



## GRAIN SIZE AND DOMAIN SIZE RELATIONS IN BULK CERAMIC FERROELECTRIC MATERIALS

WENWU CAO and CLIVE A. RANDALL

Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802, U.S.A.

(Received 13 March 1995; accepted 6 September 1995)

**Abstract**—A study of the ferroelastic domain size variations with grain sizes in  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  [PZT] ferroelectric ceramic has been conducted. Experimental results determined by a transmission electron microscopy (TEM) study on hard and soft PZT ceramics indicate that it is possible to observe a bulk metastable domain configuration in a thinned foil. The transmission electron microscopy observations demonstrate that the domain structures formed at the paraelectric–ferroelectric phase transition are strongly dependent on the elastic boundary conditions and crystallite sizes. Statistical analysis of the domain size distributions in PZT reveals that the traditional parabolic relation between grain size and domain size is only good for a limited size range of 1–10  $\mu\text{m}$ . For grains size  $> 10 \mu\text{m}$ , the exponent tends to be smaller than 1/2, while for grain size  $< 1 \mu\text{m}$  the exponent is larger than 1/2. We also report the analysis on poled ceramics which reveals for the first time direct evidence for transgranular domain switching mechanisms.

**Keywords:** A. ceramics, A. interfaces, C. electron microscopy, D. ferroelectricity, D. microstructures.

### INTRODUCTION

Domain structures are generated during a structural phase transition to recover the lost symmetry operations [1, 2]. In ferroic materials, these domain structures can be switched by external (elastic, electric, or magnetic) fields. The domain population distribution is strongly affected by these fields, which in effect gives the extrinsic contributions.

Stable domain configurations in ferroic materials are the result of an energy balance. In the case of a ferroelectric system, stable domain configurations reflect the balance of anisotropy energy, domain wall energy, electric and elastic energies. Previous theoretical investigations considered the energy balance of elastic interactions between the system and a semi-infinite medium and that of the domain walls, which leads to a parabolic scaling ( $m = 1/2$ ) of the grain–domain size relation [3–8],

$$\text{Domain Size} \propto (\text{Grain Size})^m. \quad (1)$$

Most previous domain size studies have focused on ceramic  $\text{BaTiO}_3$ . One of the major reasons for studying this system is the strong macroscopic dielectric constant enhancement observed in the tetragonal ferroelectric phase of 1.0  $\mu\text{m}$  grain materials compared to coarse grain ceramics and single crystals. The change of the dielectric constant with grain size has been accounted for in terms of the different stresses created under the spontaneous deformation at the cubic–tetragonal phase transition [9].

Arlt re-examined the domain size distributions in  $\text{BaTiO}_3$  ceramic and showed the departure of the domain size grain size relation from the parabolic relation for grain size below 1  $\mu\text{m}$  and about 10  $\mu\text{m}$  [7]. Domain density is higher than the value predicted using the parabolic relation for submicron grains as shown in Fig. 1. For grain sizes larger than 10  $\mu\text{m}$ , the exponent in eqn. (1),  $m$ , is found to be close to 1/3 in his experimental results. The slope becomes steeper as the grain size decreases. When the whole range of domain and grain sizes are considered, the fitting to the  $m = 1/2$  is very poor as shown in Fig. 1. The current work is in part triggered by this observation. Our intention is to find out if the parabolic relation could hold for the PZT systems.

In practice, the size effect of domain structures is of importance to the future application trends in ferroelectric based materials. In the last few years there have been rapid advances in the ability to fabricate thin and thick films for applications such as memories, micromotors, thermal imaging, multilayer capacitors, and actuators [10, 11]. The miniaturization of ferroelectric based electroceramic components is accompanied by the necessity of the reduction of grain sizes. Consequently, the domain sizes, domain configurations, and domain wall mobility will all be changed with the size reduction.

