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CONVERGENT-BEAM ELECTRON DIFFRACTION STUDIES OF DOMAINS IN RHOMBOHEDRAL PHASE OF LEAD ZIRCONATE TITANATE CERAMICS

M.L.A.Dass and Gareth Thomas*

Lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZT) ceramics are ferroelectrics formed as solid solutions between $PbTiO_3$ and $PbZrO_3$. Among the different phases in the ferroelectric state, the primary ones are the Ti^+ rich tetragonal (T) phase and the Zr^{+4} rich rhombohedral (R) phase and the phase boundary between them (x~0.53). A net polarization for the piezoelectric activity is obtained under an applied field whereby the polarization vectors of individual grains reorient and this process is called poling. The boundary composition is of great technological importance owing to the high piezo electric activity. It is suggested, that the excellent piezo electric property is due to the coexistence of both the T and R phases which favours easy poling,[1].

However there has been no systematic study of microstructure and domain structure of the PZT ceramics. The coexistence of both T and R phases at the boundary composition has been reported using the convergent beam electron diffraction method,[2]. Further in an attempt to characterize the ferroelectric domains in the different

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phases, R phase was first studied as such an analysis can be extended to the phase boundary composition to identify the different phases and to study their domain structure.

Experimental

The ceramic used in this study was prepared by conventional ceramic processing,[2] and the composition of the sample examined was $Pb(Zr_{0.65}Ti_{0.35})O_3$. The structure has been found to be rhombohedral with lattice parameters a=4.0970Å and $\alpha=89^{o}30'$ based on X-ray diffraction studies of powder samples. At the ferroelectric transition, the spontaneous polarization occurs along [111] in the rhombohedral phase and the crystal breaks into domains to compensate the depolarizing field. These domains influence the properties of ferroelectric materials to a large extent. Based upon the angle between the polarization directions in two adjacent domains they are related by either 71^{o},109^{o} and/or 180^{o}. In order to characterize and identify the possible domains it is necessary to use convergent beam electron diffraction (CBED) in order to obtain the necessary resolution.

Results and Discussions

A [001] zone axis CBED pattern obtained from the R phase is shown in Fig.1. The point group symmetry of the rhombohedral phase is 3m and the symmetry of the diffraction group,[3] is a mirror plane of type {110} in a <001> zone axis pattern (ZAP) Fig.2. The intensity variations in both the zero order Laue zone and the first order Laue zone (FOLZ) ring are not convincing enough to decide the symmetry of the pattern. However the intersection of the Kikuchi lines at the {100} band with the FOLZ ring is useful in identifying the symmetry of the pattern,[4] and these are marked by arrows in

Fig.1. Different orientations of the polarization direction across a domain wall result in a rotation of the mirror plane in the CBED patterns. For example a 71 degree domain between the polarization directions [111] and [111] is indicated by a 90 degree rotation of the mirror planes whereas a 109 degree domain between [111] and [111] is indicated by 180 degree rotation of the mirror plane in the CBED pattern. A bright field micrograph of domains thus studied is shown in Fig.3. Parts of the [001] ZAP's obtained from different domain regions at room temperature with a probe ~400Å in diameter are shown in Fig.4. The letters on the patterns correspond to the various domains shown in Fig.3. It can be seen that the polarization directions in two neighbouring domains across a domain wall are related by 71^{o}, a result which has been observed frequently in this study.

Conclusions

Domain types in the R phase of PZT ceramic have been identified using the CBED method. However, the fringe contrast at the domain boundaries indicate that the domain walls are inclined (Fig.3). The orientation relation of domain walls is being studied by conventional microscopy contrast and diffraction techniques.

