PHILOSOPHICAL MAGAZINE B, 1996, VOL. 74, NO. 1, 25–36

In-situ observation of the domain configurations during the phase transitions in barium titanate

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[*Received 3 January 1996 and accepted 23 January 1996*]

ABSTRACT

Using a polarizing optical microscope in conjunction with a charged-coupled device camera system, the domain microstructural evolution with respect to temperature in all three phases of $BaTiO_3$ was studied. Along a (001) oriented section the domains in the tetragonal phase form 90° domain patterns in an 'a–a' configuration. The transition on heating and cooling between the cubic and tetragonal phases occurred near the same temperature, 125°C. On cooling, the domain structures in the orthorhombic phase appeared as a long continuous lamellar structure, while on heating the domains formed a 'patchwork' structure. This transition temperature showed a large thermal hysteresis. The final transition temperature from orthorhombic to rhombohedral was difficult to determine using this technique. The transition on cooling occurred at −134°C based on a colour change and the disappearance of all the domains. During heating, the domains reappeared at −110°C and remained in a patchwork structure throughout the orthorhombic phase.

§ 1. INTRODUCTION

1.1. *Background of $BaTiO_3$*

Since the discovery of the barium titanate ($BaTiO_3$) crystal in the early 1940s, many researchers have studied it due to its large dielectric, piezoelectric and elastic constants. $BaTiO_3$ is used in many applications such as capacitors (Buessem, Cross and Goswami 1966), electro-optic devices (Nakao, Tomomatsu, Ajimura, Kurosaka and Tominaga 1994) and memory devices (Merz 1954, Cudney *et al.* 1993). Domains, which are caused by multivariants in the spontaneous polarization and strain (Arlt and Sasko 1980), contribute greatly to the physical properties of $BaTiO_3$ (Arlt 1990).

A domain is a uniform volume of spontaneous electrical polarization ($\mathbf{P}_s$) which can be formed on cooling from the paraelectric to ferroelectric (FE) phase or a transion between FE phases. Domains can be altered by temperature, pressure, electric field and past history of the mateial (Forsbergh 1949). Domains develop in various configurations to balance the stress in the material so that the overall elastic energy is minimized (Arlt 1987, 1990, Kim, Chung and Kim 1993). In some situations, certain kinds of domain patterns can be stabilized by defects (Cao 1995). The domain configurations depend on the crystallographic symmetry of the material. Domain structures are of basic importance in FE polycrystals since the struc-

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tures determine the mechanisms of the polarization reversal process. The presence of domain walls also affects the dielectric, elastic and piezoelectric properties since the walls are mobile under an external field (Fousek and Janovec 1969).

$BaTiO_3$ (BT) has four phase stability regions as a function of temperature. The high temperature phase (greater than $\sim 120°C$) is a cubic perovskite. Merz (1949) reported the dielectric constant as a function of temperature for BT. BT transformed from (c)ubic [paraelectric] to (t)etragonal [ferroelectric] at 120°C, to (o)rthorhombic [ferroelectric] at −7°C, and to (r)hombohedral [ferroelectric] at −90°C. On heating, the phase transitions of r → o,o → t, and t → c occurred at slightly higher temperatures than on cooling, which signified the presence of latent heat and a first order transition (Kanata, Yoshikawa and Kubota 1987). The polarization axes in the ferroelectric phases are along the [001], [110] and [111] directions for the tetragonal, orthorhombic and rhombohedral, phases, respectively (Merz 1949, Cook 1956). Since the polarization axis in each phase changes, the domain configuration also varies as the structure changes with temperature.

As BT transforms from the cubic to the tetragonal structure, the *c*-axis elongates and the lattice constant c/a ratio increases to 1·01 (DeVries and Burke 1957). Strains develop and are relieved by the formation of domains with polarization alone one of the three principal crystallographic axes. Due to the degeneracy of $\pm\mathbf{P}_s$, there are six possible orientations in the tetragonal phase. In the tetragonal phase 90° and 180° domains occur. The 90° domain walls orient along one of the {101} planes (DeVries and Burke 1957, Cao and Cross 1991). The domains with polarization vectors antiparallel to each other are 180° domains. Optical microscopy cannot distinguish the 180° domains since the change of optical indices is only related to the strain and not direction.

