Cubic to Tetragonal Martensitic Transformation in Lead Titanate (PbTiO_3) Single Crystals

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The cubic to tetragonal (C/T) phase transformation in PbTiO_3 single crystals has been studied in both the forward and reverse modes and found to show martensitic characteristics. Microstructural features were investigated by heating stage optical microscopy, and room temperature transmission electron microscopy. During transformation, a small hysteresis is involved. The phase front passes swiftly through the crystal and surface relief accompanying the transformation is seen. The twinning system involved was identified as a compound twin in the tetragonal phase with $K_1 = \{110\}$, $\eta_1 = \langle \bar{1}10 \rangle$, $K_2 = \{1\bar{1}0\}$, and $\eta_2 = \langle 110 \rangle$. The phase boundaries (habit planes) were frozen by controlling the temperature profile. It is found that the habit planes vary within a certain range. Not only different specimens show this real variation, but also the same specimen under different transformations follows this, indicating the importance of local arrangements near the habit plane interfaces. Theoretical predictions, with only a minute change of lattice parameters, show that experimental data appear to fit calculated results fairly well, if one considers interfacial conditions. The results show a certain degree of consistency, which implies that the martensitic phenomenological crystallographic theory applies. Discussions on the microstructural features as well as previous work on perovskite materials are presented.

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I. Introduction

Martensite was originally used to designate the hard microconstituent found in quenched steels. Since then, other materials have been found to exhibit the same type of solid state phase transformation, known as a martensitic transformation. The most distinct feature of a martensitic transformation is its crystallographic characteristics, which imply a "military" (as opposed to "civilian") mode of atomic transfer from the parent to the product phase⁽¹⁾. These transformations feature a coordinated structural change involving a lattice correspondence and a planar semicoherent parent-product interface which, during transformation movement, produces an invariant plane strain shape deformation. Microstructural inhomogeneities on a fine scale during a martensitic reaction—slip, twinning, or faulting—are usually observed at the electron microscope scale. This secondary deformation provides the invariant plane condition at the macroscopic scale and maintains a semicoherent glissile interface between the martensite and the parent phase.

The phenomenological crystallographic theory of martensitic transformations⁽²⁾⁻⁽⁴⁾ is well established, and has been applied successfully to many metallic alloy systems⁽⁵⁾⁻⁽⁷⁾, and more recently to ceramics and other systems⁽⁸⁾. It has been reported that the Wechsler-Lieberman-Read (WLR) theory can be applied to the cubic-tetragonal phase transition of semiconducting perovskite-type crystals⁽⁹⁾, which have sufficient free

charge available to provide a termination for the spontaneous polarization at the interface. On the other hand, crystals with high resistivity, though showing sharp first order phase boundaries, apparently do not follow theoretical predictions⁽¹⁰⁾⁽¹¹⁾. In their interpretation, the reason for this is that the free charges present in (semi-)conducting crystals neutralize the bound polarization charges inside the crystal. Whereas in highly insulating crystals, the absence of free charges imposes the restriction that phase boundaries be free of any excess polarization charge. The accumulated polarization charge at a phase boundary results in stored electrical energy which dominates the crystallographic characteristics once it prevails. However, the evidence here is thin because no other crystallographic data were used other than very limited habit plane data.

Lead titanate has a ferroelectric phase transition temperature, T_c , near 500°C ⁽¹²⁾⁽¹³⁾. PbTiO_3 is cubic above T_c and exhibits a strong tetragonal distortion at 20°C : $c/a = 1.06$ which persists up to T_c ($c/a = 1.01$)⁽¹⁴⁾⁽¹⁵⁾. The lattice constant a increases smoothly upon heating, while the constants c and c/a decrease. At T_c , the lattice constants c and a change abruptly and the structure becomes cubic. Since the volume of the unit cell decreases sharply as a result of this transition, the linear expansion coefficient of a polycrystalline sample is negative below T_c ⁽¹²⁾⁻⁽¹⁵⁾. The transformation is first order⁽¹⁰⁾. PbTiO_3 single crystals present a highly polar structure with very high spontaneous polarization in the perovskite family⁽¹²⁾⁽¹³⁾⁽¹⁶⁾. Because of its large tetragonality and detectable negative volume change near T_c , PbTiO_3 provides a more sensitive indication of the role of lattice variation during transformation. In the present experiments, we study microstructural features to understand basic

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crystallographic characteristics in this material, present a real scatter of the habit plane, and verify the applicability of the phenomenological crystallographic theory to this perovskite system.

