Lattice Parameters and Birefringence in PbTiO$_3$ Single Crystals

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Abstract

Measurements of lattice parameters and birefringence of PbTiO$_3$ single crystals are described as a function of temperature. The anomalous rise in birefringence with temperature is interpreted in terms of lattice strain and dielectric polarization.

Introduction

PbTiO$_3$ is a simple perovskite ferroelectric undergoing a displacive phase transition (tetragonal to cubic) at around 490°C. At room temperature the structure has the space group $P4mm$($C_{4h}$), with a tetragonal distortion of $c/a$ = 1.06. Neutron diffraction work shows that at room temperature the Ti and O atoms are displaced by 0.50 and 0.32 Å respectively in the same direction (Glazer & Mabud, 1978). The shifts of Ti and O are found to decrease with rise in temperature. There exists a great deal of published work on powdered PbTiO$_3$ (e.g. Shirane, Hoshino & Suzuki, 1950; Shirane & Suzuki, 1952; Smolenskii, 1951; Kobayashi, Okamoto & Ueda, 1956; Ikegami, Ueda & Miyazawa, 1969), but comparatively little work has been done on single crystals. This is mainly due to the difficulty in growing single crystals of the required quality.

Single crystals of PbTiO$_3$ have been grown (Nomura & Sawada, 1952; Rogers, 1952; Kobayashi, 1958; Bhide, Deshmukh & Hegde, 1962; Remeika & Glass, 1970; Gavrilyachenko, Spinko, Martynenko & Fesenko, 1970), but in most cases they have either been grown from fluxes that could impart impurities to the crystals or they have been prepared with dopants to meet special requirements. Some electrical and optical properties of this crystal have been reported by a number of workers (Fesenko & Kolesova, 1960; Fesenko, Gavrilyachenko, Spinko, Martynenko, Semenchev & Lapin, 1973; Turik, Fesenko, Gavrilyachenko & Khasabova, 1975; Bhide, Hegde & Deshmukh, 1968). However, no lattice-parameter measurements of single crystals have been reported to date. Birefringence of this material was measured by several authors (e.g. Forsburgh, 1952; Shirane, Pepinsky & Frazer, 1955). The birefringence is found to be anomalous in that as the temperature is increased it rises before eventually falling to zero at the ferroelectric–paraelectric transition. A theoretical discussion of this behaviour was given by Kobayashi & Yamada (1959) in terms of local fields at each atom site and lattice deformation. This led to an expression for the birefringence containing high-order terms in $(c/a - 1)$.

In this paper we show measurements of lattice parameters as a function of temperature and use them, together with previously measured values of the spontaneous polarization, to explain the anomalous birefringence results.

Specimen preparation

The phase diagram in the system PbO–TiO$_2$ has two eutectics and a congruently-melting PbTiO$_3$ phase (Jaffe, Cook & Jaffe, 1971). From the diagram it is evident that it may be possible to grow good PbTiO$_3$ crystals by using a flux method, provided one starts with PbO and TiO$_2$ in the molar ratio 3:1. Starting materials (> 99999% purity) were weighed out in appropriate proportions and were then placed in a 30 ml platinum crucible (Johnson Matthey Ltd, 'ZGS' crucibles). The crucible was sealed with a flat platinum lid, which was tightly crimped in position, and then it was placed inside an alumina crucible. The crucible was heated to approximately 1170°C to dissolve the PbO and then cooled at $\sim 3°C\ h^{-1}$ to 950°C. At this temperature the crucible was turned over to pour off the flux. This facilitated the removal of the crystals which had formed on the sides.

Lattice-parameter measurements

The continuous-recording technique (Glazer, 1972, 1975) was employed for the automatic recording of reflections as a function of temperature. This involved the observation of a group of reflections which are particularly sensitive to variation in lattice parameters. Some electrical and optical properties of this crystal have been reported by a number of workers (e.g. Forsburgh, 1952; Shirane, Pepinsky & Frazer, 1955). The birefringence is found to be anomalous in that as the temperature is increased it rises before eventually falling to zero at the ferroelectric–paraelectric transition. A theoretical discussion of this behaviour was given by Kobayashi & Yamada (1959) in terms of local fields at each atom site and lattice deformation. This led to an expression for the birefringence containing high-order terms in $(c/a - 1)$.