Owing to the large contribution of the elastodielectric properties from the extrinsic mechanisms, i.e. domain walls motion, it is imperative to advance the

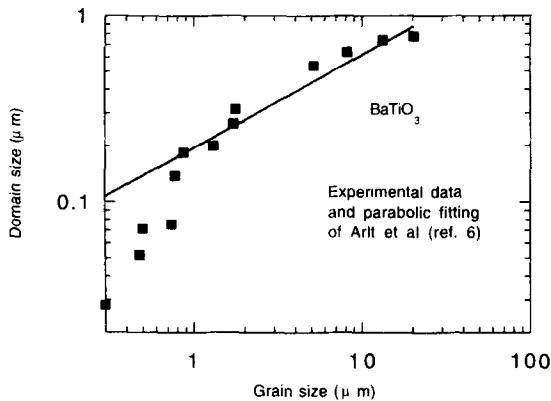


Fig. 1. Domain size vs grain size for BaTiO<sub>3</sub> ceramics, experimental results compared to parabolic relation (after-Ref. [7]).

understanding of domain size effects in the submicron grain size ceramics [12, 13]. In this paper, we present some experimental studies on the domain size distributions in poled and unpoled PZT ceramics. In addition, thermally cycling effects on the domain populations in the thin foil samples used in the TEM experiments were also examined.

## EXPERIMENTAL

### Ceramic processing

Morphotropic phase boundary composition PZT has been investigated in sintered ceramics with a grain size variation from 0.2 to 14 μm. Starting powder size variations were obtained from solid state reactions using conventional and reactive calcination techniques [14, 15]. Grain size variations were obtained by controlling densification and grain growth during the sintering process. The submicron grain size ceramics were fabricated using hot pressing techniques; namely, hot uniaxial pressure (HUP) and hot isostatic pressure (HIP). The larger grain size ceramics (>1 μm) were sintered using conventional methods by varying temperature and time in closed crucibles and controlling the lead atmosphere with PbZrO<sub>3</sub> sources.

Two systems with the morphotropic composition were investigated in this study: one is undoped Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub>, and the other is Nb-doped PZT based on compositional formula of Pb<sub>0.988</sub>(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)<sub>0.976</sub>Nb<sub>0.024</sub>O<sub>3</sub> [16]. The undoped PZT is naturally a hard piezoelectric material owing to the superoxidation processes creating an excess of acceptor lead vacancies over oxygen vacancies. The Nb-donor doping is commonly used in commercial soft PZT for piezoelectric applications and is therefore regarded as a model system for this study.

### Transmission electron microscopy

The domain size distributions and structures were investigated using analytical transmission electron microscopy (TEM); Phillips-420 STEM operated at 120 kV. TEM is most suited for microstructural investigations in the nanometer to micrometer size regime. Ferroelectric domains can be directly imaged using diffraction contrast imaging techniques [17, 18]. The observations were made on dense (>95% theoretical density) ceramic samples which were cut and polished to a thickness of 70 μm. Samples were epoxied to 3 mm copper grids before ion-beam thinning a 3 kV, with a 12° glancing angle until electron transparent. The poled samples were prepared after exposure to a poling field of 40 kV/cm in a heated oil bath at 120°C for 20 min. Samples were prepared with the poling direction in the plane of the thin foil. A Gatan single tilt hot stage was used to heat thinned samples through the transition temperature to re-equilibrate the domain configurations in the foils used for TEM studies.

## RESULTS AND DISCUSSION

In the nature of this experiment we must ensure that the obtained domain sizes by the TEM technique are representative of the bulk ceramic but not the ion-beam thinned foils. We found that in order for this to be true, the ferroelectric material must have a moderately high transition temperature compared with sample preparation and observation temperatures. The thermal and mechanical stresses have to be kept to a minimum during the cutting, polishing and ion-beam thinning processes. Under these conditions, samples prepared may preserve the bulk domain structures (which are metastable configurations in the thin foil).