II. Experimental Procedure

PbTiO₃ crystals were grown⁽¹⁷⁾ by slow cooling from a flux, containing KF, Pb₃O₄, PbF₂, KBF₄, and TiO₂, at a temperature below the transformation temperature in a 50 cm³ platinum crucible. A vertical tube furnace with sealed-end quartz tube was programmed to give a controlled cooling rate to below 300°C. Crystal growth proceeds in an oxygen atmosphere and at a very slow cooling rate. The as-grown crystals were mostly cubic in shape or elongated cubic or orthogonal forms. After washing in hot concentrated acetic acid, in order to dissolve any attached solidified flux, and polishing with Al₂O₃ powders of various sizes, the crystals show a transparent amber tint.

Transformation characteristics were studied using heating stage optical microscopy and conventional transmission electron microscopy at room temperature. Specimens for optical microscopy were ground by hand to a thickness about 80 μm or less and polished using Al₂O₃ powder. Some coarser scratches were intentionally retained as fiducial lines. *In situ* transformation experiments were performed using heating stage optical microscopy. The specimens used were high quality crystals with sharp flat {100} surfaces and the microscope used was a Nikon UM-2. The specimens were investigated using polarized light and put in a heating stage which was designed to be able to control the temperature profile quickly and to “freeze” phase boundaries. TEM specimens were hand ground and then treated by a commercial dimpling machine down to 10 μm. An ion miller was employed at 6 kV, 0.5 mA, each gun with tilting angle at 18° for further thinning. After perforation, the specimens were further ion bombarded at reduced voltage and tilting angle for several minutes. TEM investigations were conducted using a Hitachi H800 microscope at 200 kV with a double-tilt specimen holder.

III. Results

The results obtained can be divided into two major parts: experimental determination of crystallographic characteristics, and theoretical calculations.

1. Crystallographic characteristics

The single crystals used show lower transformation temperatures than those previously reported⁽¹²⁾⁽¹⁵⁾. The crystals used have transformation temperatures shown in Table 1. The reduction of T_c may be caused by solid solution of multi-elements during crystal growth. The resistance of the crystals measured is as high as $1.0 \times 10^{-8} \Omega/\text{cm}^2$ or more⁽¹⁷⁾. Surface relief of the tetragonal phase is often seen in as grown crystals and/or crystals after C/T transformation. A typical example is

Table 1 Transformation temperatures of PbTiO₃ specimens studied.

Specimen No.	M_s (°C)	A_s (°C)
1	451	460
2	450	455
3	451	455
4	455	462
5	453	457
6	450	454
7	455	460

shown in Fig. 1. Surface relief forms along two directions which are closely related to two variants shown in this orientation. Surface tilting is clearly observed as black and bright patches by appropriately adjusting the specimen position and orientation. Note that interfaces between variants are not exactly parallel, indicating a possible variation of habit plane trace during phase transformation.

Figure 2(a) shows PbTiO₃ lattice parameters as a function of temperature⁽¹⁷⁾. At room temperature, the crystal is tetragonal showing lattice parameters $a=0.39029$ nm and $c=0.41344$ nm and the values of $a=0.3961$ nm, $c=0.4012$ nm and $a_0=0.3972$ nm apply at T_c ⁽¹⁷⁾. Again, the tetragonality is a little smaller than that reported in previous work⁽¹²⁾⁽¹⁴⁾. Figure 2(b) shows the PbTiO₃ volume change as a function of temperature⁽¹⁷⁾. Note the negative slope and rapid increase (and then decrease)[†] of volume change below T_c as the temperature decreases, indicating an intriguing lattice structure variation, as discussed later.

The inhomogeneous shear was introduced as internal twins in the tetragonal phase. A ferroelectric material has regions where the magnitude and direction of the polarization are the same in each region, though the polarization may differ in orientation in neighboring regions. These regions are known as ferroelectric domains which are separated by domain boundaries. From symmetry, there are two types of domain boundaries in PbTiO₃, that is, 90° and 180° boundaries. The angles refer to the angle between the domain polarization vectors on either side of the boundary. From a [100] orientation two different morphologies of 90° domain boundaries are usually seen. One is straight with sharp images, and the other shows wavy morphology and fringe contrast, as shown in Fig. 3(a) and (b) respectively. The sharp boundaries are termed a-a type domain boundaries, because the polarization vectors in two adjacent domains are all perpendicular to the viewing direction and the a -axis in each domain points to the viewing direction. On the other hand, the fringed boundaries are inclined to the viewing direction and the polarization

[†] The present X-ray data show slightly different characteristics from those in previous work (Ref. (12)), which may be due to impurities in the crystals. Since we use the crystals from Ref. (17), the corresponding X-ray data were adopted. The impurity effect may influence the characteristic values of a phase transformation, such as T_c , tetragonality, etc., but is believed not to affect its nature.