As the temperature decreases below 0°C, BT transforms into the orthorhombic structure. The polarization axis changes to one of the twelve [101] directions and the domains can meet with polarization vectors forming 60°, 90° and 180° angles (Smolenskii 1982). As the temperature decreases even further to −80°C, BT transforms into the rhombohedral phase where the polarization axis goes to one of the eight [111] directions, and these are 71°, 109° and 180° domain structures. Experimentally, it was observed that in contrast to the tetragonal phase, birefringence occurred in both the orthorhombic and rhombohedral phases (Smolenskii 1982). Also, the actual changes in polarization were larger than expected in the orthorhombic and rhombohedral phases. It was suggested that the increase in polarization was possibly due to both the change in crystal axes and the change in the magnitude of polarization (Merz 1949).

1.2. *Microscopy techniques used to observe domain configurations*

A significant amount of research has been conducted on BT since 1943 using various techniques such as optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in an attempt to understand the relationship between the domain structures and the properties of BT. Most of the research dealt with the effect of electric fields and compressive stresses on the tetragonal domain configurations. Owing to the low temperature necessary to observe the orthorhombic and rhombohedral domain configurations, their configurations have not been studied as frequently as the tetragonal phase configurations.

Regions in which all polarization directions are parallel to the surface of the section are called 'a' domains whereas regions perpendicular to the surface of the

section are called 'c' domains (Hooton and Merz 1955). Using polarizing optical microscopy the 'c' domains appear dark since the optic axis for a tetragonal phase is along the *c*-axis, whereas the 'a' domains are bright (Merz 1954). Hooton and Merz (1955), using optical microscopy were able to observe both 90° and 180° domains by etching BT samples with hydrochloric acid. They found that the positive end of the domain etched faster than the negative end of the polarization vector. Even though this technique proved successful for the observation of 90° and 180° domains, the method is destructive to the sample and not useful for dynamic studies.

Electron microscopic techniques have been used to obtain high resolution information concerning the domains and domain boundaries (Merz 1949). Domain patterns must be etched to be observed using SEM. Due to the preferential etching, the 'a', '+c' and '−c' domains appeared grey, dark and bright, respectively (Hu, Chan, Wen and Harmer 1986). Park and Chung (1994) using SEM observed that the 90° and 180° domains formed a herringbone pattern when all three domains ('a', '+c' and '−c') were present. They also found that the spatial forms of the 90° and 180° domain boundaries formed irregular cross-sections which appeared cylindrical.

When optical microscopy was compared to TEM, it was reported that the domain widths were much larger for bulk than thin film materials. The measured domain widths for bulk samples were tens of micrometres whereas for thin film techniques the widths were between hundredths or even thousandths of micrometres (Merz 1949). It is believed that the bulk domains contain many smaller domains which were unobservable using optical microscopy.

In this study, domain creation and orientation changes for the three phase transitions in BT were observed as a function of temperature. The technique differs from previous studies because it is *in situ*, allowing domain configurations at each phase transition as well as in each ferroelectric phase to be observed in real time. Bulk domain behaviours can be determined without etching.

