Solid State Communications, Vol. 85, No. 3, pp. 193-195, 1993.
Printed in Great Britain.

0038-1098/93$6.00+.00
Pergamon Press Ltd

A TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION OF THE R3m → R3c PHASE TRANSITION IN $Pb(Zr,Ti)O_3$ CERAMICS

C.A. Randall, M.G. Matsko, W. Cao, and A.S. Bhalla
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802, USA

(Received 28 September 1992 by A. Pinczuk)

A transmission electron microscopy (TEM) study was performed on $Pb(Zr,Ti)O_3$ compositions within the R3m → R3c phase region. The low temperature phase is owing to a displacive phase transition involving oxygen octahedral tilts. The associated superlattice reflections as a result of the tilt are detectable by electron diffraction. Dark Field diffraction contrast imaging of the superlattice reflections reveals antiphase boundaries (APB) associated with the octahedral tilt domains. Interaction between the octahedral tilt antiphase boundaries and the ferroelectric domain structures of the R3c phase is studied and discussed.

1 - Introduction

The perovskite solid-solution between end-member $PbTiO_3$ and $PbZrO_3$ is the basis of important technological ceramics used in the piezoelectric, pyroelectric and electro-optic devices.[1-3] The phase diagram of $PbTiO_3$-$PbZrO_3$ is illustrated in Figure 1. The phase diagram contains a variety of regions of displacive phase transitions and there are antiferroelectric and several ferroelectric phases in the low temperature regime. Compositions between Zr/Ti ratios 90/10 and 65/35 reveals a ferroelectric → ferroelectric transition between rhombohedral space groups R3m → R3c. This transition involves the oxygen octahedra tilt about the <111> directions.[4] The aim of this investigation is to study the inter-relationship between octahedral tilt domain structures and the high temperature ferroelectric domain structures. There have been virtually no studies regarding the domain structures of octahedral tilt systems in perovskites.[5] The transmission electron microscope offers an attractive means to study this subtle phenomena owing to electron scattering factors for oxygen being much larger than the corresponding x-ray scattering factors. The diffraction contrast imaging also allows a direct means to study the domain states and their interactions with the ceramic microstructure.[6]

2 - Experimental

Ceramic samples of $Pb(Zr,Ti)O_3$ were prepared using the conventional solid-state sintering techniques. The starting raw material powders, PbO, ZrO_2, and TiO_2, were of analytical grade quality. Two compositions were made for this study $Pb(Zr_{0.9}Ti_{0.1})O_3$ and $Pb(Zr_{0.65}Ti_{0.35})O_3$. These compositions were batched according to the stoichiometric ratios and taking into account the loss of ignitions. The raw powders were ball milled with ethanol solvent for 48 hours for complete mixing. Perovskite phases were fully formed after calcining for four hours at 900°C, as determined by X-ray diffraction studies. The calcined powder was ball milled for 24 hours. Binder and 1 wt% excess PbO was added to 80 mesh sieved powders. Green pellets with 60% theoretical density were formed using uniaxial pressure followed by binder burnout at 550°C for 1 hour. Sintering was undertaken at 1250°C for 2 hours to form pellets with 91-94% theoretical density and with less than 1% weight loss.

TEM samples were made by grinding and polishing ceramics to a thickness = 50 μm. These

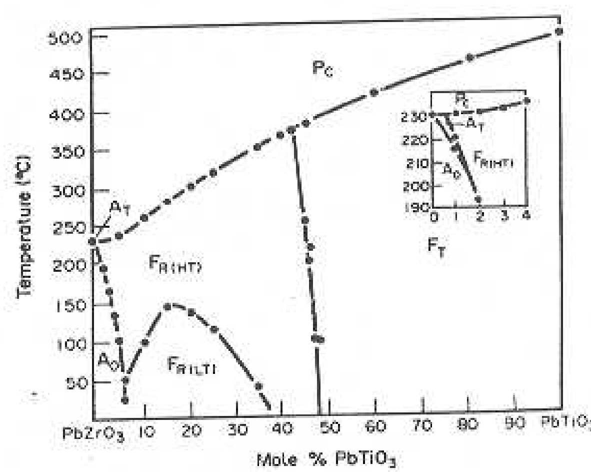

Fig. 1. The $PbZrO_3$ and $PbTiO_3$ phase diagram [Jaffe, Cook, Jaffe (1971)].

sections were mounted on 3 mm copper grids using Devcon 5-minute epoxy. Ion beam thinning was performed at 10° with argon ion beams accelerated to 4 KV and a beam current ≈ 1 mA. TEM observations were made using a Philips 420 STEM at 100 KV. A Gatan liquid nitrogen two-tilt stage was used to make in situ TEM observations between 80°C to -180°C.

