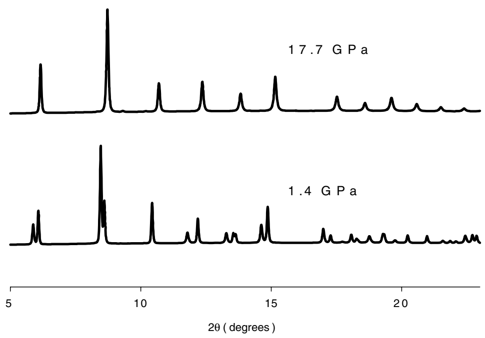

Figure 1. One-dimensional patterns of cubic (above) and tetragonal (below) PbTiO$_3$.

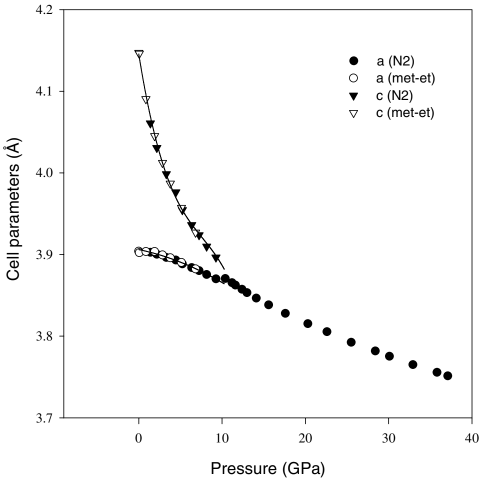

Figure 2. Variation of the cell edges with external pressure. The continuous curve relates to the polynomial fit.

of the unit-cell edges upon applying pressure and on increasing temperature [13] we find striking differences. It can be observed that the pressure induces a contraction of both unit-cell parameters; however, the opposite behaviour is seen when approaching the critical temperature: c shows a contraction and a an expansion.

The fit of the data to the Vinet equation of state [14] gives the bulk moduli for the two phases: $K_{0T} = 100(3)$ GPa, $K'_T = 4$ (implied value) and $K_{0C} = 195(3)$ GPa, $K'_C = 4$ (implied value). The tetragonal phase is more compressible than for other ferroelectric perovskites: the bulk modulus of the ferroelectric phase of KNbO$_3$ is 170 GPa [14].

The shifts of the Pb^{2+} and Ti^{4+} cations along the ferroelectric axis indicate that at pressures up to about 2 GPa, the Pb^{2+} cations are more displaced than the Ti^{4+} ones. The difference in shift tends to reduce upon increasing pressure. The decrease of the cation shift is smooth until the phase transition occurs, where no abrupt decrease was observed.

The cation displacement is directly related to the ferroelectric character of the perovskite-type structure. If we assume that the crystal is purely ionic and neglect the electronic polarization, the spontaneous polarization is proportional to $\sum_i (\delta z_i q_i / V)$, where δz_i is the displacement of the ith ion carrying a charge q_i from the centre of the oxygen environment and V is the volume of the unit cell [15]. Figure 4 shows the dependence of the spontaneous polarization P on pressure using the displacement of the ith cation of the structural refinement and an estimation of the cationic charge from the evaluation of the electronegativity. Despite the naïvety of this calculation (the electronic polarization is not considered), the value of the spontaneous polarization obtained at room conditions (59 μC cm^{-2}) is in perfect agreement with the value of 57 μC cm^{-2} obtained by pyroelectric measurements [16]. The evolution of the spontaneous polarization calculated in this way shows a continuous decrease towards the zero, which evidences a second-order (or at least weakly first-order) phase transition.

4. Conclusions

In this work we have reported the structural study of PbTiO$_3$ up to 37 GPa. This study accessed the critical pressure (11.2 GPa) at which the ferroelectric–paraelectric phase transition takes

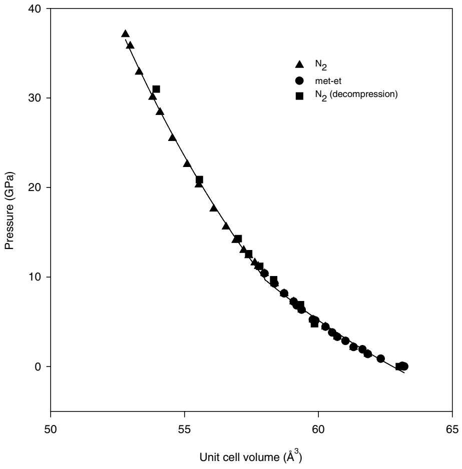

Figure 3. Volume variations in compression and decompression. The continuous curve relates to the fit of the Vinet equation of state function.

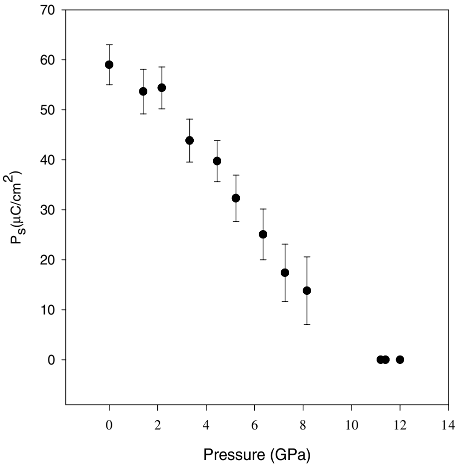

Figure 4. Spontaneous polarization as a function of applied pressure.

place. The behaviour of the spontaneous polarization calculated from the ionic displacements indicates that the phase transition has a second-order character. In agreement with the suppositions of Samara [17], a crossover in the order of the phase transition (from first to second order) occurs upon increasing pressure.

References

[1] Ravel B *et al* 1995 *Ferroelectrics* **164** 265
[2] García A and Vanderbildt D 1996 *Phys. Rev.* B **54** 3817
[3] Fontana M D *et al* 1990 *Europhys. Lett.* **11** 419
[4] Ramirez R *et al* 1991 *Solid State Commun.* **77** 927
[5] Nelmes R J and Katrusiak A 1986 *J. Phys. C: Solid State Phys.* **19** L725
[6] Inoue K and Asada T 1973 *Japan. J. Appl. Phys.* **12** 1786
[7] Sanjurio J A *et al* 1983 *Solid State Commun.* **48** 221
[8] Mao H K *et al* 1986 *J. Geophys. Res.* **91** 4673
[9] Shultze C *et al* 1998 *J. Synchrotron Radiat.* **5** 77
[10] Hammersley A *et al* 1996 *High Pressure Res.* **14** 235
[11] Larrson A C and von Dreele R B 1994 General structure analysis system *Los Alamos National Laboratory Report* LAUR 86-748
[12] Kobayshi K *et al* 2000 *Phys. Rev.* B **61** 5819
[13] Vinet P *et al* 1989 *J. Phys.: Condens. Matter* **1** 1941
[14] Chervin J C *et al* 1999 *Solid State Commun.* **110** 247
[15] Kuprianov M F *et al* 1983 *Phase Transit.* **4** 55
[16] Rameika J P and Glass A M 1970 *Mater. Res. Bull.* **5** 37
[17] Samara G A 1971 *Ferroelectrics* **2** 277