Fig. 1 Optical micrograph showing surface relief of tetragonal phase in an as-grown PbTiO_3 single crystal. Similar features can be observed after other C/T transformations. Note that interfaces are not exactly parallel.

Fig. 2 X-ray data showing (a) lattice parameters; (b) unit cell volume of PbTiO_3 as a function of temperature.

Fig. 3 Electron micrographs showing 90° domain boundaries. (a) a-c domain boundaries; (b) a-a domain boundaries.

vectors in two adjacent domains are alternatively parallel to or perpendicular to the viewing direction. The a -axis and c -axis point to the viewing direction and hence the domain boundaries are called a-c type. Actually, from a crystallographic viewpoint, a 90° domain boundary is a twinning plane between two adjacent domains. For a-a domains, this is readily seen, as shown in Fig. 4(a). The symmetrically distributed diffraction reflections imply that the two adjacent domains are twin-related. Diffraction patterns as shown in Fig. 4(b) were derived by tilting a-c type domain boundaries from a $[100]$ zone to a $[111]$ zone. Again, a twinning relation was derived from the symmetrical distribution of diffraction reflections. In both cases, the twinning planes, K_1 , are $\{110\}$ type planes. The corresponding schematic models showing atomic arrangements are in Fig. 4(c) and (d). Figure 4(c) clearly shows that the twinning direction, η_1 , is along a $\langle \bar{1}10 \rangle$ type direction due to the tetragonal distortion during transformation. The invariant plane, K_2 , is the $\{\bar{1}10\}$ plane which is the other diagonal plane of the tetragonal cell. Figure 4(d) is more complex, but can be immediately

Fig. 4 (a) Diffraction pattern taken from a $[100]_c$ orientation showing a-a type domain arrangements; two adjacent domains are twin related; (b) diffraction pattern derived by tilting an a-c domain to a $[111]$ orientation and corresponding stereographic projection showing the twinning relation; (c) corresponding atomic model describing the twinning relation for (a); (d) schematic model showing atomic arrangements corresponding to (b).

realized by studying the stereographic projection in (b). The result of the twinning system is the same as that derived from Fig. 4(c). Therefore the elements for the twinning system in PbTiO_3 crystals are determined. The twinning magnitude can also be determined from splitting in the diffraction pattern, Fig. 4(a), or from X-ray data. The results are shown in Table 2. It is found that this is a compound twinning system[†]. The result can be seen in a stereographic projection, Fig. 5.

Phase transformation characteristics were partly derived by heating stage optical microscopy. Figure 6(a) shows a single interface type phase transformation. This is a typical habit plane (or phase boundary) in a PbTiO_3 crystal during transformation as seen using polarized light. The phase boundary is sharp and straight with an angle about 30° to a $[010]$ direction. This sharp boundary implies that the boundary is almost in an edge-on position. One can easily distinguish the cubic phase by

Fig. 5 $[001]$ stereographic projection showing the relation between twinning elements for PbTiO_3 tetragonal phase.

[†] When K_1 is a rational plane and η_2 a rational direction, this is twinning of the first kind; when K_2 is a rational plane and η_1 a rational direction, this is a twin of the second kind; when all four elements K_1 , K_2 , η_1 and η_2 are rational, the twin is compound.

Fig. 6 Optical micrographs using polarized light showing (a) a sharp single C/T phase boundary during transformation, making an angle about 30° from a $\{100\}$ plane; (b) the same specimen rotated to a position where the cubic phase becomes extinct; (c) double C/T phase boundaries during transformation, showing distorted region at phase front intersection and non-uniform contrast distribution in the tetragonal phase; (d) a habit plane affected by microstructural inhomogeneity which is in the form of a-a type domains; (e) another single C/T phase boundary in a different specimen, making an angle of about 35° from a $\{100\}$ plane.

Table 2 Twinning elements in PbTiO_3 tetragonal phase.

