

## SPATIAL VARIATIONS OF POLARIZATION IN FERROELECTRICS AND RELATED MATERIALS

C. A. RANDALL, G. A. ROSSETTI, JR., and W. CAO

*Materials Research Laboratory, The Pennsylvania State University,  
University Park, PA 16802 USA*

*(Received February 10, 1993; in final form August 26, 1993)*

Electron microscopy studies in lanthanum doped lead titanate reveals the evolution of a spatial modulation in the magnitude of the spontaneous polarization with the increase of the lanthanum dopant. On the incorporation of ~25 atom percent lanthanum, the conventional domain structure becomes ill-defined, and tweed microstructures are observed. The structural information can be associated with the change from normal ferroelectric to diffuse ferroelectric phase transition behavior. Different from twin structures, these modulated structures represent a new type of polarization variation existing within a single domain. Further understanding of the observed spatial variation in polarization requires structural analysis at the atomic scale. Holographic electron microscopy is proposed as a potential tool to study various polarization gradients in ferroelectric materials. Understanding the spatial variations in polarization is essential to better comprehend the extrinsic contributions to the elasto-dielectric properties in ferroelectrics.

*Keywords: polarization gradient, modulations, PLZT, ferroelectrics*

### INTRODUCTION

Mesoscopic structures within ferroelectrics and related materials have important consequences with respect to the macroscopic elasto-dielectric properties. These structures exist on a scale of a few tens to a few thousands of angstroms and include defect structures within the lattice as well as the polarization domain structures associated with the ferroic phase transition. In general, there are two contributions to the elasto-dielectric properties: the intrinsic contribution, which is related to the ferroelectric (antiferroelectric) atomic structure, and the extrinsic contribution, which is associated with domains and defects.<sup>1,2</sup> In technologically important materials, such as  $\text{Pb}(\text{Zr,Ti})\text{O}_3$ , the extrinsic factors can contribute as much as 70% to the total elasto-dielectric response (see Figure 1). Therefore, it is necessary to develop a greater understanding of all the possible defect and polarization mechanisms which could contribute to the extrinsic elasto-dielectric properties. However, a comprehensive theoretical description of the extrinsic contributions is currently not in place.

The most common mesoscopic structures associated with ferroelectric and related materials are domains and domain walls. Domains form at the phase transition and relate the low temperature phase to the high temperature prototype phase via certain symmetry constraints. In the example of "normal" first- or second-order ferroelectric transitions, each domain is a volume of uniform polarization, and the boundary which divides two domains (i.e. a twin structure) is known as the domain wall. The domain wall is a region of distorted crystal structure in which there exists a spatial transition of the polarization from one orientation state to another.

There are two main types of twin structures. One type is a twin with inversion

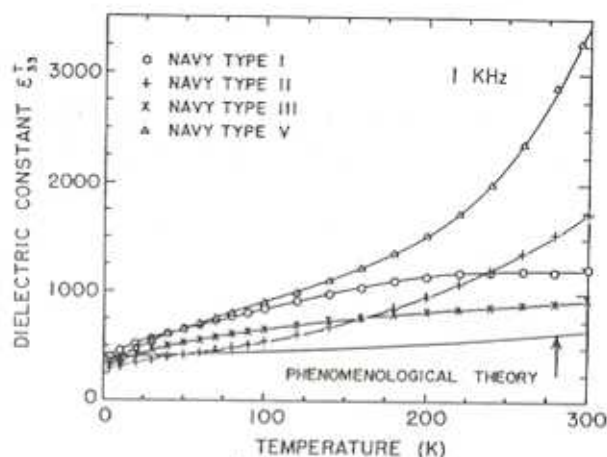


FIGURE 1 Temperature dependence of the dielectric permittivity of doped-PZT ceramics. The theoretical value from the Landau-Devonshire theory is also shown (reproduced from 1985 ONR Annual Report, Materials Research Laboratory, The Pennsylvania State University).