3 - Results

Figures 2(a) and (b) show the [110] zone axis diffraction patterns revealing {h+1/2, k+1/2, l+1/2} pseudo cubic superlattice reflections in $Pb(Zr_{0.9}Ti_{0.1})O_3$ and $Pb(Zr_{0.65}Ti_{0.35})O_3$ respectively. It is found that by heating the $Pb(Zr_{0.65}Ti_{0.35})O_3$ sample to 80°C the superlattice reflections disappear, figure 2(c), and conversely cooling to lower temperatures with the Gatan liquid nitrogen stage the intensity of the diffraction spots increases. This suggests that these reflections are, therefore, associated with a displacive phase transition in the material. The {h+1/2, k+1/2, l+1/2} diffractions are consistent with the neutron diffraction study performed by

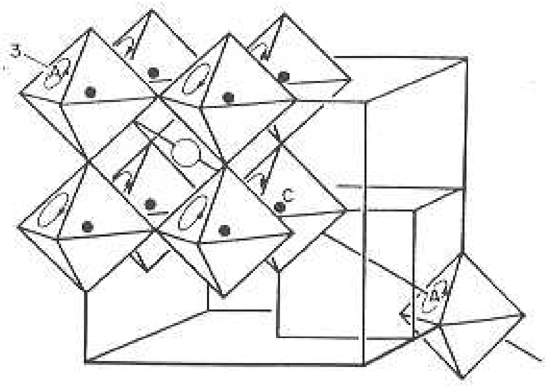

Fig 3. Schematic representation of the oxygen octahedral-tilting in R3c phase.

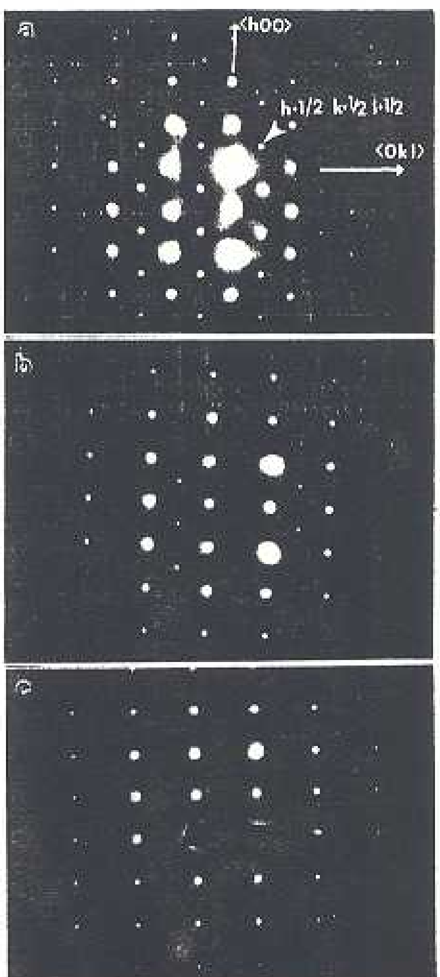

Fig. 2. [110] Zone axis diffraction patterns (a) $Pb(Zr_{0.9}Ti_{0.1})O_3$, (b) $Pb(Zr_{0.65}Ti_{0.35})O_3$, both at room temperature, and (c) $Pb(Zr_{0.65}Ti_{0.35})O_3$ at 80°C.

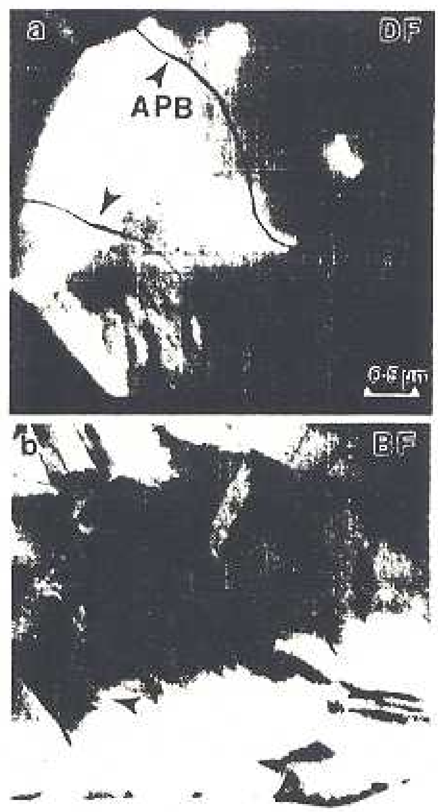

Fig. 4. (a) Dark field image of octahedral-tilt superlattice reflection revealing antiphase boundaries (APB); (b) multiple bright field image of same area revealing typical 180° domain wall contrast.

Glazer.[4] Glazer predicted the origin of this superlattice to be oxygen octahedral tilts within the simple perovskite structure. The oxygen octahedral shifts with equal components about the pseudo-cubic perovskite axis as to give an effective clockwise and anticlockwise rotation of oxygen octahedra about the <111> directions parallel to the ferroelectric dipole displacements of the R3m phase, Figure 4.