	K_1	η_1	K_2	η_2	s
Room temp	$\{110\}$	$\langle \bar{1}10 \rangle$	$\{\bar{1}10\}$	$\langle 110 \rangle$	0.115
T_c	$\{110\}$	$\langle \bar{1}10 \rangle$	$\{\bar{1}10\}$	$\langle 110 \rangle$	0.0256

rotating the crystal. The cubic phase becomes extinct because of isotropy, Fig. 6(b). One notices that the contrast near the boundary is different from regions farther away, indicating that a local distortion exists. This distorted region appears to vary case by case. For instance, the intersection of two interfaces shows a broader

contrast region; the contrast near the specimen center may be different from that of the edge. Figure 6(c) shows a two-interface type phase transformation where the two interfaces are not symmetrically distributed along a (010) plane. The angles between the two interfaces and the (010) plane are 38.5° and 35.7° respectively. It is clear that at the intersection of the two phase fronts a distorted region with different contrast is generated, and this changes the original habit plane configuration. In the tetragonal region, one sees a non-uniform contrast distribution, indicating birefringence variation which is closely related to the lattice parameter variation. We point out that brighter patches sometime show up in the

cubic region before the habit plane approaches it, suggesting some local perturbation in the crystal. Figure 6(d) shows a typical situation where the habit plane may be affected by microstructural inhomogeneity, as indicated. a-a type domains form at this region which show 45° stripes from a {100} plane. The habit plane is bent when it reaches this region. Similarly, a habit plane may be influenced by other factors, such as temperature inhomogeneity, impurity effects etc., which may substantially change the habit plane orientation during transformation. Other single crystals were also used to measure the habit planes. We found that the habit plane appears to vary from crystal to crystal, Fig. 6(e); more interestingly, the same crystal may show a habit plane a little deviated from a previous one or even a little change in orientation during phase front movement. All the angles from a {100} plane to the habit planes were measured and the results are collected in Table 3.

Because of the difficulty of performing two surface analysis of the habit plane in this case, we used another method to derive three dimensional information. In some transformations, the traces of phase boundaries are parallel to {100} planes or with several degrees deviation, shown in Fig. 7. These boundaries often show inclined features, i.e., the boundaries show a bright color at their edges under polarized light as indicated. From such boundaries, we derive the distribution of the third direction cosine, and accordingly the largest angle from a {100} plane is not more than 5°, and most are within 2°. Therefore, we are able to construct the distribution of the habit planes. The results are shown in Fig. 8. It is clear that the habit plane during transformation scatters around a range.

To determine the shape strain, the scratch displacement technique is ordinarily used⁽¹⁸⁾⁽¹⁹⁾. However the displacements in the present case are extremely small, Fig. 9. Straight fiducial lines were not seen bent across the boundary, indicating a very small shape strain during transformation.

2. Theoretical calculations

The crystallography of the cubic to tetragonal phase transformation was analyzed using phenomenological crystallographic theory formulated by Bowles and Mackenzie⁽³⁾, but treatments of Wechsler-Lieberman-Read⁽²⁾ and Bullough-Bilby⁽²⁰⁾ are equivalent. A computer program based upon the Bowles-Mackenzie formulation⁽²¹⁾ was used in this work.

The fundamental basis of the phenomenological theories is the experimental observation that the transformation is macroscopically a homogeneous distortion in which the habit plane between the parent and martensite crystals is both undistorted and unrotated. Upon the requirement that the martensitic transformation is observed as an invariant plane strain, the theory also incorporates a lattice invariant shear, and a rotation with the Bain (structural) distortion to derive a final invariant plane strain. The basic equation of the phenomenological theories can be expressed as

Table 3 Angles of habit planes (during transformation) from {110} planes.

Specimen No.	Angle 1	Angle 2
1-1	59.3	30.7
1-2	60.3	29.7
2-1	55.0	35.0
	56.0	34.0
2-2*	51.0 (53.0)	39.0 (37.0)
3-1	57.0	33.0
3-2**	51.5	38.5
	54.3	35.7
3-3	50.5	39.5
4-1	55.0	35.0
4-2	55.0	35.0
4-3	57.0	33.0
5-1	56.0	34.0
	57.0	33.0
5-2	58.8	31.2
6-1	65.0	25.0
	63.0	27.0
6-2*	50.0 (57.0)	40.0 (33.0)
	55.0	35.0
6-3	61.0	29.0
	63.0	27.0
	58.5	31.5
7-1***	58.0	32.0