symmetry of the polarization but in which the strain is the same in both variants. The second type is a twin of two variants with different orientation for both polarization and strain. Ferroelectric twins are typically of the head to tail configuration. There are reports of other domain configurations, such as head-to-head types, but these have not been extensively investigated.<sup>3,4</sup>

The fine structure of the ferroelectric domain walls depends on a number of inter-related parameters: including the symmetry, temperature, order of the phase transition, spontaneous polarization, and the electrostrictive and elastic compliances. A number of analytical descriptions now exist to describe the spatial variation of the order parameter in a ferroelectric domain wall.<sup>5-7</sup> However, some of the parameters required by the theory cannot be easily acquired with current experimental techniques, and so there is a need to develop new experimental methods to study polarization variations in these materials.

Defects and dopants are known to have a strong influence on the elasto-dielectric properties of ferroelectrics and related materials. Theoretical treatments of the role of defects near structural phase transitions are usually restricted to defect densities that are much less than the reciprocal correlation volume ( $\sim 10^{18} \text{ cm}^{-3}$ ).<sup>8</sup> In the perovskite ferroelectrics of commercial interest, such a situation is almost never realized.

This article outlines some of the results observed by diffraction contrast electron microscopy<sup>10</sup> in perovskite-based ferroelectrics. From these results, and the requirements of the theoretical developments, there is an urgent need to experimentally investigate the polarization gradients, both within the domain and in the region of the domain wall. Electron holography is discussed as a technique potentially capable of quantifying the polarization gradients in these materials.

## RESULTS AND DISCUSSION

### *La-Doping in PZT-based Perovskites*

Doping in  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ -based materials by lanthanum is used as a means to soften the switching characteristics of piezoelectric materials.<sup>11</sup> Additionally, the incor-

poration of lanthanum facilitates the fabrication of transparent ceramics for optoelectronic applications.<sup>12</sup> In general, doping with lanthanum has a significant influence on many of the elasto-dielectric properties. For sufficiently high levels of doping in Zr-rich PZT compositions, this leads to the observation of diffuse phase transition behavior having strong dielectric dispersion. Ferroelectrics with this behavior are generally referred to as relaxors, and are of technological importance owing to their unique electrostrictive, capacitive, and optoelectronic properties. The domain structures of relaxor (Pb,La)(Zr,Ti)O<sub>3</sub> (PLZT) ceramics are difficult to study using transmission electron microscopy. However, by carefully cooling a 8.2/70/30 composition, a microdomain contrast could be detected, as shown in Figure 2(a). Under the irradiation of the electron beam, the domain structure is unstable. By agitating the structure through focusing/defocusing the beam, the domain configuration transforms to a more stable ordered structure, Figure 2(b). It is believed that thermally-induced stresses switch the microdomain structure to a new domain configuration.<sup>13</sup>

The end-member of the PZT solid solution, PbTiO<sub>3</sub>, has the highest transition temperature ( $T_c = 490^\circ\text{C}$ ) and the largest strain [ $(c/a - 1) \sim 6.5\%$ ] within the perovskite family. This makes PbTiO<sub>3</sub> an ideal material to study by transmission electron microscopy. Doping PbTiO<sub>3</sub> with lanthanum (PLT) reduces both the phase transition temperature and the characteristic discontinuity of the first-order transition. A systematic study of the structural effect of lanthanum on the polar domain structure in PLT ceramic reveals the development of a strain texture within the normal domains (Figure 3(a), (b), and (c)). Using diffraction contrast invisibility conditions, we were able to deduce that the texture is the result of a non-uniform spontaneous deformation along the *c*-axis within the domain. As shown in Figure 3(a), for a sample doped with 1 atom % La, there is no evidence of a texture. As