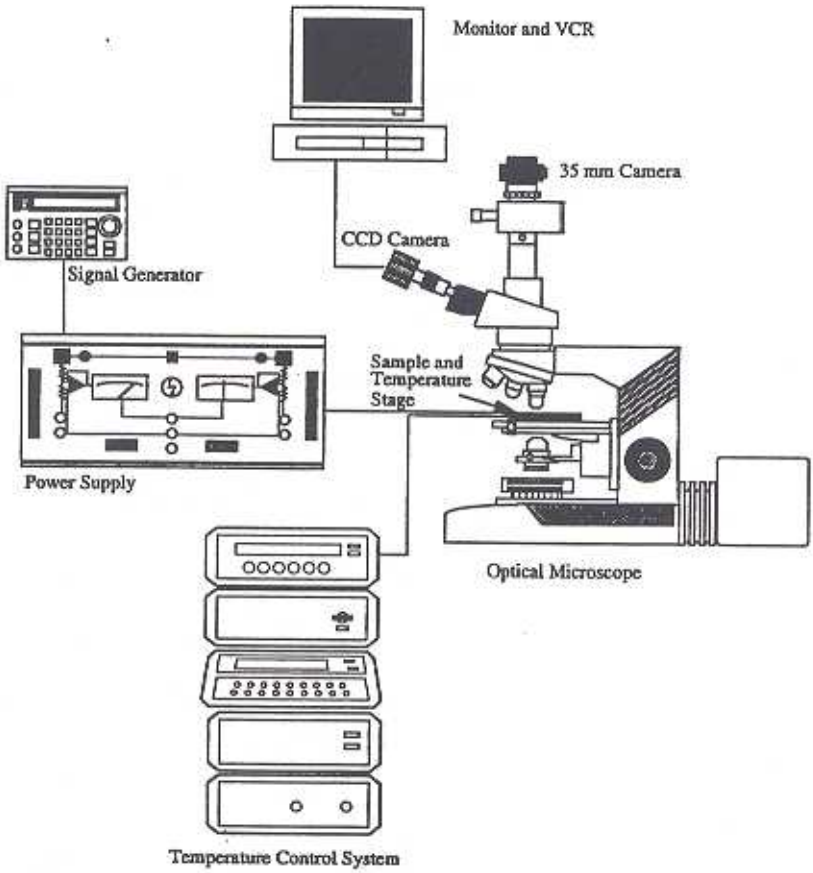
§ 2. Experimental procedure

The high quality BT single crystal used in this study was obtained from the Institute of Physics, Chinese Academy of Science, Beijing China. The crystal was grown by the top seed solution method. As received, it was optically clear, free of imperfections, and untwinned when examined under cross polarizers.

The Laué X-ray technique was used to precisely determine the [001] family of directions in the crystal. The crystal was then sliced parallel to the (001) plane, ground to a thickness of 100 μm, and polished with 0·5 μm gamma-alumina in kerosene. The samples were gold sputtered on one side leaving a 400 μm gap on the surface. Silver leads were attached to the electrodes with air dry silver paste. The samples were annealed above 200°C to remove any internal stresses in the material which were produced during the cutting and polishing operation.

A high resolution charged coupled device (CCD) camera attached to a Nikon transmission optical microscope was connected to a monitor and VCR as illustrated in fig. 1. The birefringence between the domains permitted the observation of the domains with the polarizing light microscope. Magnifications up to 1300× can be observed on the monitor. The temperature-controlled sample stage (Linkam Inc.) in conjunction with the deep focal point of the objective lenses allows the observation of domain behaviour as a function of temperature between +200°C and −185°C at a rate of 10°C min^{-1}. The stationary and changing domains were instantaneously recorded by the VCR and observed on the monitor.

Fig. 1



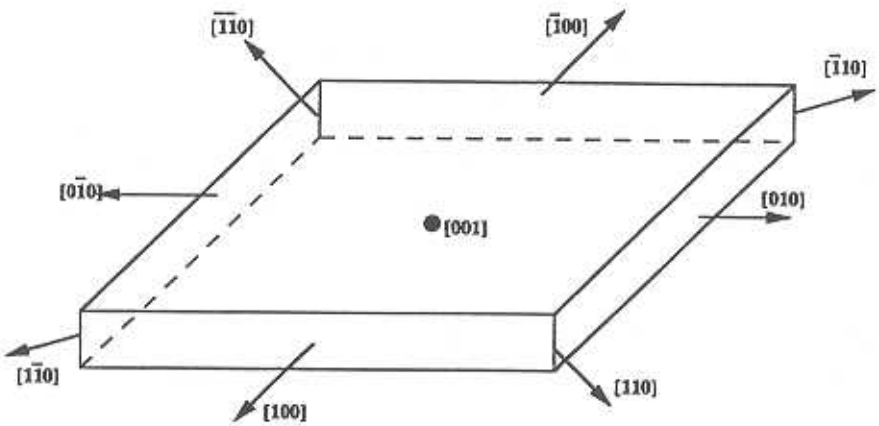
Experimental set-up of CCD microscope system used in this study.

For the dielectric constant versus temperature measurements, the crystals were cut and polished to 100 μm thick sections. Circular gold electrodes were sputtered on parallel surfaces with diameters of 1 to approx. 2 mm. The capacitance and loss of an unpoled crystal section were measured as functions of temperature and frequency in a computer controlled furnace system using a Hewlett Packard Programmable 4275A Multi-frequency LCR meter. The samples were measured on cooling from 200°C down to −160°C at 1°C min^{-1}, then heated back to 200°C at 1°C min^{-1}.

§ 3. Results and discussion

A high quality BT single crystal section with (001) orientation was measured under transmission optical microscopy (TOM) as a function of temperature during several temperature cycles to determine domain configuration changes through the three ferroelectric phase transitions. These phase transitions were observed by the changes in the domain configurations and then compared with the measured dielectric constant. The (001) section contains several directions, as illustrated in fig. 2.

Fig. 2



An illustration of the directions contained in the (001) section.

