

MICROSTRUCTURAL CHARACTERISTICS AND DIFFUSE PHASE TRANSITION BEHAVIOR OF LANTHANUM-MODIFIED LEAD TITANATE

G. A. ROSSETTI, JR[†], W. CAO, AND C. A. RANDALL
Materials Research Laboratory, The Pennsylvania State University
University Park, Pennsylvania 16802

[†] Now with the Department of Geological and Geophysical Sciences and
Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544
(Received August 9, 1993)

Abstract The introduction of structural disorder into perovskite ferroelectrics leads to the observation of diffuse phase transition behavior. In this paper, the microstructural characteristics and phase transition behavior of lanthanum-modified lead titanate are discussed. It is shown that the diffuse nature of the transition is connected with the appearance of ferroelectric domain structures exhibiting texture on the mesoscopic (≈ 10 nm) length scale. The theoretical implications of these results are briefly discussed.

INTRODUCTION

Diffuse phase transitions in perovskite ferroelectrics occur as a consequence of some level of structural disorder that breaks the translational invariance of the lattice. The type of diffuse transition observed depends both on the nature and scale of the structural disorder. Impurities, point defects, extended defects, incomplete or inhomogeneous cation ordering, macroscopic fluctuations in chemical composition, core/shell structures *etc.* can all lead to smearing of the ferroelectric phase transition. The physical origin of the smearing and the behavior of the ferroelectric properties in each particular case, however, may be very different. In chemically complex compounds and solid solutions, several types of structural disorder are often present simultaneously. To establish structure-property relations in these materials therefore requires characterization at all the relevant length scales, including the macroscopic (crystal symmetry, chemical homogeneity, core/shell structures), the microscopic (ferroelectric domain structures, extended defects), the mesoscopic (cation order domains, texture within ferroelectric domains), and the atomic (point defect chemistry, local environment).

For ferroelectrics such as lanthanum-modified lead zirconate-titanate (PLZT), the structural disorder arises as a consequence of the complex defect chemistry associated with the aliovalent A-site substitution of lanthanum¹. Kelzer, Lansink and Burggraaf² have shown that the nature of the ferroelectric transition in ceramic specimens of the end member $Pb_{1-\alpha}La_{\alpha}TiO_3$ (PLT) changes smoothly from that expected in a sharp first-order phase change to that of a diffuse transition as

the lanthanum concentration is increased. Figure 1 shows that, when characterized by the exponent γ in the generalized Curie-Weiss law, the anomalous dielectric behavior onsets at $y = 0.05$ and becomes typical of diffuse transitions (*i. e.* $\gamma = 2$) when $y > 0.23$. Although the numerical values of γ depend somewhat on the lead elimination factor (α) as well as on the grain size, the general trend towards increasingly diffuse behavior with lanthanum substitution is intrinsic.

In order to better understand how structural disorder evolves and relates to the dielectric properties in PLT, we have recently undertaken transmission electron microscopy (TEM) and powder x-ray/neutron studies, the details of which are reported elsewhere³⁻⁵. In this paper, we draw on these results and speculate on some possible interconnections between the microstructure, dielectric properties, and the phase transition behavior.

RESULTS AND DISCUSSION

High resolution X-ray diffraction studies⁴ of sol-gel derived powders have shown that the addition of lanthanum to lead titanate results in broadened diffraction profiles showing a marked profile asymmetry. The degree of asymmetry can be quantified by fitting the profiles to split Pearson distributions⁶. The split Pearson function gives two values for the full width at half maximum, β^L and β^H , which are characteristic of the peak shape on the low and high angle sides of the peak maximum, respectively. Figure 2 shows that both the peak asymmetry and the peak breadth renormalize as a function of lanthanum concentration. The asymmetry (β^H/β^L) changes markedly between $y = 0$ and $y = 0.01$, but then decreases and becomes constant for samples with $y > 0.05$. At the same time, the profile breadth decreases. Corresponding to the changes in the diffraction profiles, the crystal tetragonality (c/a) begins to deviate from the linear composition dependence as expected based on Vegard's law. These observations cannot be easily explained by macroscopic variations in chemical composition, nor by particle size effects.