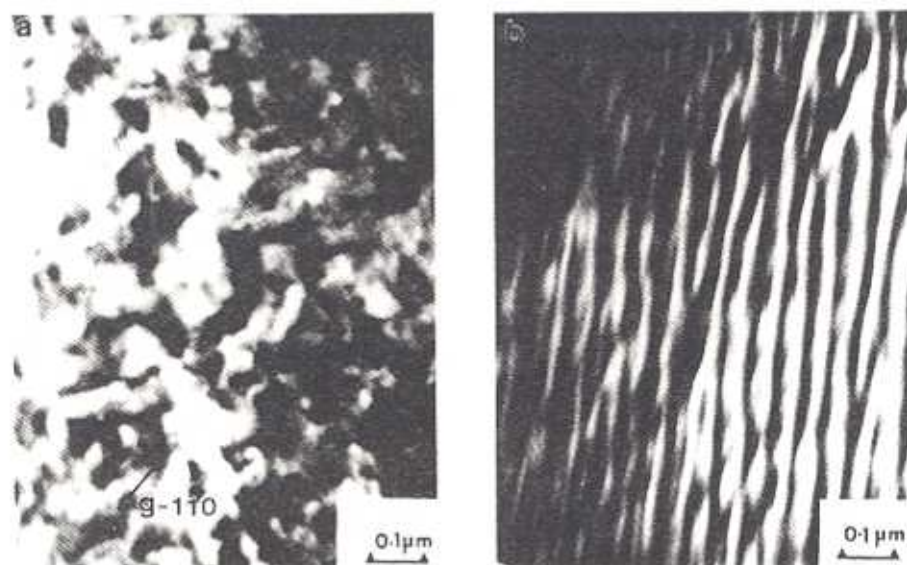


FIGURE 2 (a) Bright field image of liquid nitrogen cooled PLZT 8.2/70/30 relaxor ferroelectric revealing a microdomain structure. (b) An *in situ* switched pseudo-domain structure of (a).