In this paper we show measurements of lattice parameters as a function of temperature and use them, together with previously measured values of the spontaneous polarization, to explain the anomalous birefringence results.
posed for 13.3 min. As can be seen from the photograph, the separation of the reflections 400 and 004 increases as the temperature is decreased. The positions of these reflections give an estimate of the $a$ and $c$ axes respectively. The separation on the other hand gives a measure of the tetragonal distortion of the lattice.

Low-temperature measurements were made using the continuous-recording apparatus modified by Clarke & Morley (1976). The coolant was liquid nitrogen. The crystal was cooled from room temperature down to $-125^\circ\text{C}$ at a rate of 0.3 $^\circ\text{C} \text{min}^{-1}$. No low-temperature structural transition was observed, in contrast to the claims of several earlier workers (Smolenskii, 1951; Kobayashi et al., 1956; Ikegami et al., 1969).

The lattice parameters measured from the photographs are plotted in Fig. 2. In order to have a closer look at the transition region, another photograph was taken over the range of temperature 520 to 460$^\circ\text{C}$. The lattice parameters measured from this photograph are shown in the inset of Fig. 2. The variation of tetragonal distortion is shown in Fig. 3. It can be seen from the photograph in Fig. 1 that the intensity of the reflection 400 decreases near the phase transition while that of the reflection 004 increases as the temperature is decreased. This shows that surface domains favouring the reflection 400 are created at the cost of those favouring the reflection 004. An increase in intensity is again observed in the case of the 104 reflection, which is also sensitive to the variation of the $c$ axis of the unit cell. It may be possible that reciprocal domains which have been reported to play a part during the phase transition (Fesenko et al., 1973) are involved in this domain reorientation. This behaviour has also been observed in our optical studies of the sample at high temperature. The small ‘wiggle’ evident in the cubic phase in the inset of Fig. 2 was observed in all runs on this particular crystal. With a different crystal this behaviour was not encountered.

Room-temperature lattice parameters of PbTiO$_3$ crystals were also measured with the help of a Debye–Scherrer camera. They are shown in Table 1.

<table>
<thead>
<tr>
<th>Continuous-recording camera</th>
<th>Debye–Scherrer camera</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.902 ± 0.003</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.156 ± 0.003</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.065</td>
</tr>
</tbody>
</table>

Fig. 2. Unit-cell axes of a PbTiO$_3$ crystal as a function of temperature.

Fig. 1. X-ray continuous recording of reflections of PbTiO$_3$ undergoing a first-order phase transition. Interchange of relative intensities of the 004 and 400 reflections at $A$ and $B$ shows reorientation of twin domains just below the transition.
Measurement of Birefringence

The birefringence of PbTiO₃ was measured as a function of temperature with a Berek compensator and the results are shown in Fig. 5. In contrast to most ferroelectrics, Δn initially rises with increase of temperature, peaks at around 350°C and then decreases until it disappears at the transition. No microscopic theory has so far been developed to explain this unusual phenomenon. However, an approach to the problem in macroscopic terms may be useful. This kind of attempt was first made by Pockets (1906). It is easy to show that the birefringence is related to the tetragonal strain and spontaneous polarization (see Appendix). Equation (6) represents a straight line of slope \( g_{11} - g_{12} \) and intercept \( p_{11} - p_{12} \). The values of \( (c/a-1) \) at different temperatures are known from the X-ray diffraction work, those of \( P_s \) from the work of Remeika & Glass (1970) and that of \( n_0 \) from the work of Kobayashi & Yamada (1959). With these values a straight line was fitted to equation (6) (Fig. 4), the agreement factor being \( r = 0.99 \). The overall values of \( (g_{11} - g_{12}) \) and \( (p_{11} - p_{12}) \) as obtained from the least-squares fitting using all the points are

\[
\begin{align*}
g_{11} - g_{12} & = -0.013 \text{ m}^4 \text{ C}^{-2} \\
p_{11} - p_{12} & = 0.078.
\end{align*}
\]