Alternatively, recent TEM studies³ (Figure 3) reveal that the development of sub-domain texture in PLT materials closely parallels the changes observed both in the X-ray studies and in the dielectric behavior. For samples with $y < 0.05$, no sub-domain texture is observed, and the transition behavior is sharp. For samples with $y \geq 0.05$, sub-domain texture becomes apparent, and increases in degree with lanthanum concentration. As the sub-domain texture becomes more pronounced, the dielectric behavior near the transition becomes correspondingly more

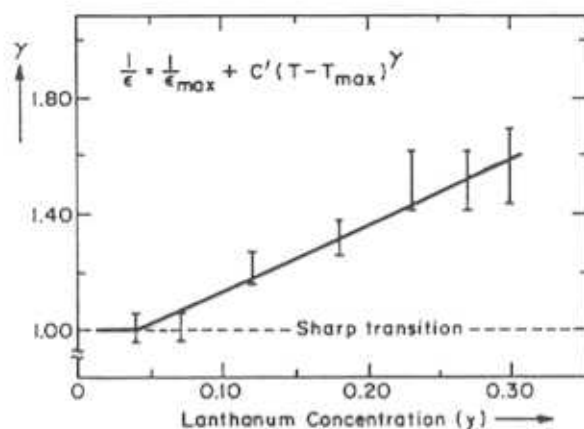


Figure 1. Composition dependence of the exponent γ in the generalized Curie-Weiss law for $\text{Pb}_{1-y}\text{La}_y\text{TlO}_3$ (After Reference 2).

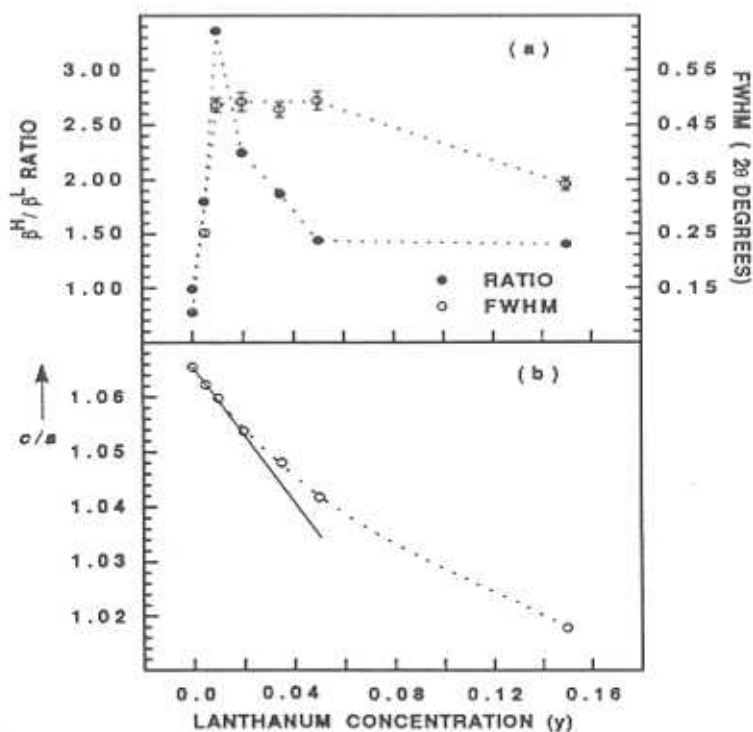


Figure 2. Breadth and asymmetry of the 002 powder XRD profile (a) and crystal tetragonality (b) of $\text{Pb}_{1-y}\text{La}_y\text{TlO}_3$.