Two tests were performed in the PZT samples to verify this fact. First, poled Nb-doped piezoelectric ceramics were thinned and shown to preserve an aligned domain configuration which is expected only in poled sample, as shown in Fig. 2 (a-c), indicating there were no major redistribution of the domains during the sample preparation procedure. Second, unpoled ceramic samples were analyzed for domain size distribution after ion beam thinning and later after being heated and cooled slowly through the transition temperature inside the TEM with a hot stage. A difference in the mode and shape of the distribution function of the domain sizes was observed before and after the foils were heated through the transition temperature. The domain sizes are shifted to multimodal distributions with the majority of domains smaller in the thin foil samples after the



Fig. 2. (a)–(c) Multi-beam bright field TEM images of domain structures in a poled PZT ceramic foil. RAIN SIZE IN BULK

heat treatment, suggesting the domain patterns before heating are metastable. These test results support the claim that carefully prepared TEM samples can preserve domain structures representative of the bulk ceramic in systems with moderately high transition temperatures.

Figure 3 shows a selection of domain structures in a variety of grain size for PZT piezoelectric ceramics. We note in the finer grain ceramics ( $0.2\ \mu\text{m}$ ) the domain walls generally have preferred orientations, in other words, the number of variants becomes less within each grain. The domain walls are generally periodic as shown in Figure 3(a) and transverse across the entire grain to pin on the grain boundaries. Figure 3(b) shows a typical domain structure for the soft PZT with a mean grain size  $0.8\ \mu\text{m}$ . Figure 3(c) shows a multimodal domain size distribution in soft PZT with

$1.8\ \mu\text{m}$  mean grain size after the thinned TEM foil was heated above the transition temperature and then slowly cooled in the microscope. Figure 3(d) is a typical complex multiple variant domain configuration for larger grain sized PZT.

A statistical analysis of the grain and domain sizes is determined directly by measuring scanning electron microscope (SEM) micrographs of etched ceramics and TEM micrographs, respectively. The domains measured were limited to those tilted such that no  $\delta$  fringes are observed; i.e. domain wall planes are parallel to the electron beam direction [17, 18]. The histograms for the grain size are in general symmetric and therefore the mode and the mean are almost the same as observed in the typical histograms [see Fig. 4(a)]. However, the histograms of the domain size distributions are often skewed, an example is given in