Figure 4(a) shows the dark field diffraction contrast image associated with the superlattice reflection in a $Pb(Zr_{0.9},Ti_{0.1})O_3$ subgrain. A dark ribbon-like boundary is observed under these imaging conditiors, and this is believed to be a wall separating out-of-phase octahedral tilt variants. Figure 4(b) shows the same subgrain imaged under a multiple beam bright field spatial perturbation between the 180° ferroelectric domain walls and the octahedral antiphase boundaries.

Figure 5(a) shows a bright field image which reveals ferroelectric twin structures and inversion 180° ferroelectric domains in a rhombohedral ferroelectrics.[7] Figure 5(b) shows the same crystallite imaged in dark field with a superlattice reflection. The antiphase boundary contrast is again observed and shows a strong interaction with the twin boundaries. generally was found antiphase boundaries are terminated on the twin boundaries, grain boundaries, or alternatively contained within the closed loops. The antiphase boundaries in the $Pb(Zr,Ti)O_3$ ceramics predominantly terminates on either twin boundaries or grain boundaries. Region X in Figure 5(b) shows an example of the antiphase boundary terminating at a (110) twin domain region and Y shows an antiphase boundary coincident with a (001) domain wall.

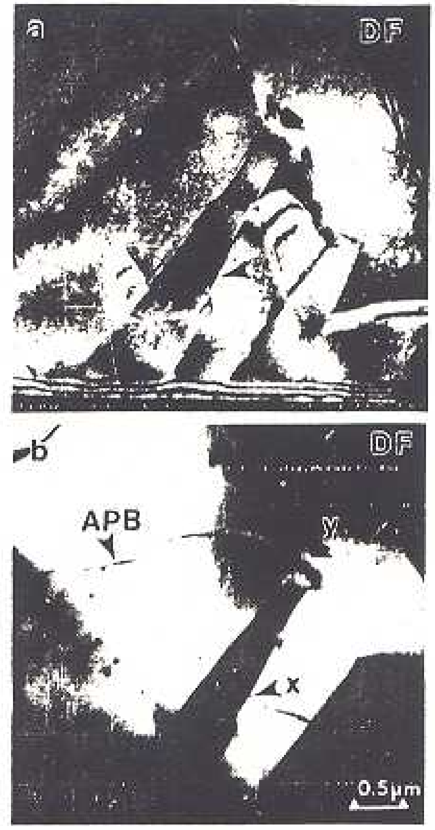

Fig. 5. (a) Dark field image of ferroelectric domain walls; (b) Dark field image of supperlattice reflection revealing interaction of APBs with twin domain walls.

4 - Discussion

From the above results we can infer that the R3m ferroelectric phase has only twin and inversion domains. Twin domains being 109° or 71° type and twin on habit planes (110) and (100), respectively. These observations are consistent with earlier observations on modified rhombohedral $Pb(Zr,Ti)O_3$ ceramics.[8] The octahedral tilt transition is driven by a zone boundary soft mode resulting in the doubling of the unit cell. This transition gives rise to two additional variants which are separate from each other with antiphase boundaries. The antiphase boundaries are slightly perturbed by 180° domain walls and are strongly perturbed by the twin boundaries. In some incidents we noted that the antiphase boundaries were joined with the walls in which case it may imply that a coupling between the gradients of the tilt and the polarization may be present.

Acknowledgements

This research was supported by Air Force Office of Scientific Research under Grant No. AFOSR-91-0433 and by Office of Naval Research under Grant No. N00014-92-J-1510. We also wish to thank Dr. Ian Reany for many discussions during his work and also JoAnn Mantz for typing this manuscript.

References

1. B. Jaffe, W.R. Cook, and H. Jaffe, *Piezoelectric Ceramics*, Academic Press, London, New York (1971).

2. M.E. Lines and A.M. Glass, *Principles and Applications of ferroelectrics and Related Methods*, Clarendon Press, Oxford (1977).

3. A. Moulson and S. Herbert, *Electroceramics-Materials-Properties-Applications*, Chapman and Hall, London, New York, Tokyo, Melbourne, Madras.

4. A.M. Glazer, Acta Cryst. A31, 756-762 (1975).

5. E.L. Colla, I.M. Reaney, and N. Setter, European Conference on the Applications of Polar Dielectrics, Conf. Proc, In press, (1992).

6. P.B. Hirsch, A. Howie, R.B. Nicholson, D.W. Pashley, and M.J. Whelan, *Electron Microscopy of Thin Crystals*, Butterworth, London (1977).

7. I.M. Reaney, Private Communication.

8. C.A. Randall, D.J. Barber, and R.W. Whatmore, J. Mat. Sci. 22 935 (1987).