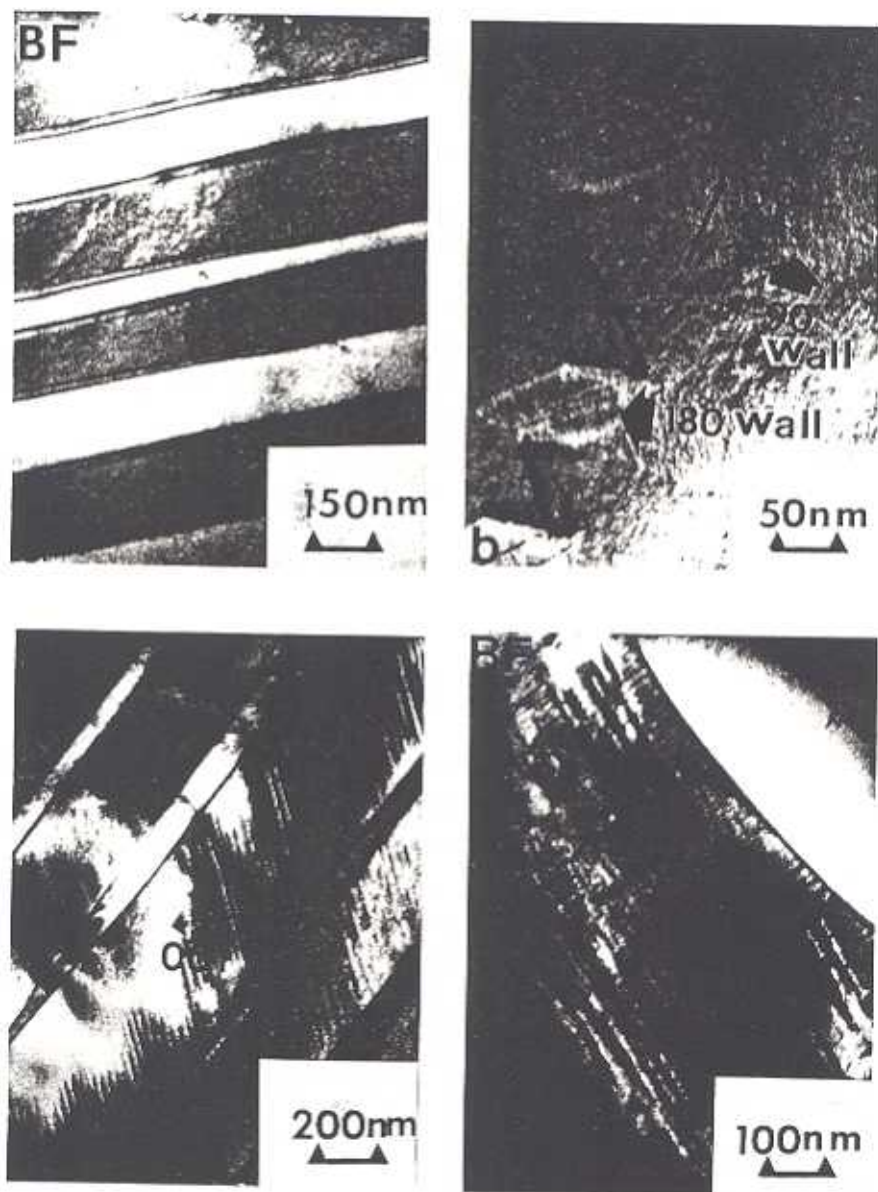


Figure 3. Transmission electron micrographs of $\text{Pb}_{1-y}\text{La}_y\text{TiO}_3$: (a) $y = 0.01$ (b) $y = 0.05$ (c) $y = 0.10$ and (d) $y = 0.25$.

anomalous. For compositions with $y > 0.25$, the microstructure degenerates into a cross-hatched or tweed texture. For these compositions, the dielectric behavior is typical of that for diffuse phase transitions. Note that these textures disappear on heating above the transition temperature, and so cannot be identified with exsolution lamellae.

The tweed structures observed for the higher lanthanum concentrations would appear to be precursors for the mottled and poorly defined vestiges of sub-domain texture as observed for PLZT⁷. The Zr-rich PLZT compositions exhibit strongly frequency-dispersive diffuse transitions similar to those of the complex B-site perovskites such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) and related compounds. In the later case, however, it is the cation order domains persisting on a ~ 10 nm length scale that lead to the breakdown of the ferroelectric domain structure⁸⁻¹⁰. The similarity in mesoscopic domain texture of the PLZT and PMN type materials¹¹⁻¹³ is intriguing, since at the atomic level, the origin of the structural disorder in these two materials is very different.

With regard to the nature of the phase transition in PLT, the first-order character also follows the changes in structural properties as revealed in the X-ray data. The development of a Landau-Devonshire¹⁴ formulation for the phase transition in PLT requires the expansion coefficients to depend on spatial variables, which results in a distribution of transition temperature. As a macroscopic average, one expects that the first-order discontinuity of the transition will be drastically reduced as the transition becomes diffused. The Landau theory is valid, however, only when the sub-domain modulations are weak, otherwise the gradient related (Ginsburg) terms must be included. Using the methodology described previously¹⁵, the coefficients in the Landau-Devonshire expansion were estimated for compositions with $y < 0.05$, where judging from Figure 3, this condition is approximately satisfied. As shown in Figure 4, the coefficient of the quartic term in the elastic Gibbs function (α_{11}^X) increases rapidly toward zero between $y = 0$ and $y = 0.01$ but then changes at a much lower rate. This increase reflects the apparent loss in the first-order character of the transition as the structure relaxes to the defects and the long range order is disrupted. The coefficient of the sixth-rank term also renormalizes, but to a much lesser extent. Large changes in the coefficient of the quartic term were also observed for PLZT compositions¹⁶.

