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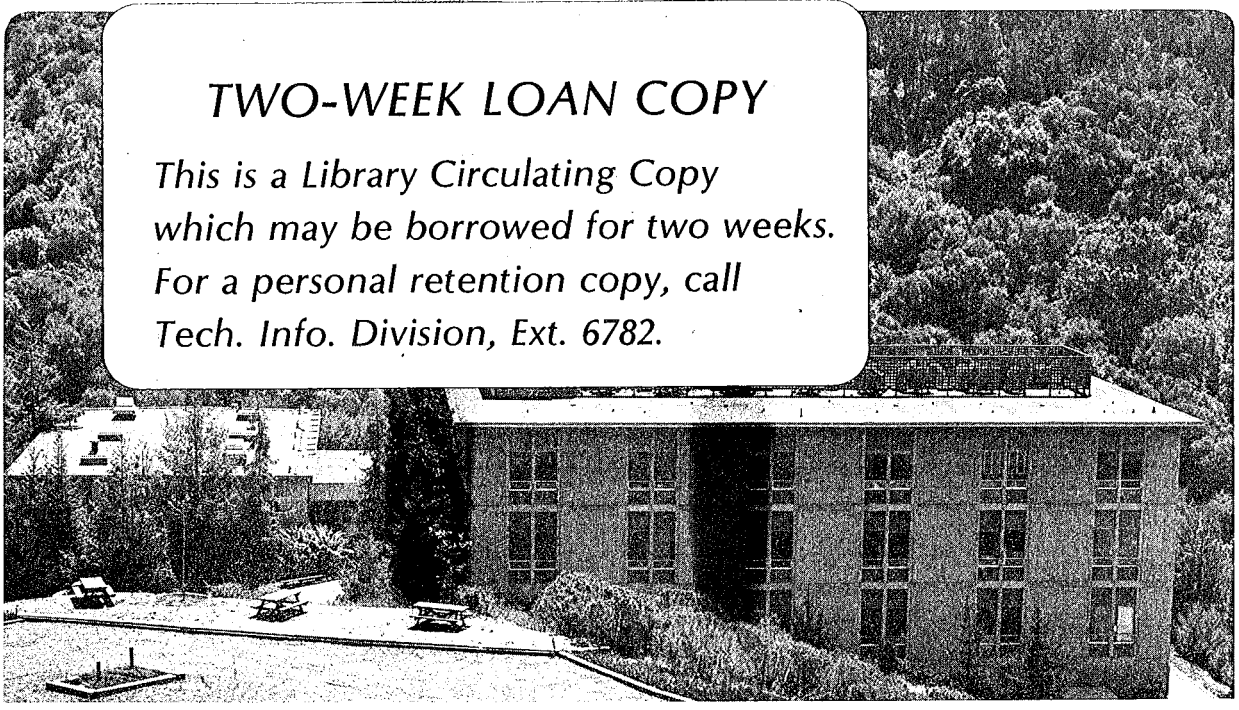

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ABSTRACT

The crystallography of the domains and domain walls in PZT are studied using electron diffraction and transmission electron microscopy. Both 90° and 180° domains are observed and the 90° domains are shown to be deformation twins with displacement along <110> on {110}. The thickness of the 90° domain wall is determined to be $\lesssim$ 100 Å.

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I. INTRODUCTION

Lead Zirconate Titanate (PZT) is a ferroelectric material at room temperature and it is used extensively in piezoelectric devices.[1] Above its Curie temperature (375°C),[2] PZT is a cubic solid solution of lead titanate and lead zirconate. It undergoes a phase transformation[1] from cubic to tetragonal phase on cooling below the Curie temperature. The strain, resulting from this transformation is accommodated by the formation of twins. Each of the twin plates is a ferroelectric domain. These domains have been examined by etching technique[3] or by replica technique,[4] both of which cannot provide any crystallographic information about the structure. The purpose of the present study is to characterize the nature of the domains in PZT and also to study the structure of the domain walls using transmission electron microscopy methods.

II. EXPERIMENT

Samples of PZT were prepared by conventional sintering process from 99.9% pure PbO, ZrO_2, and TiO_2 powders. Electron transparent specimens were prepared from the bulk material by mechanical thinning followed by ion bombardment. These specimens were coated with carbon to prevent charging in the microscope. The microscopy was done using a Philips EM301 microscope operating at 100kV.

III. RESULTS AND DISCUSSION

Fig. 1 shows the typical domain configuration inside a grain of PZT. Two kinds of domains can be seen in this figure. The predominant category of domains are 90° domains. The adjacent domains of this kind are twin-related.[4] The twin boundary is the domain boundary and the twin plates are ferroelectric domains. The twin planes are {110} and the polarization vectors (parallel to the C-axis of the tetragonal lattice) in adjacent domains are perpendicular to each other. The selected area

diffraction pattern from several domains shows the splitting of spots along [$1\bar{1}0$] in Fig. 1, due to twinning on ($1\bar{1}0$). The contrasts from the domain walls depend on the operating diffraction condition and the domain walls are out of contrast when the operating reflection is normal to the domain boundary. Thus, the domain boundary can be described by a small displacement vector, parallel to the boundary plane. This confirms that the twins are displacement twins,[5] created due to stress in the material during the paraelectric to ferroelectric transformation.