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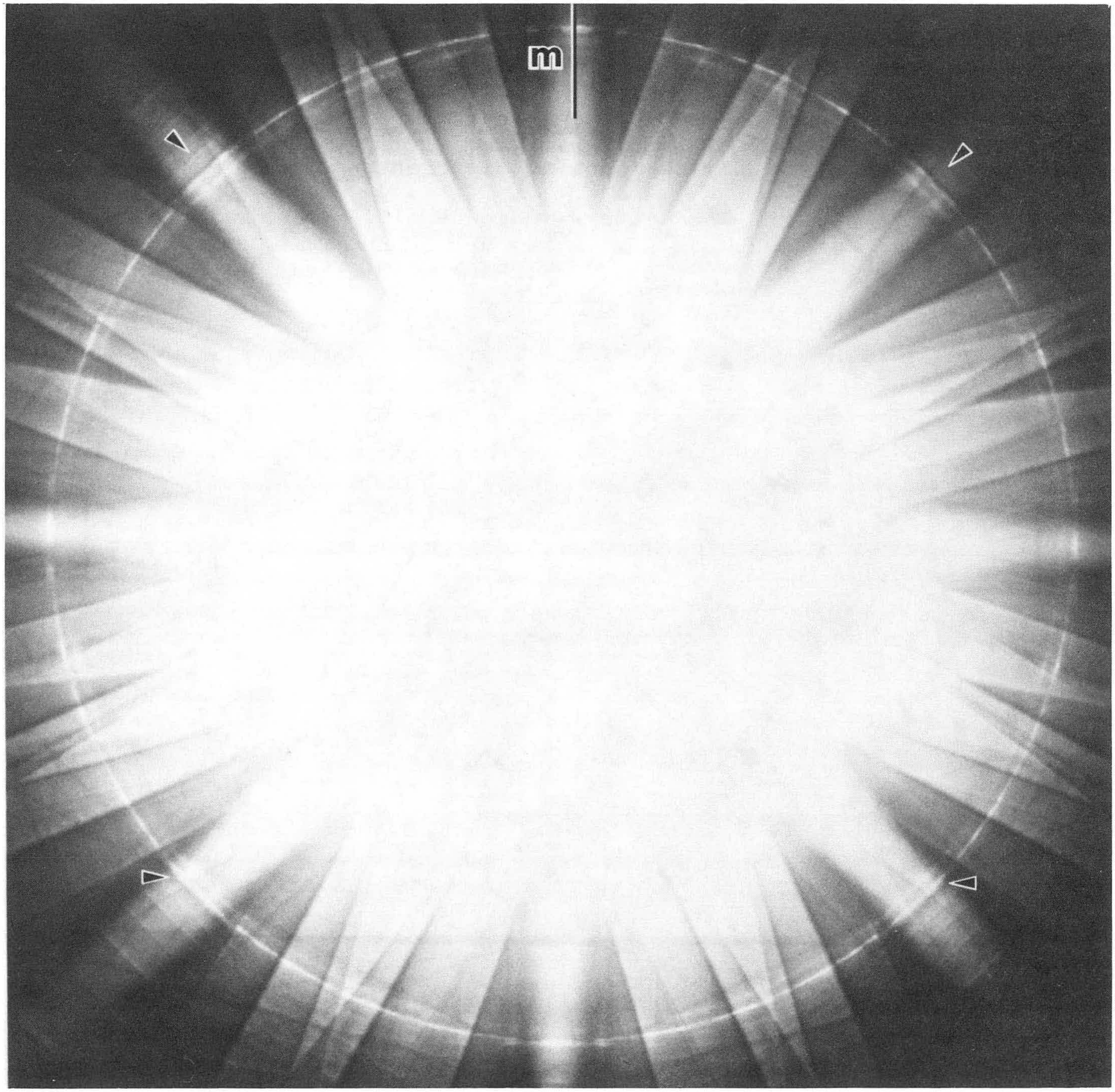
Figure captions

Fig.1.--[001] zone axis pattern. The pointers indicate the features of the mirror symmetry.

FIG.2.--[001] Stereographic projection of the R phase with 3m point group symmetry.

FIG.3.--Bright field image of domains in R phase.