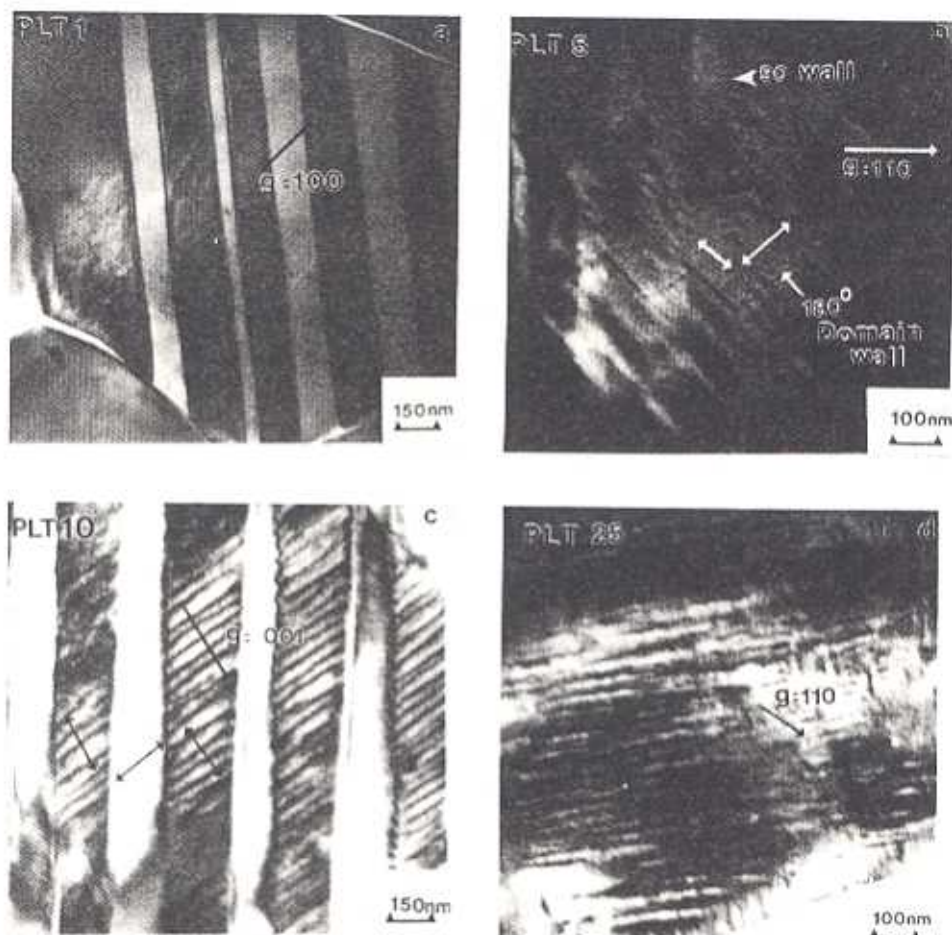


FIGURE 3 Bright field image of domain structures in a solid solution series  $(\text{Pb}_{1-x/2}\text{La}_x)\text{TiO}_3$  with four different La contents.

the lanthanum concentration is increased from 5 to 10 atom %, texturing appears, and this becomes progressively more pronounced with increasing dopant concentration. When the dopant concentration reaches 25 atom %, a normal domain structure is not identified, and a full cross-hatched or "tweed" domain structure is observed below the transition temperature (Figure 3(d)). Similar structures have been observed in ferroelastic systems such as  $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.03})_3\text{O}_{7-\delta}$  and Mg-Cordierite.<sup>14,15</sup> Inhomogeneous polarization distributions are not unique to the PLZT system, but also exist in the complex lead  $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$  perovskite systems. In these systems, the intermediate scale-B-site cation ordering is the source of the polarization modulation.<sup>16</sup> In order to further our understanding of the polarization variation in these materials, we need to develop a technique to quantify the polarization gradients and defect structures. In this regard, the potential of the electron holography technique is discussed below.

### *Electron Holography*

The idea of using coherent electrons in electron microscopy was proposed in 1949 by Gabor in an attempt to extend the limits of electron microscope resolution.<sup>17</sup> However, the realization of electron holography was achieved only in the 1980's owing to the development of a coherent field-emission electron beam. Commercial instruments for electron holography have been developed by Hitachi Ltd. and Philips but have only recently become available. The principle of electron holography is similar to that of optical holography, in which the phase and amplitude of the electron beam are recorded simultaneously. The addition of phase shift information which is highly sensitive to local changes makes electron holography a more attractive method compared to conventional electron microscopy techniques. There have been a variety of applications for this new technique starting since 1980, especially in the study of magnetic domains and fluxons in superconducting materials.<sup>18</sup>

Recently the possibility of using the holography technique to study ferroelectric domain walls and other defect structures in ferroelectrics was recognized. Some encouraging results have been reported on the profiles of domain walls, as shown in Figure 4.<sup>19</sup> The kink-like electron interference fringe pattern closely resembles the space profile of the polarization vector across a domain wall as predicted by the Landau-Ginzburg model.<sup>5,6</sup> Although a complete theoretical description of the fringe profile in Reference 18 is not currently available, the fact that the electric field variation can be probed on a scale less than 1 Å is both exciting and promising.

It has been demonstrated that the electron holography technique may also be used to study the location of aliovalent dopants inside crystal structures through the perturbed local electric fields.<sup>20</sup> As shown in Figure 5(a) the fringe bifurcations occurred across the domain wall. The potential contours reveal that there are charge centers attracted to the domain wall (see Figure 5(b)).<sup>20</sup> This information may lead

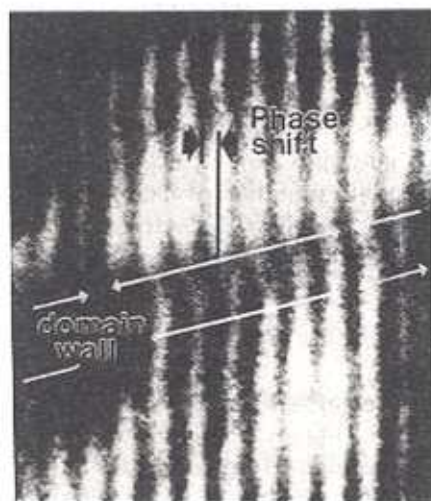


FIGURE 4 An electron hologram of a 90° domain wall in BaTiO<sub>3</sub>, the fringe bending is related to the polarization difference across the domain wall (Reference 19).