3.1. *Measured dielectric constant as a function of temperature*

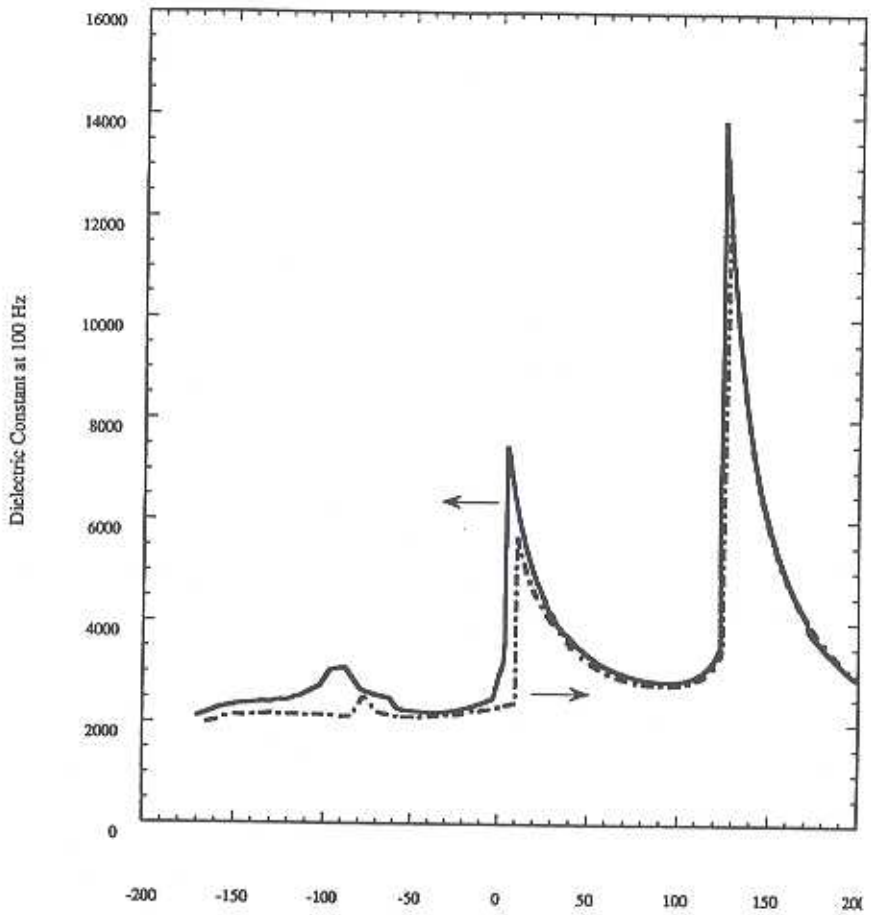
The dielectric constant as a function of temperature during heating and cooling for an unpoled BT single crystal measured along the [001] direction is shown in fig. 3. The phase transition temperatures of this crystal occurred at slightly higher temperatures than those measured by Merz (1949). In this experiment, the c → t phase transition occurred at 125°C on cooling while the t → c transition occurred at 127°C on heating (the c ↔ t phase transition reported by Merz was 120°C). The other two phase transitions, i.e. t ↔ o and o ↔ r showed larger thermal hystereses. The t ↔ o phase transitions occurred near 2·5°C on cooling and 10°C on heating, and the o ↔ r phase transitions occurred at −100°C on cooling and −90°C on heating.

3.2. *Optical observation of the cubic ↔ tetragonal phase transitions*

For each of the three thermal cycles, the cubic to tetragonal phases transition occurred at the same temperature of 125°C on cooling which was in agreement with the c ↔ t phase transition temperature of the measured dielectric constant shown in fig. 3. A small thermal hysteresis was observed as the sample was heated back through the tetragonal to cubic transition which occurred near 127°C.

In the cubic phase above 125°C, the sample appeared to be a uniform colour. On cooling, wedge-shaped domains appeared at 125°C as shown in fig. 4(*a*). These wedge-shaped domains elongated and widened with further cooling as shown in fig. 4(*b*) at 124·4°C. The isolated wedge domains grew into a more uniform twin band with domain walls oriented in [1$\bar{1}$0]. Another set of twin bands is formed with the domain walls oriented along the [110] direction. At 122·3°C the entire sample contains tetragonal 90° domains as shown in fig. 4(*c*). One set of twin bands disappeared leaving only the twin band with domain walls oriented along [1$\bar{1}$0]. The lamellar domains had a wedge shape which travelled across the sample slowly as the temperature decreased until the entire sample was covered. Most of the domain growth occurred by 120°C. Afterwards, the domain width (1–5 μm) appeared to be saturated and did not change with temperature down to 2·4°C. The 90° domains

Fig. 3



The measured dielectric constant versus temperature for an unpoled BT single crystal.

