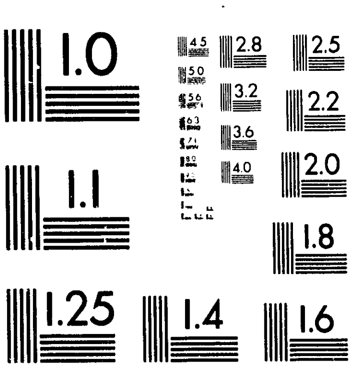

1.0
4.5
5.0
5.6
6.3
7.1
8.0
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

1 of 1

ANL/MSD/CP--78507
CONF-930852--2

The Electromechanical Properties of Tetragonal $BaTiO_3$ and $PbTiO_3$ Single Crystals*

Z. Li, C. M. Foster, M. Grimsditch, and S.-K. Chan
Materials Science Division
Argonne National Laboratory, Argonne, IL 60439

RECEIVED
AUG 1
OSTI

July 1993

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

To be presented at the Eighth International Meeting on Ferroelectricity (IMF8), Gaithersburg, MD, August 8-13, 1993, and published in the Proceedings.

---

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under contract #W-31-109-ENG-38.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

THE ELECTROMECHANICAL PROPERTIES OF TETRAGONAL $BaTiO_3$ AND $PbTiO_3$ SINGLE CRYSTALS*

Z.LI, C.M.FOSTER, M.GRIMSDITCH AND S.-K.CHAN
Materials Science Division, Argonne National Laboratory,
Argonne IL 60439, USA

Abstract The velocities of propagation for longitudinal and transverse sound waves in various directions have been measured by Brillouin scattering on high-quality mono-domain single crystals of $BaTiO_3$ and $PbTiO_3$. Using these velocities and also the dielectric permittivities measured by the impedance method and by Raman spectroscopy, a complete set of elastic stiffness moduli, C_{ijkl}, piezoelectric constants, e_{rij} and dielectric permittivity, ε_{ij}, has been determined at ambient temperature. The dependence of the electromechanical properties on orientation and frequency will be presented for both materials and the physical implications will be discussed.

INTRODUCTION

$BaTiO_3$ and $PbTiO_3$ that have similar ABO_3 perovskite structures are two of the most important ferroelectric materials. At high temperature, both materials are paraelectric with the cubic structure (Pm3m). On cooling, $BaTiO_3$ undergoes successive structural phase transitions with its symmetry changing from cubic to tetragonal (131°C), then to orthorhombic (5°C) and finally to rhombohedral (-90°C), whereas $PbTiO_3$ has only one transformation from cubic to tetragonal (490°C). The nature of the phase transformations for these two materials are, however, different. It is generally believed that the origin of the phase transition for $PbTiO_3$ is displacive, whereas that for $BaTiO_3$ is order-disorder type[1,2]. Both materials are ferroelectric with tetragonal structures at room temperature, but the lattice strain c/a ratios are quite different, about 1% for $BaTiO_3$ and 6% for $PbTiO_3$. The technological importance of both materials has been demonstrated repeatedly in the literature, and the physical properties of materials in

---

* Work supported by the U.S.Department of Energy, BES-Materials Sciences, under Contract #W-31-109-ENG-38.

ceramic form have been extensively studied. Only recently, however, have anisotropic elastic, piezoelectric and dielectric properties of mono-domain single crystals of $BaTiO_3$ and $PbTiO_3$ been accurately measured[3,4]. These not only provide us with basic parameters for practical applications but also enable us to further understand the different nature of phase transformations in these two materials. In this paper we present a complete set of elastic, piezoelectric and dielectric constants and discuss the orientation and frequency dependence of the electromechanical properties for both $BaTiO_3$ and $PbTiO_3$ mono-domain single crystals.