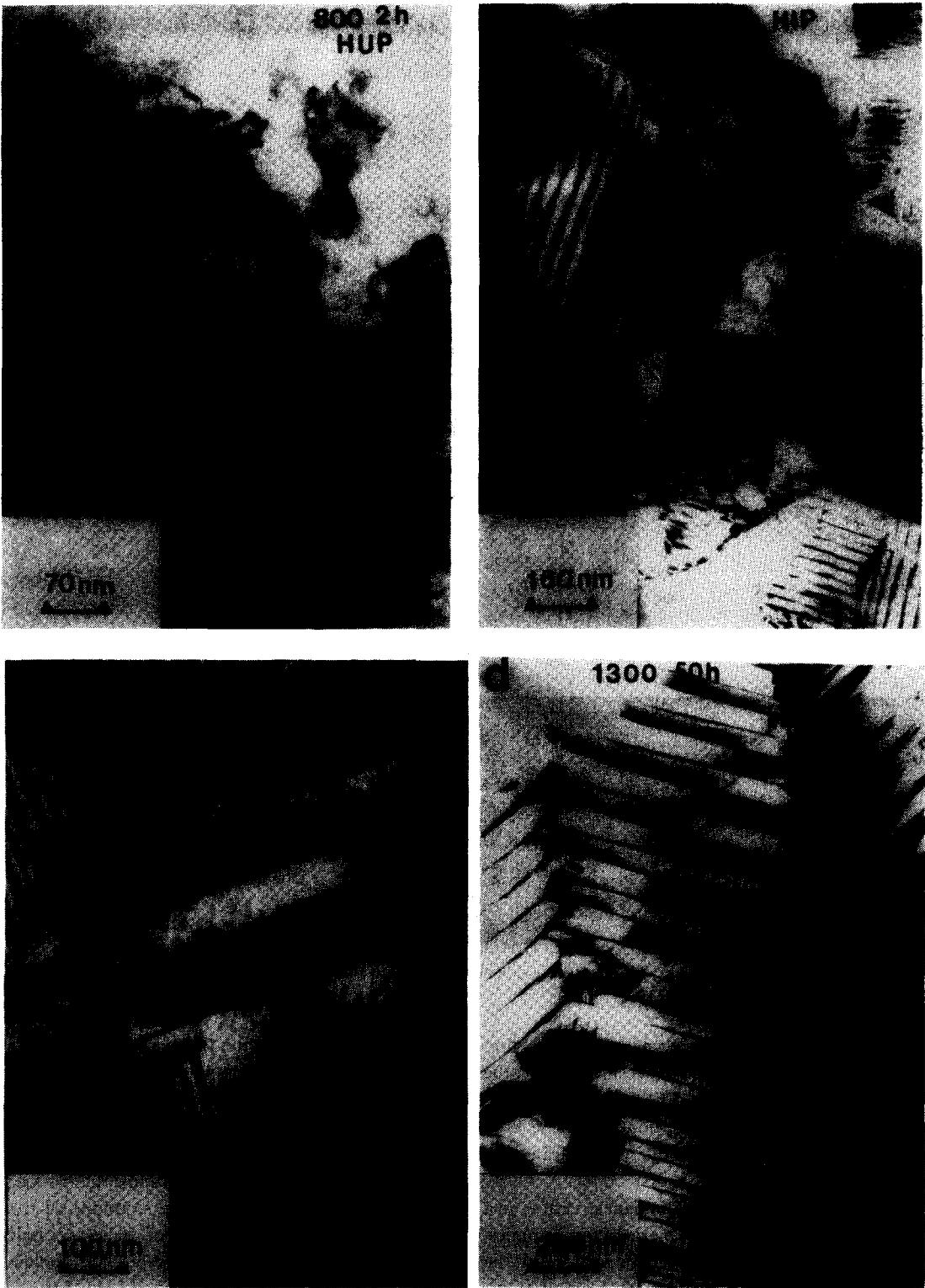


Fig. 3. Typical bright field images of ferroelectric domain structures in (a)  $0.2 \mu\text{m}$ , (b)  $0.8 \mu\text{m}$ , (c)  $1.8 \mu\text{m}$ , and (d)  $14 \mu\text{m}$  bulk ceramics.

Fig. 4(b), therefore, the modes of the domain distribution are selected for comparison. The mode in the distribution corresponding to the most probable domain size as indicated in Fig. 4(a), but not the

mean value. The mode values and the errors based on a full width half maximum distribution are listed in Table 1.

The experimental values for the domain sizes are

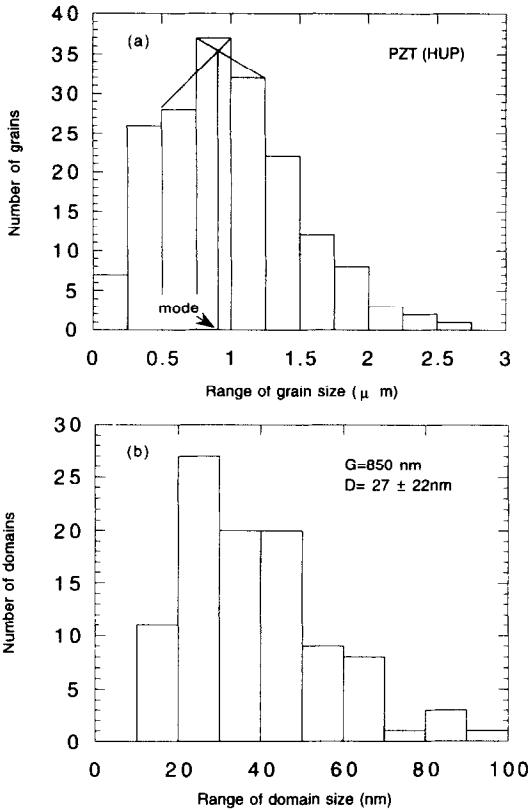


Fig. 4. Typical histograms of (a) grain size distribution of undoped PZT,  $G_{mode} = 0.8\mu\text{m}$  and (b) domain size distribution of Nb-doped PZT,  $D_{mode} = 0.2\mu\text{m}$ .