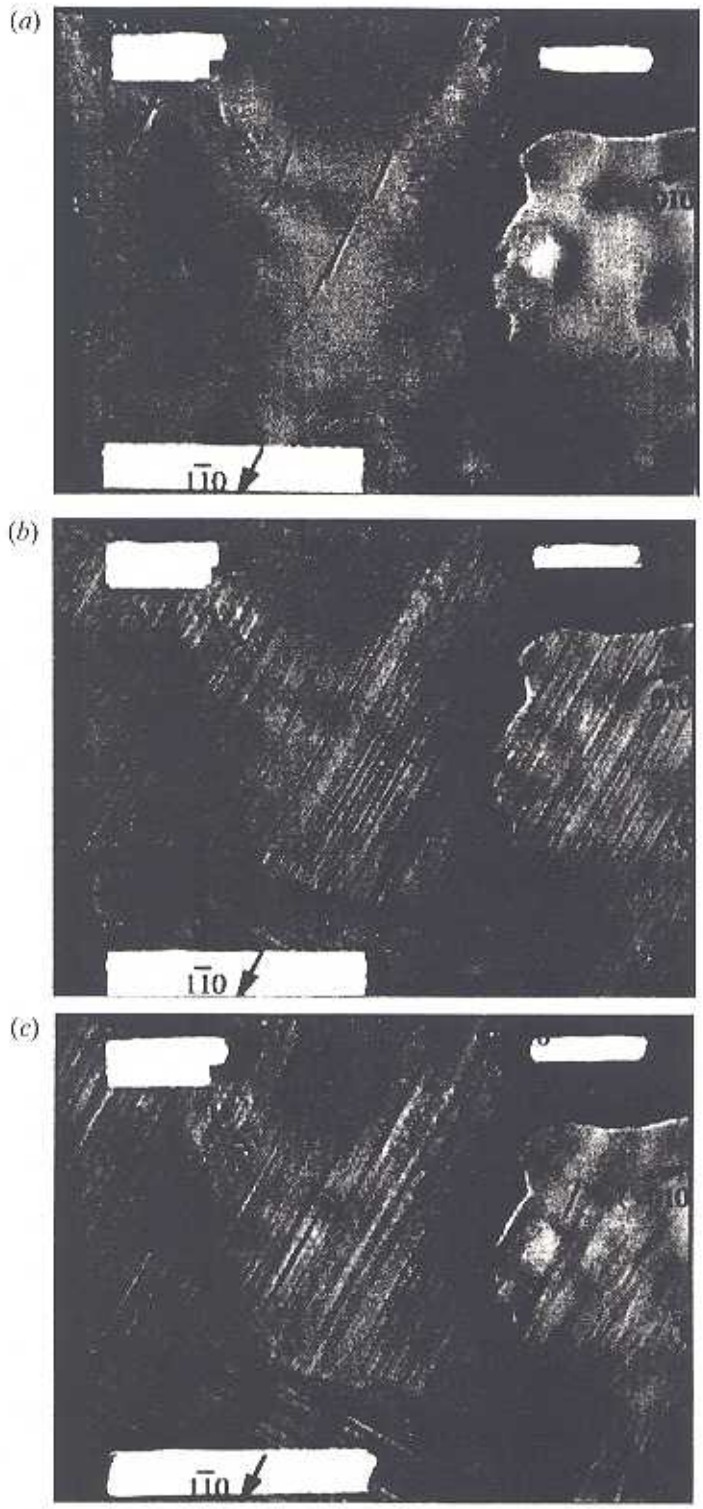
formed an 'a–a' configuration on the plane. The sample contained a high density of the long and sharp 90° domains. The colours of domains alternated yellow and green.

On heating, the tetragonal to cubic phase transition began at 124°C, signified by the disappearance of some domains. At 125°C the domains became very difficult to distinguish. At 126°C a swift shift to cubic phase occurred and all domains disappeared in a sweeping motion. However, even at 127°C, the sample still shows some birefringence. Uniform colour appeared only at 128°C.

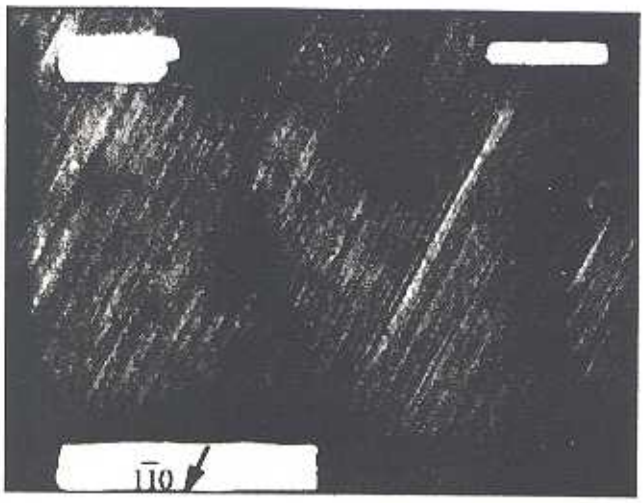
3.3. *Optical observation of the tegragonal ↔ orthorhombic phase transitions*