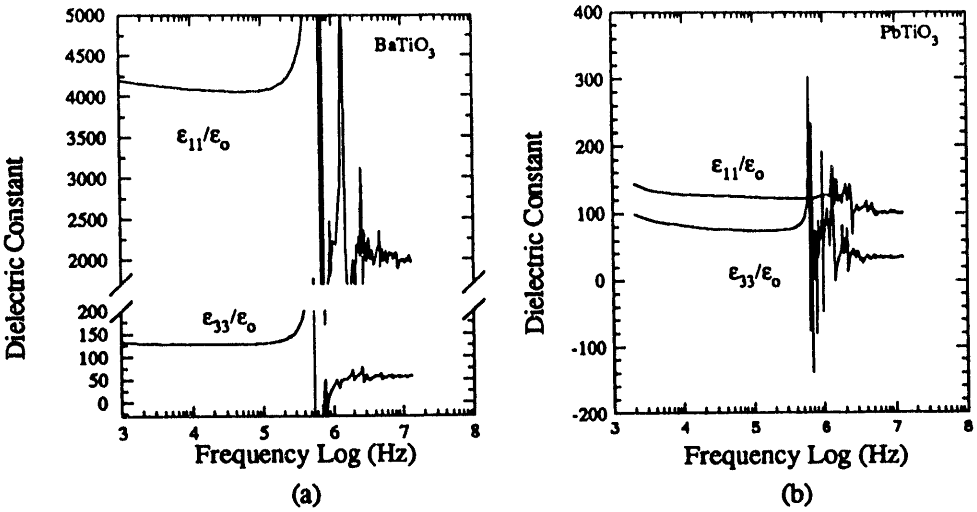
SAMPLE PREPARATION

Tetragonal $BaTiO_3$ single crystals were obtained from the Institute of Physics, Chinese Academy of Science, Beijing, China. The crystals were grown by the top seed solution method and have been poled in a dc electric field to obtain a mono-domain crystal. The dimensions of the samples were approximately 3 x 3 x 3 mm. The $PbTiO_3$ single crystals were grown by a flux solution method. The PbO was used as a flux and the mole ratio of PbO to TiO_2 was about two. The as-grown single crystals then underwent a series of treatments that included (1) mechanical detwinning to eliminate 90° domains, (2) heat treatment to reduce dielectric frequency dispersion and dielectric loss, and (3) electrical poling to remove 180° domains. Detailed information of growth and preparation of mono-domain single crystals of $PbTiO_3$ is reported elsewhere [5]. The final dimensions of the $PbTiO_3$ samples were about 3 x 3 x1.5.

For both materials, three sets of parallel crystallographic planes, (100), (010) and (001), of the crystals were obtained by polishing on a standard metallographic disc, using 9, 6, 3, and 1 mm diamond pastes to achieve a mirror-like surface. Several samples were electroded with silver paint on the (100) or (001) faces for dielectric measurements.

DIELECTRIC CONSTANTS

For dielectric measurements, the sample was held in a HP 16034 test fixture, which was connected to a computer controlled HP4192A LF Impedance Analyzer. The anisotropic dielectric permittivities, ε_{11} and ε_{33}, were determined automatically with the frequency sweeping from 1kHz to 13 MHz. Figures 1a and 1b illustrate the dielectric constants, $\varepsilon_{11}/\varepsilon_o$ and $\varepsilon_{33}/\varepsilon_o$, as a function of frequency for $BaTiO_3$ and $PbTiO_3$, respectively. The ε_o is the permittivity of vacuum which is 8.8542×10^{-12} F/m. The values of $\varepsilon_{11}/\varepsilon_o$ and



(a) (b)

FIGURE 1. Dielectric constants as a function of frequency for (a) BaTiO$_3$ and PbTiO$_3$

$\varepsilon_{33}/\varepsilon_o$ decrease slightly as the frequency increases up to the resonant frequencies of the crystals. Over this frequency range the dielectric constants are those at constant stress, $\varepsilon_{ij}^T/\varepsilon_o$. Above the resonant frequencies, $\varepsilon_{11}/\varepsilon_o$ and $\varepsilon_{33}/\varepsilon_o$ remain constant and they are the dielectric constants at constant strain, $\varepsilon_{ij}^S/\varepsilon_o$.