In order to see whether these values were temperature-independent, straight lines were also fitted for different temperature intervals over the range 25 to 490°C. The corresponding values of \( (g_{11} - g_{12}) \) and \( (p_{11} - p_{12}) \) are shown in Table 2. It can be seen that both \( (g_{11} - g_{12}) \) and \( (p_{11} - p_{12}) \) are almost temperature independent over the range 75°C to the transition temperature. The values of \( Δn \) obtained from equation (6) using the overall values of \( (g_{11} - g_{12}) \) and \( (p_{11} - p_{12}) \) and the observed \( Δn \) are plotted in Fig. 5. The fit between the observed and calculated \( Δn \)'s is quite satisfactory.

### Table 2. Values of \( (g_{11} - g_{12}) \) and \( (p_{11} - p_{12}) \) for a PbTiO₃ crystal over different temperature ranges

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( (g_{11} - g_{12}) ) (m⁴ C⁻²)</th>
<th>( (p_{11} - p_{12}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25–75</td>
<td>-0.005</td>
<td>0.040</td>
</tr>
<tr>
<td>25–125</td>
<td>-0.007</td>
<td>0.050</td>
</tr>
<tr>
<td>75–175</td>
<td>-0.012</td>
<td>0.071</td>
</tr>
<tr>
<td>150–250</td>
<td>-0.012</td>
<td>0.074</td>
</tr>
<tr>
<td>275–375</td>
<td>-0.014</td>
<td>0.080</td>
</tr>
<tr>
<td>400–490</td>
<td>-0.014</td>
<td>0.079</td>
</tr>
<tr>
<td>25–490</td>
<td>-0.013</td>
<td>0.078</td>
</tr>
</tbody>
</table>

The value of \( (p_{11} - p_{12}) \) obtained above can be compared with the values for some perovskites quoted by Di Domenico & Wemple (1969): -0.2 in SrTiO₃, 0.05 in KTaO₃ and 0.5 in KTa₀.₆₅Nb₀.₃₅O₃. The value of \( (p_{11} - p_{12}) \) obtained by Whatmore (1977) for antiferroelectric PbZrO₃ is 0.88, and by Ishida & Glazer (1974) for antiferroelectric NaNbO₃ is 0.25. Di Domenico & Wemple found that for the perovskites they studied \( g_{11} - g_{12} \simeq 0.12 \text{ m}^4 \text{ C}^{-2} \), whereas for PbZrO₃, this value is 0.04 m⁴ C⁻² (Whatmore, 1977). The negative value of \( g_{11} - g_{12} \) for PbTiO₃ is probably due to the high polarizability of the Pb atom.
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APPENDIX

The refractive index of a material (not necessarily crystalline) which is subjected to a homogeneous strain \( \xi \) and an electric field \( E \) is given by

\[
n = n_0 + aE + b\xi + a'E^2 + b'\xi^2 + cE \xi , \tag{1}
\]

where \( a, b, \text{ etc.} \) are constants and \( n_0 \) is the refractive index for \( E = 0 \) and \( \xi = 0 \). The refractive index obtained is for light with the electric vector in a particular direction. This equation can be applied to a ferroelectric where the spontaneous strain replaces the external strain and the spontaneous polarization the external field. Considering only the first-order strain term and the quadratic term in electric field (Kerr effect), the change, on going through the phase transition, in the dielectric impermeability tensor is given by

\[
\Delta B_{ij} = p_{ijk}\xi_{ki} + g_{ijmn}P_mP_n , \tag{2}
\]

where the strains \( \xi_{ki} \) are defined in relation to the cubic phase and \( P_m \) and \( P_n \) are the components of the spontaneous polarization along the cubic cell axes. \( p_{ijk} \) and \( g_{ijmn} \) are the 'elasto-optical' and 'quadratic electro-optical' coefficients respectively.