For the compositions with $y > 0.05$, the Ginsburg terms must be included in the formalism. The inclusion of the gradient energy can describe both the domains and their modulations. Periodic domain structures can be excited for a finite

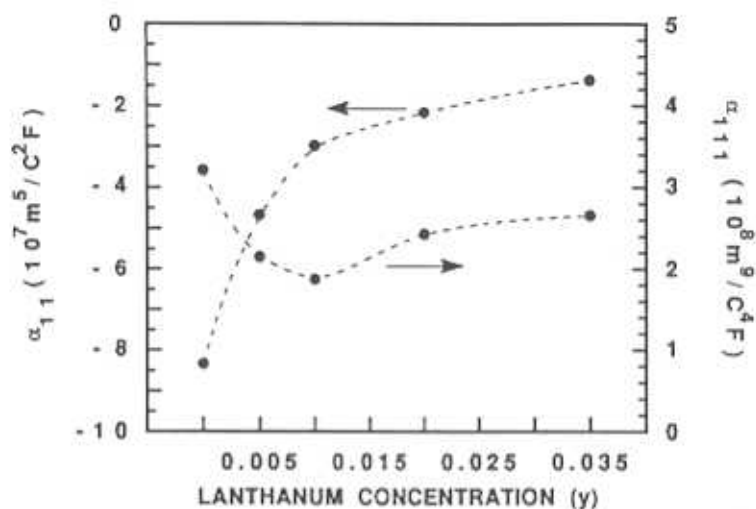


Figure 4. Coefficients of the elastic Gibbs free energy density function of $\text{Pb}_{1-\alpha}\text{La}_\alpha\text{TiO}_3$.

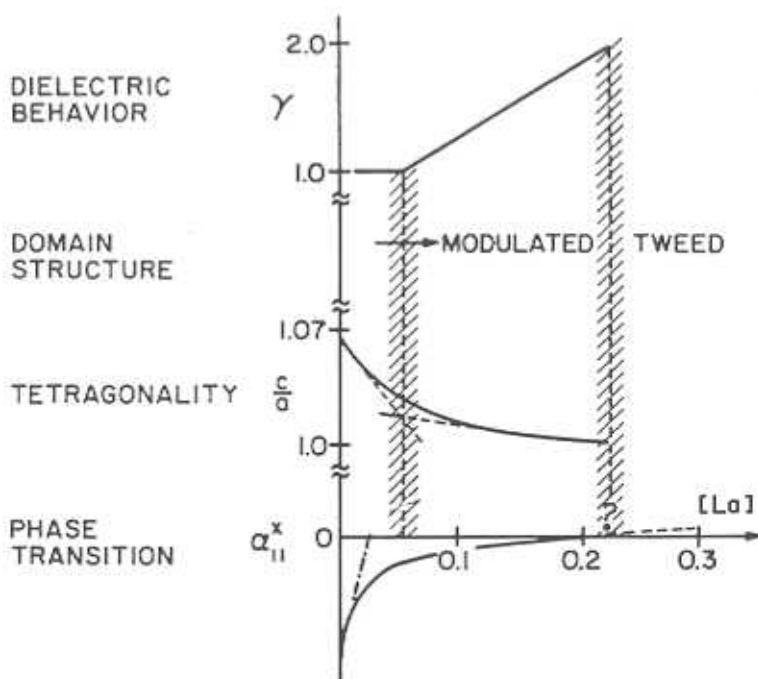


Figure 5. Observed relationships between the first-order character of the transition, the crystal tetragonality, the sub-domain texture, and the dielectric properties of $\text{Pb}_{1-\alpha}\text{La}_\alpha\text{TiO}_3$.

system due to the competition between nonlinearity and nonlocality. Modulated structures and tweed textures can be described in terms of crest riding periodons^{17,18}. However, the modulated structures such as those in Figure 3c do not seem to follow the expected temperature variation pattern of the crest riding periodon excitations, which are unstable and can survive only in a finite temperature range near the transition. One possible explanation could involve an interaction of the defects with the periodons. These excitations might be stabilized by the lanthanum/vacancies if the defects are appropriately aligned. The alignment can be driven, on the other hand, by the field gradient created at the walls of the periodons. Consistent with this notion, the modulations have preferred orientations (although not perfect), and are nearly periodic, as shown in Figure 3. Further studies will be required to confirm this picture.