* Curved interface

** Two phase fronts

*** Some phase front traces nearly parallel to {100} type planes, as discussed in the text.

$$\mathbf{P}_1 = \mathbf{R}\mathbf{B}\mathbf{P}_2 \quad (1)$$

where $\mathbf{P}_1$, is the shape deformation, and $\mathbf{P}_2$, $\mathbf{B}$ and $\mathbf{R}$ represent the lattice invariant shear, the Bain distortion and the rigid body rotation, respectively. Since both $\mathbf{P}_1$ and $\mathbf{P}_2$ are invariant plane strains, they can be represented as:

$$\mathbf{P}_i = \mathbf{I} + m_i \mathbf{d}_i \mathbf{p}_i' \quad (2)$$

where $\mathbf{I}$ is the unit matrix, m_i is the magnitude of the displacement, $\mathbf{d}_i$ is a unit column vector in the direction of the displacement, and $\mathbf{p}_i'$ is a unit row vector representing the normal to the invariant plane.

Bowles and Mackenzie utilized an equivalent expression to eq. (1)

$$\mathbf{P}_1 \mathbf{P}_2^{-1} = \mathbf{R}\mathbf{B} = \mathbf{S} \quad (3)$$

where the matrix $\mathbf{S}$, the resultant of two invariant plane strains, is an invariant line strain.

From the experimental lattice parameters of the parent and martensite phases and the assumed Bain (lattice) correspondence, the principal distortions and thus the matrix $\mathbf{B}$ are determined. Invariant lines and invariant normals are calculated from $\mathbf{B}$, and their combinations applied with the appropriate rigid body rotations $\mathbf{R}$ give four invariant planes. The rigid body rotation matrix to put undistorted lines and normals into their original positions is given by Euler's theorem. Once $\mathbf{S} = \mathbf{R}\mathbf{B}$ is determined, $\mathbf{P}_1$ and $\mathbf{P}_2$ can be determined from eq. (3) and the assumed (or known) $\mathbf{p}_2'$ and $\mathbf{d}_2$.

Fig. 7 Optical micrographs using polarized light showing (a) phase boundary spikes nearly parallel to a (100) plane; during transformation, these spikes nucleate from the lower part and extend to the whole specimen; (b) rectangular shaped phase boundary formed during C/T transformation. Note that these boundaries are nearly parallel to {100} planes or with only several degrees deviation.

In the present case, we assume transformation occurs from cubic to tetragonal structures. The lattice correspondences and lattice invariant shear systems in PbTiO₃ are listed in Tables 4 and 5. Since we know that PbTiO₃ has a negative linear expansion coefficient (therefore negative volume change) below T_c , and the lattice parameter c decreases and a increases as the temperature increases, we can derive

$$(a/a_0)^2(c/a_0) > 1, \text{ when } C \rightarrow T \quad (4)$$

That is, the increasing rate of c/a_0 is greater than that of $(a/a_0)^2$. Considering the lattice parameters of PbTiO₃ carefully, one realizes that the “lattice parameters at T_c ” derived by X-ray may be different from those when

transformation actually occurs, since the transformation occurs swiftly and the nature of X-ray measurements is not really “on-time”. We need to consider the local lattice conditions, such as: real lattice parameters when transformation occurs, lattice perturbations, temperature inhomogeneity, etc. However, we do not know the “real” conditions around the habit plane at transformation, but can estimate the principal strains as follows. Based upon the lattice constants mentioned before and the relation shown in eq. (4), we calculate possible habit planes by holding η_{11} constant ($\eta_{11} = \eta_{22}$) and varying η_{33} . The ranges of η_{11} and η_{33} are: $1 > \eta_{11} > 0.994949$ and $1 < \eta_{33} < 1.012626$. We find that the habit plane shows the same tendency for each set of η_{11} and η_{33} . That is, the

Fig. 8 Experimental and calculated habit plane distribution shown in stereographic projection.

habit plane scatters linearly over a range, and is very sensitive to the relative values of $(\eta_{33}-1)/(\eta_{11}-1)$, i.e., the principal strains. Moreover, if η_{11} is different from η_{22} when transformation occurs, the habit plane normal may deviate sideways from the $\{001\}$ - $\{011\}$ zone which explains the lateral scatter of experimental data seen in Fig. 8. We summarize a set of calculations using lattice correspondence I and lattice invariant shear system (101)