Figure 1a shows that the dielectric anisotropy is very large for BaTiO$_3$ single crystals. The ratio of $\varepsilon_{11}/\varepsilon_{33}$ is about 30. The reason of this is unknown. However, we have found that the $\varepsilon_{11}^T/\varepsilon_o$ decreases significantly with temperature, from 4000 to 3000, as the temperature increases from 22° to 40°C[6]. This may be related to the phase transformation of BaTiO$_3$ at 5°C. In contrast, the dielectric anisotropy is small for PbTiO$_3$ and the ratio is less than 2. Table 1 lists the dielectric constants at constant stress, $\varepsilon_{ij}^T/\varepsilon_o$, and at constant strain, $\varepsilon_{ij}^S/\varepsilon_o$, which are determined at 10 kHz and 12 MHz, respectively. The $\varepsilon_{33}/\varepsilon_o$ of BaTiO$_3$ measured from our study are significantly smaller than the values reported previously in the literature, which are 170 and 110 for $\varepsilon_{33}^T/\varepsilon_o$ and $\varepsilon_{33}^S/\varepsilon_o$, respectively[7,8]. Since BaTiO$_3$ has a large dielectric anisotropy, we have found that any residual 90° domains will significantly affect the dielectric properties. The dielectric constants of PbTiO$_3$ from this study are in good agreement with the calculated values using a Landau-Ginsburg-Devonshire type thermodynamic approach by Haun et al[9], but are much smaller than those measured on single crystals by Fesenko et al[10] and on polycrystalline ceramics by Ikegami et al[11]. Table 1 also lists the high frequency dielectric constants calculated from the A and E optical modes of Raman spectroscopy using the Lyddane-Sacks-Teller (LST) relation[12,13]. The

TABLE 1 Dielectric Constants of $BaTiO_3$ and $PbTiO_3$.

	$\varepsilon^T_{11}/\varepsilon_0$ (10kHz)	$\varepsilon^T_{33}/\varepsilon_0$ (10kHz)	$\varepsilon^S_{11}/\varepsilon_0$ (12MHz)	$\varepsilon^S_{33}/\varepsilon_0$ 12MHz)	$\varepsilon^S_{11}/\varepsilon_0$ (Raman)	$\varepsilon^S_{33}/\varepsilon_0$ (Raman)
$BaTiO_3$	4100	127	1980	56	2000*	37+
$PbTiO_3$	130	80	101	34	107	28.6

*** Ref 12, + Ref 13**

dielectric constants determined along the polar direction (c-axis) from the impedance method and from Raman spectroscopy are similar for $PbTiO_3$ but different for $BaTiO_3$. This difference indicates that contrary to $BaTiO_3$, a jump due to atomic relaxation does not occur at high frequency for $PbTiO_3$ single crystals.

ELASTIC AND PIEZOELECTRIC CONSTANTS

Sound velocities were measured using the Brillouin scattering technique. Brillouin scattering is the inelastic scattering of light by acoustic phonons. The frequency shifts $\Delta\nu$ observed in Brillouin scattering are directly related to the sound velocity V[14]. The elastic and piezoelectric constants may then be calculated from the sound velocities using Christoffel's equation as

$$\rho V_q^2 u_i = \Gamma_{ijkl} q_j q_l u_k , \tag{1}$$

where u_i is the polarization (displacement) of the wave, Γ_{ijkl} is the piezoelectrically stiffened elastic modulus given by

$$\Gamma_{ijkl} = C^E_{ijkl} + [(e_{rij} q_r)(e_{skl} q_s)/(\varepsilon^S_{mn} q_m q_n)] , \tag{2}$$