At the higher lanthanum concentrations ($y > 0.25$) the microstructure breaks down on still finer scales and more degenerate states are created. This will effectively increase the dielectric response of the system, as observed. For these materials, however, arguments based on the continuum theory as summarized above may not be used because the density representation (both in terms of energy and polarization) is no longer valid. Instead, discrete models must be developed.

The results described above can be represented schematically as shown in Figure 5, where the observed relationships between the first-order character of the transition, the crystal tetragonality, the sub-domain texture, and the dielectric properties are shown. Here it is worth mentioning that, in the Landau-Devonshire formalism, close inter-relationships exist between the curvature of the energy surface, the order of the transition, and the symmetry of the ferroelectric phase. In this connection, it is of interest to consider how the scenario depicted in Figure 5 may change as zirconium, which lowers the tetragonality of the system and further flattens the energy surface, is added to the system. Based on the above discussion, we might expect that lanthanum will become more effective at breaking down the domain structure as the rhombohedral side of the PLZT diagram is approached, leading to a large number of degenerate states and additional contributions to the dielectric response even at modest lanthanum concentrations.

SUMMARY

The breakdown of conventional ferroelectric phase transition behavior in lanthanum-modified lead titanate has been correlated with the appearance of

domain structures exhibiting texture on a nanometer scale. It was suggested that this type of mesoscopic sub-domain texture is a common feature of ferroelectrics showing diffuse/frequency dispersive transitions. The theoretical implications of the relationships existing between the curvature of the energy surface, the order of the transition, the symmetry of the ferroelectric phase, the development of the sub-domain texture, and the resulting dielectric properties were discussed.

ACKNOWLEDGEMENT

This work was supported by contracts administered through the Office of Naval Research. The authors are grateful to Professor L. E. Cross for his support of, and interest in, this study. Thanks also to Mr. N. Kim for fabricating the ceramic specimens used in the TEM studies.

REFERENCES

1. K. H. Härdtl and D. Hennings, *J. Am. Ceram. Soc.*, **55** 230 (1972).
2. K. Keizer, G. J. Lansink, and A. J. Burggraaf, *J. Phys. Chem Solids*, **39** 59 (1978).
3. C. A. Randall, G. A. Rossetti, Jr., and W. Cao, *Ferroelectrics* (in press).
4. G. A. Rossetti, Jr., L. E. Cross, and J. P. Cline, *J. Phys: Cond. Mat.*, (submitted).
5. G. A. Rossetti, Jr., M. A. Rodriguez, A. Navrotsky, L. E. Cross, and R. E. Newnham, *Acta Cryst. C*, (submitted).
6. M. M. Hall, Jr., V. G. Veeraghavan, H. Rubin, and P. G. Winchell, *J. Appl. Cryst.*, **10** 66 (1977).
7. C. A. Randall, D. J. Barber, and R. W. Whatmore, *J. Microscopy*, **145** 275 (1987).
8. H. B. Krause, J. M. Cosley, and J. Wheatly, *Acta Cryst.*, **C35** 1015 (1979).
9. C. A. Randall, D. J. Barber, and R. W. Whatmore, *J. Mater. Sci.*, **22** 935 (1987).
10. C. A. Randall and A. S. Bhalla, *Jap. J. Appl. Phys.*, **29** 327 (1990).
11. C. A. Randall, D. J. Barber, R. W. Whatmore, and P. Groves *Ferroelectrics*, **76** 265 (1987).
12. A. D. Hilton, C. A. Randall, D. J. Barber, and R. W. Whatmore, *Inst. Phys. Conference Series, No. 90*, Chapter 9, 315 (1987).
13. A. D. Hilton, C. A. Randall, D. J. Barber, and T. R. ShROUT, *Ferroelectrics*, **93** 379 (1989).
14. A. F. Devonshire, *Advances in Physics*, **3** 85 (1954).
15. G. A. Rossetti, Jr., *Ferroelectrics*, **133** 103 (1992).
16. G. A. Rossetti, Jr., T. Nishimura, and L. E. Cross, *J. Appl. Phys.*, **70** 1630 (1991).
17. G. R. Barsch and J. A. Krumhansl, *Met. Trans. A.*, **19A** 761 (1988).
18. W. Cao (to be published).