With further cooling down to 2·4°C the second phase transition started, which is from the tetragonal phase to the orthorhombic phase as shown in fig. 4(*d*). This phase transition took place within 0·4°C. It was also in agreement with the t ↔ o phase transition temperature in fig. 3. The orthorhombic phase domains grew across the sample in a sweeping motion with a narrow but finite temperature interval as illustrated in figs. 4(*d*), (*e*), and (*f*). The orthorhombic domains were long and well

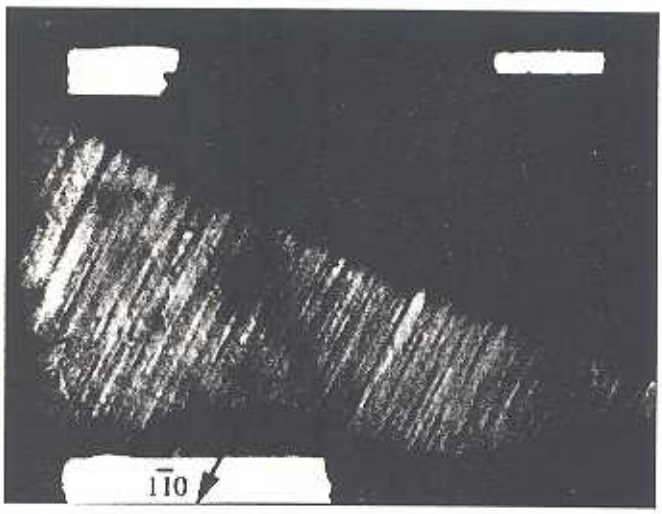
Fig. 4



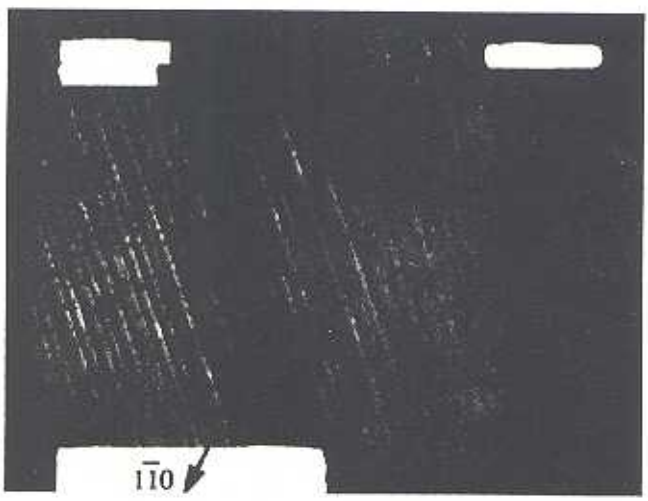
(*d*)



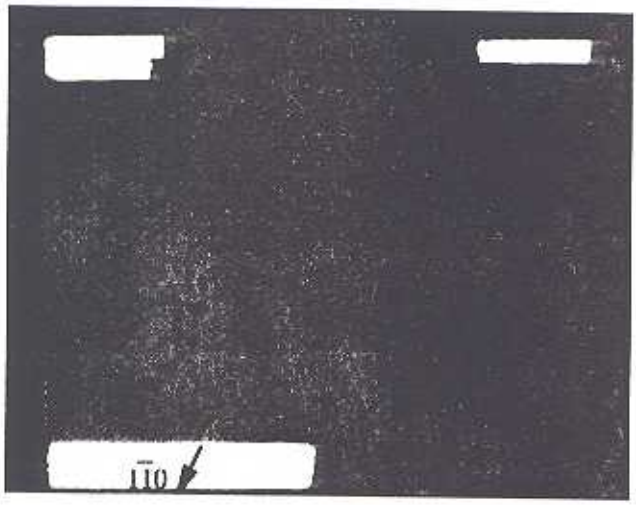
(*e*)