Table 4 Lattice correspondence (LC) and transformation matrix for cubic and tetragonal phases of PbTiO_3 .*

Lattice correspondence	[UVW]	[uvw]	T
I	1 0 0	1 0 0	1 0 0
	0 1 0	0 1 0	0 1 0
	0 0 1	0 0 1	0 0 1
II	1 0 0	0 1 0	0 0 1
	0 1 0	0 0 1	1 0 0
	0 0 1	1 0 0	0 1 0
III	1 0 0	0 0 1	0 1 0
	0 1 0	1 0 0	0 0 1
	0 0 1	0 1 0	1 0 0
IV	1 0 0	0 1 0	0 1 0
	0 1 0	1 0 0	1 0 0
	0 0 1	0 0 1	0 0 1
V	1 0 0	1 0 0	1 0 0
	0 1 0	0 0 1	0 0 1
	0 0 1	0 1 0	0 1 0
VI	1 0 0	0 0 1	0 0 1
	0 1 0	0 1 0	0 1 0
	0 0 1	1 0 0	1 0 0

* where

$$\begin{bmatrix} u \\ v \\ w \end{bmatrix}_{\text{Tetra}} = T \begin{bmatrix} U \\ V \\ W \end{bmatrix}_{\text{Cubic}}$$

$[\bar{1}01]$ to show the general characteristics of the calculated crystallography, as listed in Table 6. The calculated habit plane varies within a range similar to that observed in the experiments if we input reasonable values of principal distortions based upon available lattice parameters and take into account a possible local lattice perturbation. Similar scatter characteristics can also be derived by varying a dilatational parameter, $\delta^{(3)}$, which describes a uniform lattice distortion at the boundary as discussed

Fig. 9 Optical micrograph showing fiducial lines across a phase boundary. The fiducial lines appear not to be bent due to the very small transformation shape strain.

Table 5 Lattice invariant shear systems employed for PbTiO₃.

LC I (101)[$\bar{1}$ 01] ($\bar{1}$ 01)[$\bar{1}$ 01] (011)[0 $\bar{1}$ 1] (0 $\bar{1}$ 1)[011]	LC II (011)[0 $\bar{1}$ 1] (110)[$\bar{1}$ 10] (0 $\bar{1}$ 1)[011] ($\bar{1}$ 10)[110]	LC III (110)[$\bar{1}$ 10] (101)[0 $\bar{1}$ 1] ($\bar{1}$ 10)[110] (10 $\bar{1}$)[101]
LC IV (10 $\bar{1}$)[$\bar{1}$ 01] ($\bar{1}$ 0 $\bar{1}$)[101] (0 $\bar{1}$ 1)[0 $\bar{1}$ 1] (0 $\bar{1}$ 1)[011]	LC V (1 $\bar{1}$ 0)[$\bar{1}$ 10] (0 $\bar{1}$ 1)[0 $\bar{1}$ 1] ($\bar{1}$ 10)[110] (0 $\bar{1}$ 1)[011]	LC VI ($\bar{1}$ 10)[$\bar{1}$ 10] ($\bar{1}$ 01)[0 $\bar{1}$ 1] ($\bar{1}$ 10)[110] ($\bar{1}$ 0 $\bar{1}$)[101]

Table 6 Effect of principal distortion values on the results of crystallographic analysis (LCI-1).

η_{11}	0.998317	0.998317	0.998317	0.998317	0.998317
η_{33}	1.004209	1.005261	1.006313	1.007365	1.009470
Solution 1					
$V-V_0$	0.000652	0.001880	0.002929	0.003977	0.006075
m_1	0.004022	0.005252	0.006302	0.007353	0.009454
$\mathbf{p}_1$	-0.762924 -0.646485 0.002263	-0.824731 -0.565521 0.002090	-0.856502 -0.516140 0.002053	-0.878487 -0.477761 0.001956	-0.907004 -0.421117 0.001945
$\mathbf{d}_1$	-0.761653 0.647981 0.002176	-0.823282 0.567630 0.002026	-0.855040 0.518559 0.001906	-0.877020 0.480451 0.001900	-0.905487 0.424370 0.001773
Angle from [010]	40.3°	34.4°	31.1°	28.5°	24.9°

later. The calculated shape strain magnitude m_1 is about one tenth to one twentieth that in ferrous martensitic transformations. This is the reason why we can hardly see any obvious bending of fiducial lines. It is seen that the theoretical calculations appear to fit experimental results quite well if we consider the interfacial properties of the habit plane. A more complete set of calculations will be published elsewhere.