FIG.4.-- Parts of [001] ZAP showing different amounts of rotation of the mirror plane. The letters indicate different sampling points in Fig.3.



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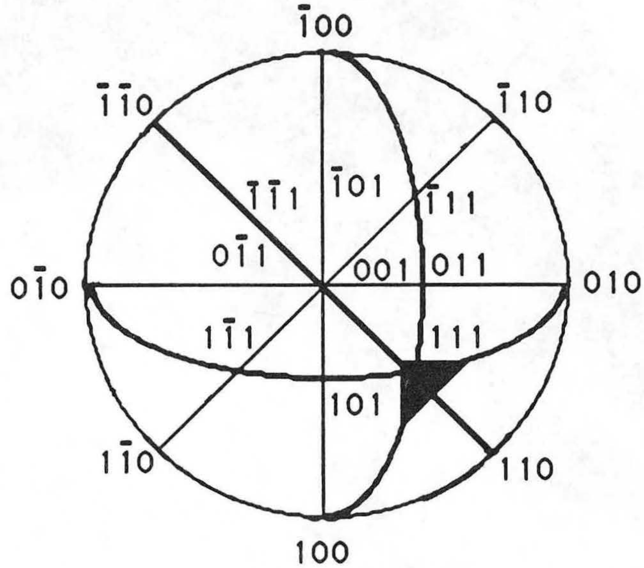
[001] STEREOGRAPHIC PROJECTION OF RHOMBOHEDRAL PHASE WITH POINT GROUP 3m



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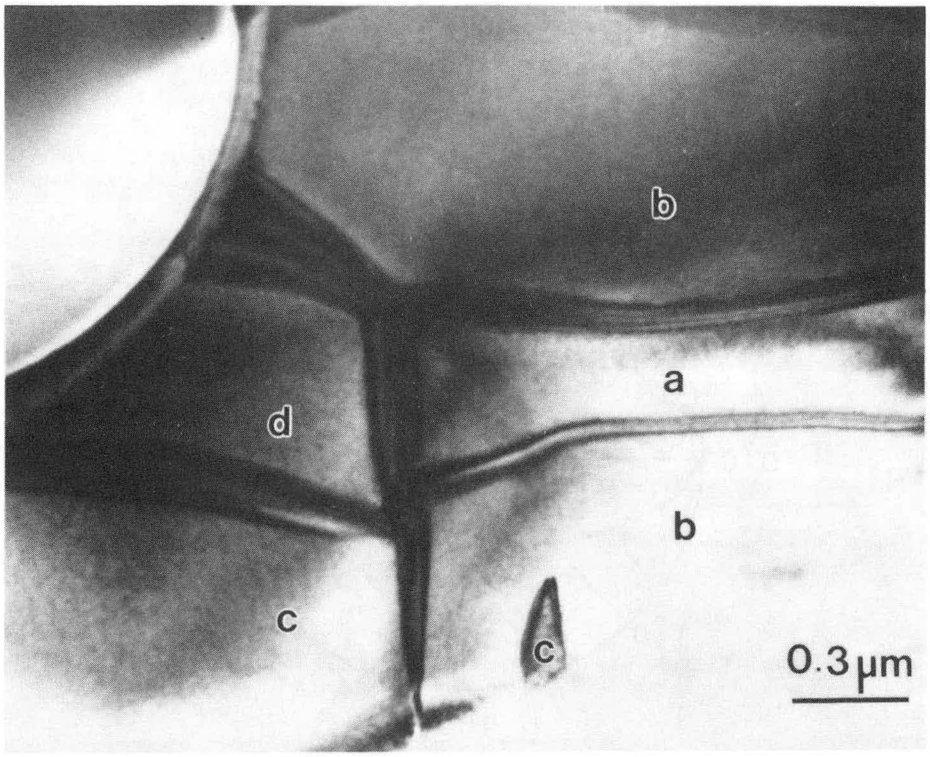