In a perovskite ferroelectric such as \( \text{BaTiO}_3 \) it is found that strain is related closely to polarization squared, thus allowing the formula for dielectric impermeability to be cast entirely in terms of either strain or polarization. However, in \( \text{PbTiO}_3 \) the high polarizability of the \( \text{Pb} \) ions does not allow such a simple change and we have to keep the strain and polarization terms separated. Nevertheless, this will be a small difference and so the second-order term in the product of strain and field will look approximately like a function of field cubed and can therefore be ignored.

If equation (2) is written in matrix form using the reduced-suffix notation of Nye (1957), we have

\[
\begin{bmatrix}
\Delta B_1 \\
\Delta B_2 \\
\Delta B_3 \\
\Delta B_4 \\
\Delta B_5 \\
\Delta B_6 \\
\end{bmatrix} = \begin{bmatrix}
p_{11} & p_{12} & p_{12} & - & - & - \\
p_{12} & p_{11} & p_{12} & - & - & - \\
p_{12} & p_{12} & p_{11} & - & - & - \\
- & - & - & p_{44} & - & - \\
- & - & - & - & p_{44} & - \\
- & - & - & - & - & p_{44} \\
\end{bmatrix} \begin{bmatrix}
\xi_1 \\
\xi_2 \\
\xi_3 \\
\xi_4 \\
\xi_5 \\
\xi_6 \\
\end{bmatrix} + \begin{bmatrix}
g_{11} & g_{12} & g_{12} & - & - & - \\
g_{12} & g_{11} & g_{12} & - & - & - \\
g_{12} & g_{12} & g_{11} & - & - & - \\
- & - & - & g_{44} & - & - \\
- & - & - & - & g_{44} & - \\
- & - & - & - & - & g_{44} \\
\end{bmatrix} \begin{bmatrix}
P_{11}P_1 \\
P_{12}P_2 \\
P_{12}P_3 \\
P_{11}P_4 \\
P_{12}P_5 \\
P_{12}P_6 \\
\end{bmatrix}. \tag{3}
\]

Now, in the tetragonal phase of \( \text{PbTiO}_3 \), \( \xi_1 = \xi_2 \) and \( \xi_4 = \xi_5 = \xi_6 = 0 \); also \( P_1 = P_2 = 0 \) and \( P_3 = P_5 \). Therefore, expanding equation (3), we have the following values for \( \Delta B_i \):

\[
\begin{align*}
\Delta B_1 &= p_{11}\xi_1 + p_{12}\xi_2 + p_{12}\xi_3 + g_{12}P_2^2 \\
\Delta B_2 &= p_{12}\xi_1 + p_{11}\xi_2 + p_{12}\xi_3 + g_{12}P_2^2 \\
\Delta B_3 &= p_{12}\xi_1 + p_{12}\xi_2 + p_{11}\xi_3 + g_{11}P_1^2 \\
\Delta B_4 &= \Delta B_5 = \Delta B_6 = 0 .
\end{align*}
\]

Now \( B_i = 1/n_i^2 \), implying that

\[
\Delta n_1 = -\Delta B_n n_1^3/2 , \tag{i.e.}
\]

\[
\Delta n_1 \approx -\Delta B_n n_0^3/2 .
\]

The birefringence of interest is

\[
\Delta n = \Delta n_3 - \Delta n_1
\]

\[
= -\frac{n_0^3}{2} \left[ (p_{11} - p_{12})(\xi_3 - \xi_1) + (g_{11} - g_{12})P_2^2 \right] . \tag{4}
\]

For a tetragonal crystal such as \( \text{PbTiO}_3 \) the value of \( (\xi_3 - \xi_1) \) is approximately given by \( (\xi_3 - \xi_1) = (c/a - 1) \). Therefore equation (4) becomes

\[
\Delta n = -\frac{n_0^3}{2} \left[ (p_{11} - p_{12})(c/a - 1) + (g_{11} - g_{12})P_2^2 \right] . \tag{5}
\]

Rearranging equation (5), we have

\[
\frac{2|\Delta n|}{n_0(c/a - 1)} = (g_{11} - g_{12})\frac{P_2^2}{(c/a - 1)} + (p_{11} - p_{12}) . \tag{6}
\]

References