IV. Discussion

It has been suggested that the WLR theory should be applicable to perovskite-type ferroelectric crystals⁽⁴⁾. DiDomenico and Wemple⁽⁹⁾ did present evidence on semiconducting perovskite-type crystals showing habit planes quantitatively explainable in terms of the WLR crystallographic theory. However, crystals with high resistivity were reported not always with predicted habit plane normals⁽¹⁰⁾⁽¹¹⁾. Since then, it has been considered that the cubic to tetragonal transformation in perovskite crystals with high resistivity can not be classified in the family of martensitic transformations⁽²²⁾. However, the microstructural characteristics of PbTiO₃ in the present experiment have shown: (i) reversible surface upheavals; (ii) irrational habit planes; (iii) a fine inhomogeneous structure which is twinning in this case; (iv) that all atoms move less than an interatomic distance; and (v) the transformation process is clearly first order. Although

the precise orientation relationship between the two phases is not determined quantitatively in the present experiments, the relationship between the principal axes in both phases is easily derived. That is, the three orthogonal axes in the cubic phase are essentially parallel to certain orthogonal axes in the tetragonal phase. All the above crystallographic features fall within the classification scheme for martensitic transformations⁽¹⁾⁽²³⁾.

During the cubic to tetragonal transformation in PbTiO₃, several features were observed. Most significantly, some of the cubic-tetragonal interfaces (or habit plane) show sharp, straight first order phase boundaries which scatter within a certain range, and some show bright and broader edges. If we consider this using a three dimensional construction, as shown in Fig. 10, the morphology of the habit plane depends on the viewing direction. For instance, viewing from direction **c**, a sharp interface can be seen; from direction **a**, a broad interface appears; on the other hand, one may not see any phase boundary or only some faint feature from direction **b**. Boundaries shown in Fig. 6 are those viewing from a direction similar to **c**, and Fig. 7 shows boundaries viewing from an **a** direction. Interpretation in this way explains fairly well the morphology of habit planes observed in PbTiO₃, and the habit plane distribution can be fit with theoretical calculations by considering local lattice parameter perturbations. However, previous works on BaTiO₃ claimed that in some high resistivity BaTiO₃ crystals the cubic-tetragonal phase boundary is of the W-L-R type, but contrary to theoretical predictions⁽¹⁰⁾⁽¹¹⁾. The cubic-tetragonal phase transition in about 20 BaTiO₃ single crystals was investigated⁽¹⁰⁾⁽¹¹⁾ and about 30% of the crystals exhibited phase boundaries at angles very close to that predicted by theory; 60% of them showed a broad phase boundary approximately perpendicular to the 90° domain walls of the a-c domain structure and the remaining 10% changed from cubic to tetragonal via a broad and complicated square net pattern⁽¹¹⁾⁽²⁴⁾. In all cases the a-c domain structure was clearly visible right up

Fig. 10 Three dimensional arrangement of a habit plane. Viewing from three different cube directions reveals different morphological characteristics. See text for discussion.

to the phase boundary and in all cases a strain pattern with the same period as the a-c domain structure was clearly visible in the cubic phase on the high temperature side of the phase boundary. Reviewing these previous results carefully, we can see that the situation in BaTiO₃ is quite similar to that in PbTiO₃. Besides the 30% habit planes which show sharp interfaces and are consistent with the theoretical calculations, the 60% habit planes approximately perpendicular to the 90° domain walls of the a-c domain structure are actually parallel to a {100} plane since the traces of a-c domain boundaries should be parallel to a {100} plane, which may be just the case shown in Figure 7 and can be derived viewing from an appropriate direction, like *c* in Fig. 10. We do not see complicated square net patterns in PbTiO₃ and therefore it is difficult to compare the remaining 10% of the habit planes. It seems that the apparent inconsistency in previous works is because three dimensional considerations were not taken into account.