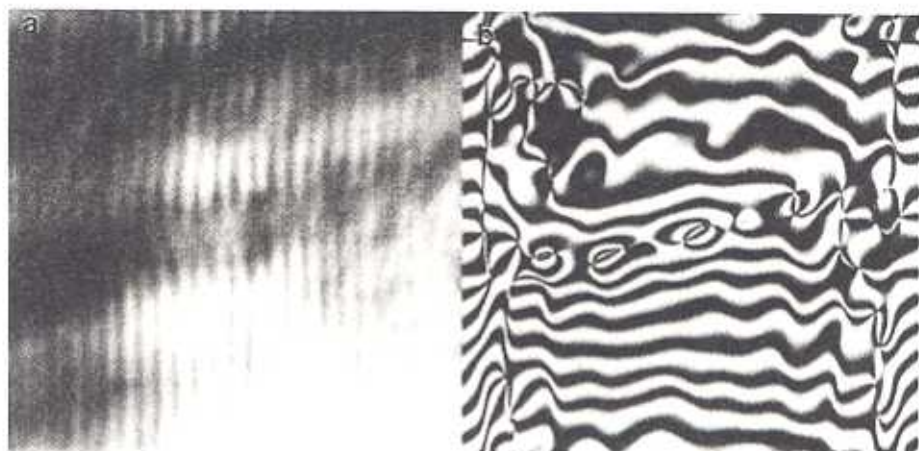


FIGURE 5 (a) An electron hologram showing anomalous fringe bifurcations in a  $90^\circ$  domain wall in  $\text{BaTiO}_3$ , (b) Electron interferogram of the same area of (a) shows charge defect centers within the wall (courtesy of Drs. D. Joy and X. Zhang).<sup>20</sup>

significant advance in the understanding of the effect of dopants, and may shed new light on the study of interactions between the dopants and domain walls and other polarization modulations as described above.

Quantitative study of the polarization profiles can have a significant impact on the fundamental understanding of ferroelectrics. Once the relationship between the fringe variation and the polarization space profile is established, one can obtain the polarization gradient coefficients through back fitting the observed domain profiles to the theoretical results on domain walls.<sup>7</sup> These gradient coefficients are a measure of the nonlocal coupling strength. Using lattice dynamics, one may correlate these gradient coefficients to the dispersion surface near the soft mode of the paraelectric-ferroelectric phase transition.<sup>21</sup> Hence, the electron holography technique, together with the continuum model described in Reference 6, can potentially provide a methodology to study the characteristics of the over-damped soft mode in systems such as  $\text{BaTiO}_3$ , which could not be directly probed through inelastic neutron scattering.

As a new technique, many problems still exist in the electron holography, especially with regard to the interpretation of the observed fringes. In principle, the total phase shift of high energy coherent electrons passing through a ferroelectric thin sample may be calculated from the following equation<sup>22</sup>

$$\phi(x_0, y_0) = \frac{\pi}{\lambda \Sigma} \int V(x_0, y_0, z) dz, \quad (1)$$

where  $\lambda$  is the electron wavelength,  $x_0$  and  $y_0$  define the point on the thin sample,  $\Sigma$  is the electron energy, and  $V(x_0, y_0, z)$  represents the electrical potential experienced by the traveling electrons. However,  $V(x_0, y_0, z)$  represents the total potential, and it is quite difficult to delineate contributions from the "bound" charges (relevant to the polarization) and the "free" charges (relevant to compensation). We believe this is the main reason for the inconsistencies encountered in the current

studies of ferroelectrics using electron holography.<sup>23</sup> More theoretical analysis of the interpretation of the holography results is in order.