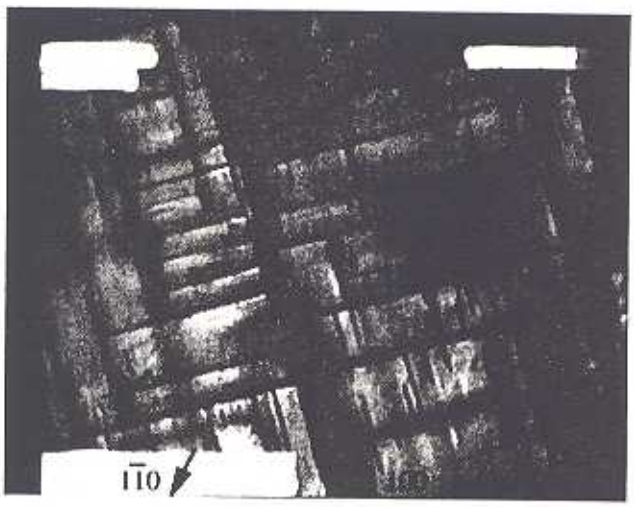
(*f*)



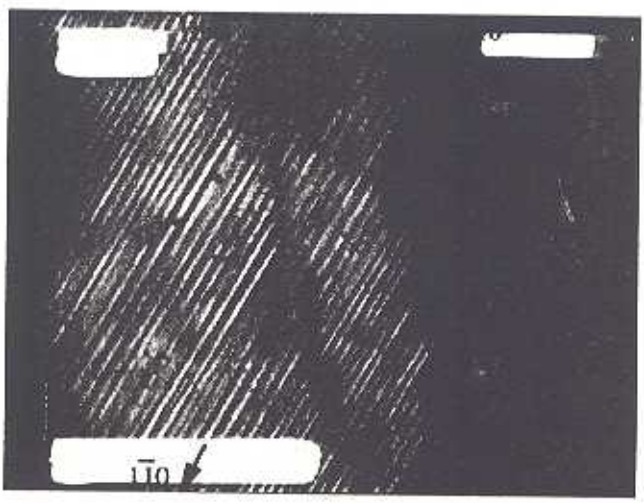
(*g*)

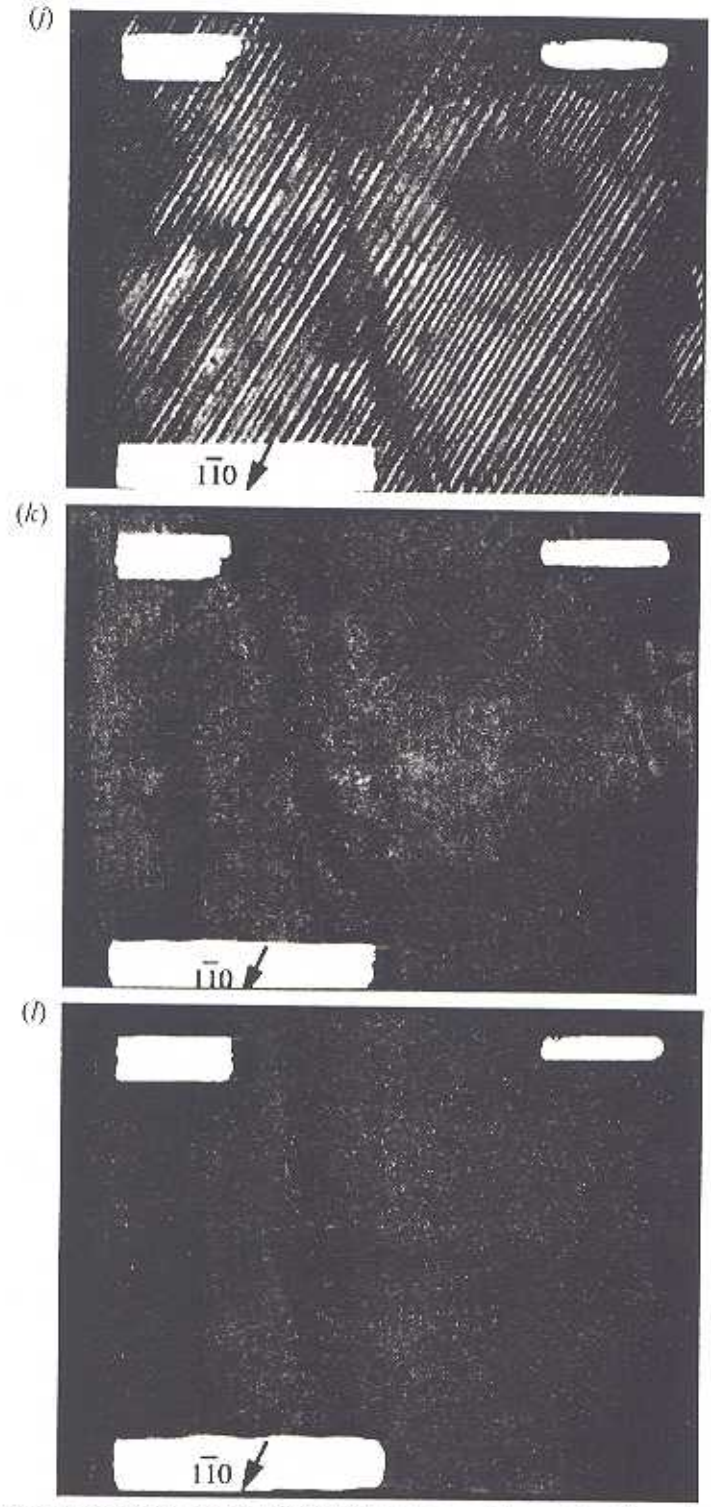


(*h*)