If the specimen is thin enough, one sees a pronounced contrast variation around the phase boundary under polarized light, as shown in Fig. 6. This is clearly related to a strain field and one further notes that this pattern appears at the tetragonal side, with a width of tens of microns. An interpretation of this is that a coherent unrotated interface forms with severe elastic strain over an appreciable distance owing to lattice-matching. However, the contrast variation regions appear to vary case by case, indicating a possibility that local lattice distortions may vary depending on the ambient conditions. To reduce the misfit strain energy to a minimum, the lower symmetry crystal phase should be twinned so that the sign of the strain reverses in going from one twin to the next along the habit plane. This then defines a plane of "zero average distortion"⁽⁴⁾. The theory of WLR is based on an interface plane between the martensite and its parent which remains macroscopically unrotated and undistorted as a result of the shape deformation. It is implicit in this account that the "fit" of the martensite to its parent is isotropic. Bowles and Mackenzie have shown that if the habit plane contains a small scale isotropic distortion, the condition of an invariant plane strain for the habit plane is slightly relaxed⁽³⁾. Therefore, the Bowles-Mackenzie theory, on the other hand, holds that the habit plane is unrotated but may be isotropically distorted by some 1 or 2 percent⁽³⁾. They introduced a dilatation parameter, δ , which in effect slightly relaxes the requirement that the habit plane is undistorted, but this modification is not without criticism⁽²³⁾. We do not know in fact if the habit plane is isotropically distorted (or not) during transformation from the present experiments. However, we can think in another way that the parameter δ is more than a "correction factor", and may contain substantial physical meaning. The significance of this is that the parameter δ may function as an indicator of local lattice arrangements causing a habit plane change. This offers a certain degree of freedom: to take into account a perturbation or local lattice distortion during transformation due to compo-

sition, defects, temperature inhomogeneity, etc., which may substantially influence the crystallographic characteristics. In the present experiments, the same crystal sometimes showed habit planes with different angles from a {100} plane, providing evidence for this consideration.

Although the transformation strains in PbTiO₃ are quite small (Table 6) compared to those of ferrous alloys, a small change in the relative values of the principal strains introduces a dramatic shift of the habit plane. That is, the tetragonality of the C/T transformation is a major factor determining the crystallographic characteristics. The tetragonality can be affected by impurities, structural inhomogeneities, a temperature perturbation, strain conditions, etc. The crystals used in the present case⁽¹⁷⁾ offer a good example. It is thus obvious that even a very small perturbation of lattice distortion during transformation will shift the habit plane. This is evidenced by the shift of the same phase front at different positions during transformation, Fig. 6(c)-(e). This consideration may explain the scattering of habit plane normals observed in experiments. The reason why the scattering phenomenon is not seen in BaTiO₃ and KTN is probably due to the very small tetragonality and distortions involved.

PbTiO₃ has a much higher polarization value than BaTiO₃ and KTN⁽¹⁶⁾ and the resistivity of the crystals used is much higher than a semiconductor. Therefore the stored electrical energy should be much higher at the phase boundary in this case according to an argument made by previous workers⁽⁹⁾⁻⁽¹¹⁾. If this is true, the electrostatic and/or electrostriction energy may overwhelm the strain energy, and dominate the transformation characteristics. We do not know the exact relation between the strain and electrical energies in the present experiment, and more detailed work is needed. However, if the electrical energy prevails and the transformation characteristics are solely dominated by this rather than by a perturbation of lattice arrangements, it appears that the same crystal could show identical habit plane characteristics because the stored electrical energy is the same. This is not the case we observe. Therefore we suggest a re-investigation of the role of electrical energy.

V. Conclusions

(i) The cubic to tetragonal (C/T) phase transformation in PbTiO₃ single crystals shows martensitic characteristics. Microstructural features investigated using heating stage optical microscopy and transmission electron microscopy show a small hysteresis involved, the difference between the *A_s* and *M_s* temperatures being about 5°C. The phase front passes swiftly through the crystal; surface relief accompanying the transformation is also seen. The twinning system involved has been identified as a compound twin in the tetragonal phase with $K_1 = \{110\}$, $\eta_1 = \langle \bar{1}10 \rangle$, $K_2 = \{1\bar{1}0\}$, $\eta_2 = \langle 110 \rangle$.

(ii) The phase boundaries (habit planes) were "frozen" by controlling the temperature profile. It was

found that the habit planes vary within a certain range. Not only did different specimens show this phenomenon, but also the same specimen under different transformations also follows this, indicating the importance of local distortion near the interfaces during transformation. The present experimental results suggest a re-investigation of the role of stored electrical energy.

(iii) Theoretical predictions with varying principal distortions show that experimental data appear to fit calculated results quite well, if one considers the effect of local lattice distortions during transformation. The results show a certain degree of consistency, which imply that the phenomenological martensitic crystallographic theory does indeed apply to PbTiO₃.

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