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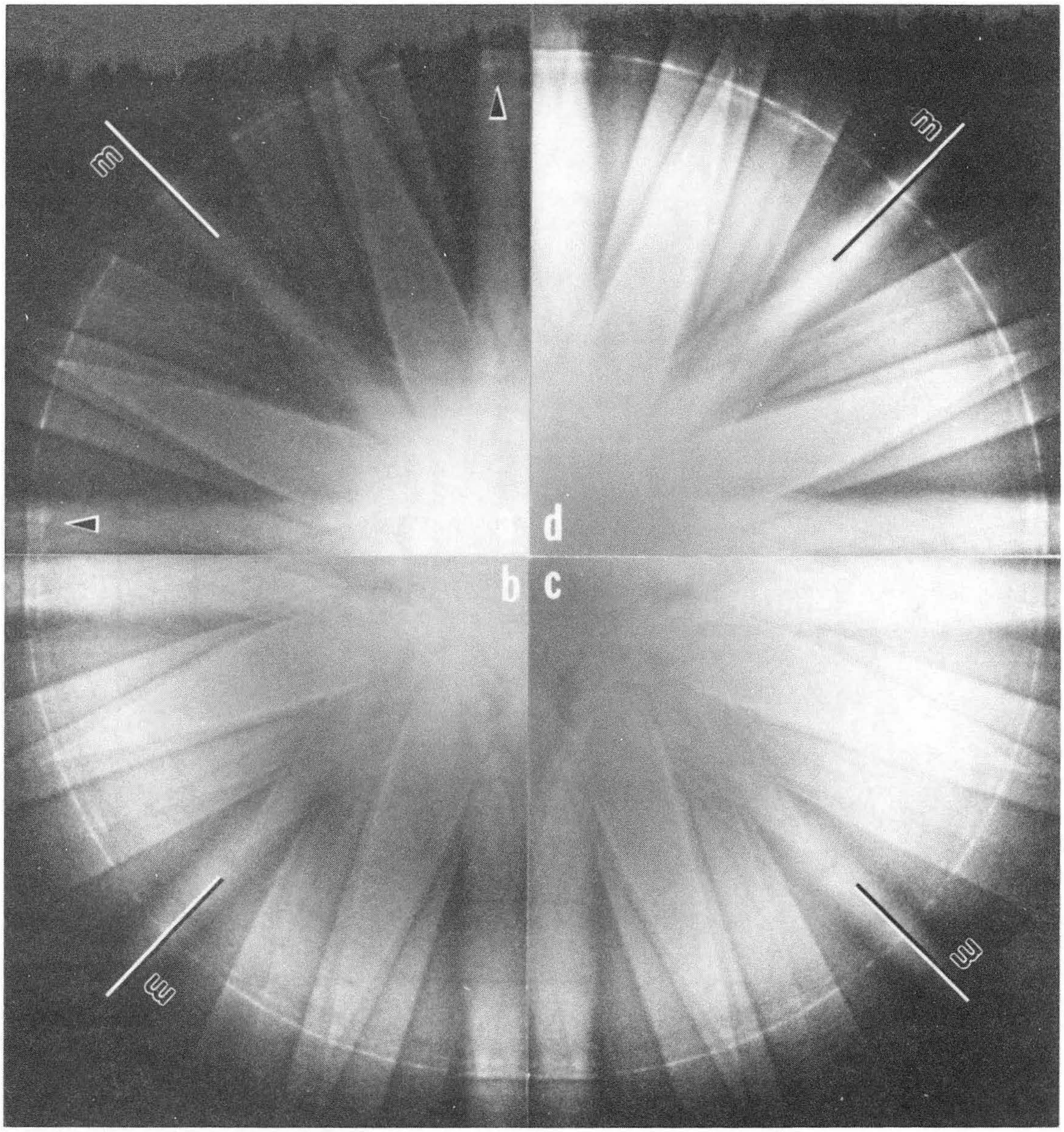

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