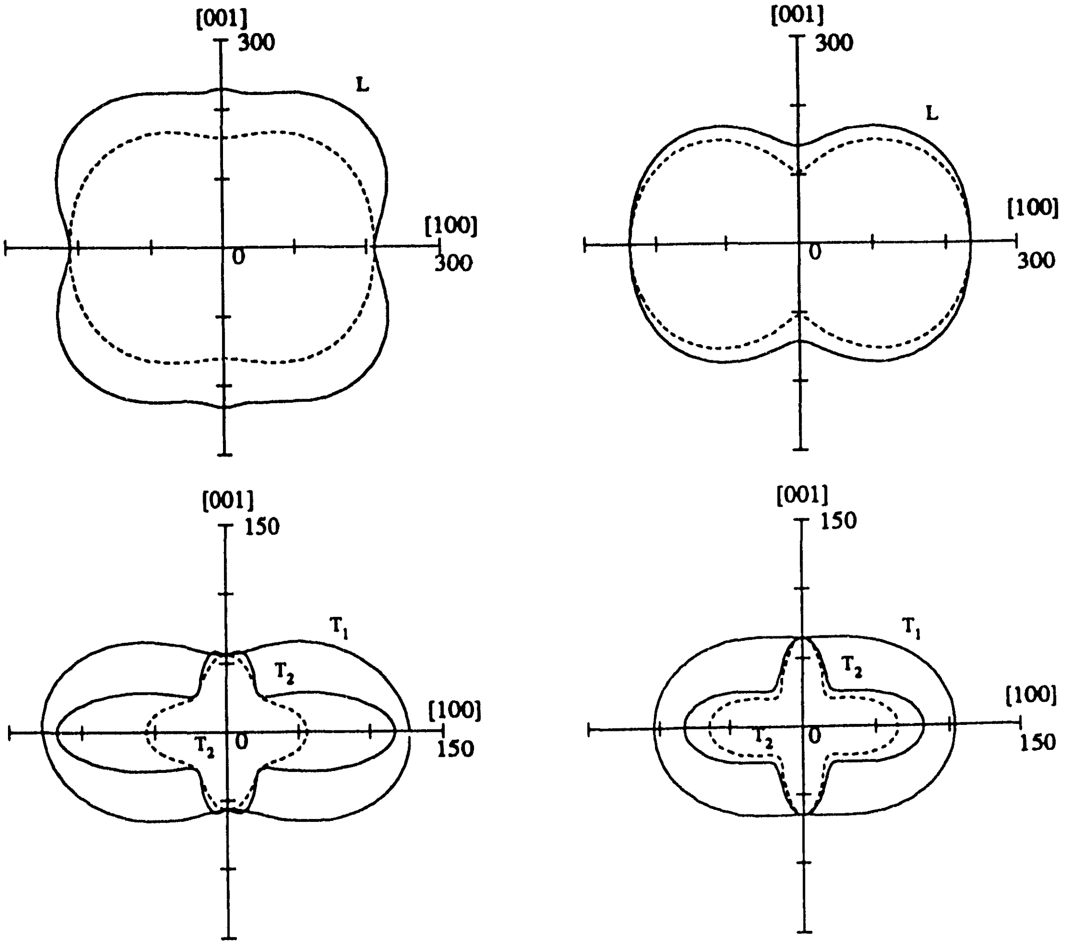
and ρ is the density of materials. In Equation (2), C^E_{ijkl} is the elastic stiffness modulus at constant electric field; e_{rij} is the piezoelectric stress constant, and ε^S_{mn} is the permittivity at constant strain. For tetragonal crystal with P4mm symmetry, the non-vanishing C^E_{ijkl},

TABLE 2 Elastic and Piezoelectric Constants of $BaTiO_3$ and $PbTiO_3$

	C^E_{11}	C^E_{33}	C^E_{12}	C^E_{13}	C^E_{44}	C_{66}	e_{15}	e_{31}	e_{33}
			(GPa)					(C/m^2)	
$BaTiO_3$	211	160	107	114	56.2	127	32.6	-3.88	5.48
$PbTiO_3$	235	105	101	98.8	65.1	104	3.92	-0.98	3.35
	S^E_{11}	S^E_{33}	S^E_{12}	S^E_{13}	S^E_{44}	S_{66}	d_{15}	d_{31}	d_{33}
			($x10^{-3}/GPa$)					($10^{-12}C/N$)	
$BaTiO_3$	8.01	12.8	-1.57	-4.60	17.8	7.91	580	-50.0	106
$PbTiO_3$	7.06	21.3	-0.40	-6.27	15.4	9.62	60.2	-27.5	83.7

e_{rij}, and ε^S_{mn} are, in Voigt notations, C^E_{11}, C^E_{12}, C^E_{13}, C^E_{33}, C^E_{44}, C^E_{66}, e_{15}, e_{31}, e_{33}, ε^S_{11} and ε^S_{33}. To obtain these eleven independent parameters, a total of fifty velocities were measured for the longitudinal, L, and the two transverse modes, T_1 and T_2 , in twenty wave propagation directions for each material[3,4]. Using Equations 1 and 2, the elastic constants and the piezoelectric constants were calculated from the velocities by combining algebraic computations with a computer-based nonlinear least-squares fitting method.