(*i*)





Domain structures of high quality 100% BT single crystal as a function of temperature: (*a*) 125°C, (*b*) 124·4°C, (*c*) 122·3°C, (*d*) 2·4°C, (*e*) 2·2°C, (*f*) 2·0°C, (*g*) −134°C, (*h*) 14·4°C, (*i*) 14·6°C, (*j*) 14·9°C, (*k*) −110·4°C and (*l*) −110·3°C.

defined. A single set of twin bands with domain walls oriented in the [010] evolved from the original tetragonal domains with domain wall oriented in [1$\bar{1}$0]. In effect, the domain walls rotated by 45°. The sample colour changed to warmer colours (red and orange). Taking into account the fact that the stripe period is similar in both the tetragonal and orthorhombic phases, this domain configuration change was to compensate the stress distribution.

On heating, the orthorhombic to tetragonal phase transition occurred at a much higher temperature, 14·4°C. The phase transition took place within 0·5°C as shown in figs. 4(*h*) to (*j*). A moving interface perpendicular to the tetragonal domain walls swept across the sample, changing the domain wall orientation back to nearly the same configuration as before the t → o transition (fig. 4(*c*)). The interface front which swept across the sample was not straight but slightly zigzagged. The period of this zigzag pattern corresponded roughly to that of a patchwork pattern. The recovered tetragonal phase consisted of long straight 90° domains similar to the 90° domains which appeared on cooling but with varying widths.

3.4. *Optical observation of the orthorhombic ↔ rhombohedral phase transitions*

The orthorhombic to rhombohedral phase transition temperature could not be clearly defined from the optical observation of the domain configurations. The observed phase transition temperatures varied from those shown in fig. 3. At −110°C the sample still contained long orthorhombic domains as in fig. 4(*j*). At −123°C the sample darkened and the colours became less orange and red, but the pattern was the same as that in fig. 4(*f*) in which the domain walls were oriented along the ⟨100⟩. The domains disappeared instantaneously at −134°C probably reflecting the orthorhombic to rhombohedral phase transition, as shown in fig. 4(*g*). However, in the area near a crack, domains were still present. These domains are possibly caused by the residual strain of the crack (Cao and Krumhansl 1990). The sample stayed a uniform colour down to −185°C.

On heating to −110·4°C no domains were observed as shown in fig. 4(*k*). At −110·3°C, a cross hatching of the twin bands or a 'patchwork' domain structure of purple colour was observed as shown in fig. 4(*l*). The domain walls were oriented along both the [$\bar{1}$00] and [010] directions. The width of the patchwork squares was approximately 10–50 μm in size. This pattern may have originated from the rhombohedral domain period which has not been clarified in this work. At −5·3°C the brightness of the sample increased dramatically but the domain patterns remain the same as shown in fig. 4(*h*). The patchwork domain patterns existed up to 14·6°C where the sample went through the orthorhombic-tetragonal phase transition, shown in fig. 4(*i*).

§ 4. Summary

A polarizing microscope in combination with a CCD camera system allowed the *in situ* observation of the phase transition in barium titanate and the associated domain structures for temperatures cycled between 200°C and −185°C. The domain configuration in each of the three phases had its own orientation and morphology. The transitions all appeared to be first order due to the existence of thermal hysteresis.

In the tetragonal phase, several twin bands were nucleated and later merged into a single set of twin bands with the domain walls oriented along the ⟨110⟩ directions. The width of the domains was in the range of 1–5 μm and did not seem to change

significantly with temperature. The orthorhombic domains were different when the system was transformed from the high temperature phase or from the low temperature phase. On cooling, the system transformed into a single set of twin bands from the twin bands of the tetragonal phase via a propagating habit plane perpendicular to the tetragonal domain walls. In contrast, a patchwork pattern formed on heating. The patchwork domain structure transformed to the tetragonal twin band via a zigzagged interface of an orientation near the [010]. No clear domain patterns were visible under TOM in the rhombohedral phase on this crystallographic section.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research under grant numbers N00014-91-J-4145 and N00014-92-J-1501.

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