## CONCLUSIONS

Observations by conventional transmission electron microscopy techniques on ferroelectric and related materials reveal a variety of polarization modulations which can be induced when there exists coupling of the primary order parameter to symmetry breaking defects. From the evolution of the modulated structures and domain structures, one can see some link between these mesoscopic structures and the extrinsic elasto-dielectric properties.

A new electron-microscopy technique using coherent electrons known as electron holography opens up opportunities in the study of domain walls and defect structures. In this technique, phase shifts can be correlated to local variations of the electrostatic fields within materials. Further development of this new technique in the study of ferroelectrics may help us to gain new insight into the mechanisms of extrinsic contributions to the macroscopic elasto-dielectric properties.

## ACKNOWLEDGEMENTS

We wish to thank the ONR via Grant No. N00014-89-J-1689 and the AFOSR via Grant No-91-0433 for partly funding this program. We also wish to thank Drs. D. C. Joy, Xiao Zhang, and Larry Allard for many useful conversations regarding electron holography and Dr. L. E. Cross for discussions on ferroelectrics in general.

## REFERENCES

1. M. Marutake, *J. Phys. Soc. Japan*, **11**, 807 (1956).
2. A. G. Luchaninov, L. Z. Potikha and V. A. Rogozin, *Zh. Tekh. Fiz.*, **50**, 616 (1980).
3. S. I. Yakunin, V. V. Shakmanov, G. V. Spivak and N. V. Vasileva, *Sov. Phys. Solid State*, **14**, 310 (1972).
4. C. A. Randall, D. J. Barber, and R. W. Whatmore, *J. Mat. Sci.*, **22**, 925 (1987).
5. V. A. Zimov, *Sov. Phys. JETP*, **35**, 822 (1959).
6. W. Cao and L. E. Cross, *Phys. Rev. B*, **44**, 5 (1990).
7. W. Cao and G. R. Barsch, *Phys. Rev. B*, **41**, 4334 (1990).
8. A. P. Levanyuk and A. S. Sigov, in "Defects and Structural Phase Transitions" Gordon and Breach Science Publisher, New York (1987).
9. E. K. H. Salje, *Acta Cryst.*, **47**, 453 (1991).
10. P. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley and M. J. Whelan "Electron Microscopy of Thin Crystals" Robert Krieger Publishing Co. New York (1965).
11. B. Jaffe, W. R. Cook and H. Jaffe, in "Piezoelectric Ceramics" Academic Press Inc., New York (1971).
12. G. H. Haertling and C. E. Land, *Am. Cer. Soc.*, **54**, 1 (1971).
13. C. A. Randall, D. J. Barber, and R. W. Whatmore, *J. Microsc.*, **145**, 275 (1987).
14. Y. Zhu, J. Taftø and M. Suenaga, *MRS Bul.*, **16**, 54 (1991).
15. E. K. H. Salje, *Phase Transitions*, **34**, 25 (1991).
16. C. A. Randall, A. S. Bhalla, T. R. Shrout and L. E. Cross, *J. Mat. Res.*, **5**, 829 (1990).
17. D. Gabor, *Proc. R. Soc. London, Ser. A*, **197**, 454 (1949).
18. see the review article by A. Tonomura, *Rev. of Mod. Phys.*, **59**, 639 (1987) and the references thereafter.
19. X. Zhang, T. Hashimoto, and D. C. Joy, *Appl. Phys. Lett.*, **60**, 784 (1992).
20. X. Zhang and D. C. Joy, Presentation in Materials Society Meeting, Boston, Massachusetts, 1992.
21. W. Cao, to be published.
22. G. F. Missiroli, G. Pozzi, and U. Valdré, *J. Phys. E*, **14**, 549 (1981).
23. W. Cao and C. A. Randall, *Solid State Comm.*, **86**, 435 (1993).