A summary of all the individual elastic constants, C^E_{ij}, and piezoelectric constants, e_{ij}, are given in Table 2. For the purpose of practical applications, the elastic compliance moduli and piezoelectric strain constants, S^E_{ij} and d_{ij}, calculated from C^E_{ij} and e_{ij} are also listed in Table 2. The elastic stiffness moduli for both materials are similar except for C^E_{33}. However, the absolute values of the piezoelectric constants of $PbTiO_3$, especially e_{15}, are much smaller than those of $BaTiO_3$, which indicates that the



(a) (b)

FIGURE 2. Directional dependence of the compressional (L) and shear (T) moduli (ρV^2) in the (010) plane, (a) $BaTiO_3$ and (b) $PbTiO_3$

electromechanical coupling of $BaTiO_3$ is stronger than that of $PbTiO_3$ at room temperature. The large value of e_{15} may result from the proximity of the tetragonal to orthorhombic phase transition of $BaTiO_3$ at 5°C[6].

The directional dependence of the compressional and shear moduli (ρV^2) in the (010) planes for $BaTiO_3$ and $PbTiO_3$ are shown in Figures 2a and 2b, respectively. The dotted curves in these figures are the values of ρV^2 calculated from elastic constants alone, ignoring piezoelectricity. For each direction, the longitudinal (L) velocity gives the compressional modulus while each of the transverse (T) velocities leads to a shear modulus. The T_1 mode leads to a shear modulus corresponding to displacement perpendicular to the plane and the T_2 mode to one corresponding to a displacement in the plane. From Figures 2a and 2b, it is evident that the electromechanical coupling is a maximum when the displacement is parallel to the polarization c-axis. At its maximum, for $PbTiO_3$, approximately one fourth of both compression and shear energies are converted into electrical energy due to the electromechanical coupling. These are relatively small in comparison with $BaTiO_3$, for which, at room temperature, one third of the compression energy and one half of the shear energy are converted as illustrated in Figure 2a. The smallness of the electromechanical coupling in $PbTiO_3$ is refelected that the larger stress is needed for switching 90° domains in $PbTiO_3$ compared to what is needed in the $BaTiO_3$[15].

REFERENCES

[1]. F.Jona and G.Shirane, Ferroelectric Crystals, (Pergamon Press, New York 1962).
[2]. R.Comes, M.Lambert, and A Guinier, Solid State Commun. **6**, 715 (1968).
[3]. Z.Li, S.-K.Chan, M.Grimsditch and E.S.Zouboulis, J. Appl. Phys. 70 7327 (1991).
[4]. Z. Li, M. Grimsditch, X. Xu and S.-K. Chan, Ferroelectrics, (1993).
[5]. Z.Li, X.Xu, X.H.Dai, D.J.Lam and S.-K.Chan, Ceramics-Adding the Value, Vol 1.Edited by M.J.Bannister, (CSIRO Publications, Melbourne, Austrlia, 1992) pp. 457-462.
[6]. Z.Li, M.Grimsditch and S.-K.Chan, in this issue.
[7]. A.V.Turik, G.I.Khasabova, and E.N.Sidorenko, Sov. Phys. Solid State 27, 653 (1985).
[8]. D Berlincourt and H. Jaffe, Phys. Rev. 111, 143 (1958).
[9]. M.J.Haun, E.Furman, S.J.Jang, H.A.McKinstry and L.E.Cross, J. Appl. Phys. 62 3331 (1987).
[10]. V.G.Garilyachenko and E.G.Fesenko, Soviet Physics - Crystall. 16 549 (1971).
[11]. S.Ikegami, I.Ueda and T.Nagata, J. Acoust. Soc. Am. 50 1060 (1971).
[12]. Y.Tominaga and T.Nakamura, J. Phy. Soc. Japan 39, 746 (1975).
[13]. G.Burns, Phy. Lett. 43A, 271 (1973).
[14]. M.Grimsditch, Physica B 150, 271 (1988).
[15]. Z.Li, C.M.Foster, X.H.Dai, X Z.Xu, S.-K.Chan and D.J.Lam, J. Appl. Phys. 71 4481 (1992).

DATE FILMED

10/15/93

END