The strain tensor during this transformation (6) can be written as:

$$S = \begin{pmatrix} -\varepsilon & 0 & 0 \\ 0 & -\varepsilon & 0 \\ 0 & 0 & 2\varepsilon \end{pmatrix}$$

with $\varepsilon = 0.01$ [7], and the tetragonality along [001]. If the fraction of the material in one twin configuration is x, then the overall strain in the material can be expressed as

$$\bar{S} = x\bar{S}_1 + (1 - x)\bar{S}_2$$

where $\bar{S}_1$ and $\bar{S}_2$ are strain tensors for adjacent domains along a 90° domain wall. Thus, for $x = 1/3$, $\bar{S} = (\varepsilon, -\varepsilon, 0)$. This is equivalent to a shear strain of magnitude $\sqrt{2}\,\varepsilon$ along [$1\bar{1}0$] on ($1\bar{1}0$) plane, consistent with the observations in Fig. 1.

From the foregoing analysis, it can be shown[6] that the macroscopic strain in the material can be zero, if, in addition to the twins on ($1\bar{1}0$), as discussed above, also twins on (101) of $\bar{S} = (-\varepsilon, \varepsilon, 0)$ are formed. Thus, if the twinning is due to the deformation stress, two sets of twins on ($1\bar{1}0$) and (101) are more likely to be formed than only one set in order to reduce the strain energy. That such is the case can be seen in Fig. 2, when the secondary twin plates are seen to be forming inside the primary twin plates.

Fig. 2 also shows that near the edge of the foil there is no domain configuration present. However, from the diffraction pattern it can be seen that the region near the edge of the foil is not cubic, but tetragonal, and hence ferroelectric. The region is so thin ($\lesssim$700Å as determined experimentally) that the strain due to the tetragonality is relaxed by the free surfaces and thus does not lead to twinning. The tip of the twin plates in Fig. 2 also does not show any stress concentration.

When the specimen is heated above the Curie temperature, the domain structure disappears as shown in Fig. 3(b), but it reappears upon cooling. The domain configuration is not reversible, and several groups of domains form inside one grain, as shown in Fig. 3(c). Thermal stresses due to beam heating also cause the domains to move. All these effects make it questionable whether the domain configurations observed in the TEM are representative of the bulk material.

The structure of the domain walls and the rotation of the polarization vectors for $BaTiO_3$ (8) are shown in Fig. 4. As can be seen from such a model, (a) the domain wall has a finite thickness,[9] (b) the structure of the wall region can be considered as a two-dimensional distorted crystal which is noncentrosymmetric, and (c) the sense of rotation of the tetragonal distortion at adjacent walls are opposite of each other. The dark field image in Fig. 5 shows that adjacent domain walls have opposite contrast, arising because of dynamical diffraction[10] from the noncentrosymmetric crystal in the boundary region. The measured thickness of the wall image is ~80Å for PZT. This thickness represents the thickness of the distorted region near the boundary (Fig. 3b)

and hence the thickness of the domain wall. It must be pointed out that the structure of the domain walls in PZT, as determined experimentally, is similar to those suggested for the structure of the domain walls in $BaTiO_3$ where the theoretical estimates for wall thickness range from 10 to 40 Å.[11,12]

In addition to the 90° domains, another kind of domain is also found. The wall A-A in Fig. 1 is such a domain wall. The adjacent domains on the opposite sides of this wall differ by an inversion and this wall is a 180° domain wall. The contrast from the wall arises due to the noncentrosymmetric structure of PZT below its Curie temperature and is characteristic of π boundaries. Although this wall lies on (001) planes, it departs from this plane significantly in certain twin plates. This kind of domain is seen very rarely. No further investigation of these walls has been done in the present case.

In the above discussions, only the strain energy is considered. Fousek and Janovec[13] have shown that the distortion in an infinite perfect crystal depends on the polarization $\vec{P}_s$, and the domain walls lie on the planes where the two distortion systems from adjacent domains mate exactly. In the present case, where the polarization lies parallel to the plane of the specimen, charges do not accumulate on the free surfaces and thus the above results can be taken as an approximation. As shown by Cross[14], the stress model is a plausible model for $BaTiO_3$ ceramic materials for a phenomenological study of ferroelectricity. In this study, no attempts have been made to separately account for the effects of the depolarizing fields on the domain formations. In view

of the good correspondence between the experimental observations and the predictions of the stress model, the latter is considered to be a good approximation.

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