plotted against the corresponding grain sizes in Fig. 5(a) and (b) for Nb-doped and undoped PZT, respectively. For both compositions of grain sizes between  $1.0\mu\text{m}$  and  $10\mu\text{m}$  the exponent is found to be approximately  $m \approx 0.5 \pm 0.03$ , consistent with previous bulk ceramic studies. However, the domain size in the

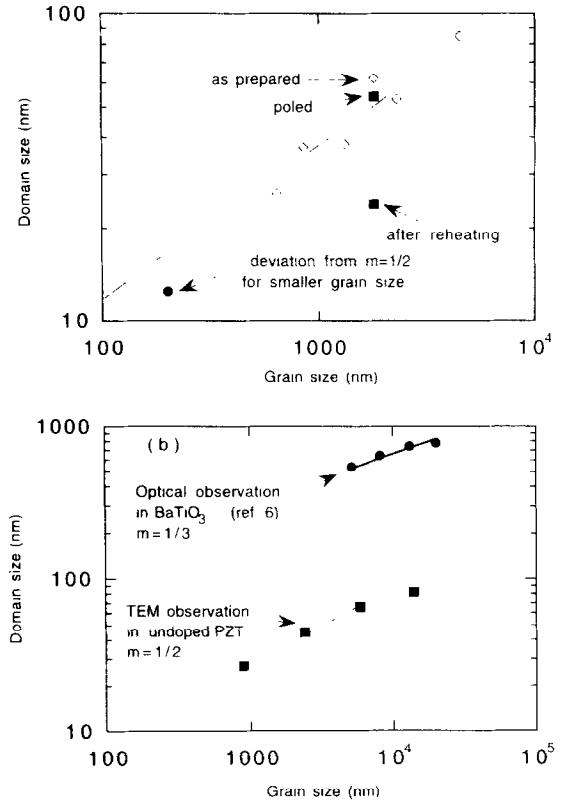


Fig. 5. (a) Logarithmic plot of measured domain size vs grain size for Nb-doped PZT ceramics and the parabolic relation. (b) Comparison of the domain size grain size relation in undoped PZT and large grain BaTiO<sub>3</sub>. The exponent,  $m$ , for BaTiO<sub>3</sub> of large grains is  $\sim 1/3$  while for PZT is  $\sim 1/2$  except the largest grain sample which shows deviation to higher domain density (not in the figure).

$0.1\mu\text{m}$  grain sample shows departure from the  $m = 1/2$  curve as shown in Fig. 6(a). Similar departures have been reported for domain structures in the

Table 1. Sintering conditions for the PZT samples, and the measured grain size, domain size and the estimated errors

Firing conditions	Mean grain size (μm)	Mode grain size (μm)	Standard error of grain size (μm)	Mode domain size (nm)	Estimated domain size error in mode (± nm)	Comments
<b>Nb-doped PZT</b>						
800/2 hr	0.17	0.16	0.005	12	3	Hot Pressed
970°C/4 hr	0.64	—	0.020	30	15	Conventional & HIP
900°C/2 hr	—	—	—	—	—	—
1000°C/4 hr	0.85	0.78	0.020	37	22	Conventional
1100°C/4 hr	1.32	1.30	0.025	38	10	Conventional
1200°C/4 hr	1.82	—	0.030	63	12.5	Conventional
1250°C/4 hr	2.30	—	0.038	53	8.5	Conventional
1300°C/50 hr	3.95	3.85	0.230	67	11	Conventional
Unknown*	4.5†	—	—	85	—	—
<b>Undoped PZT</b>						
800/2 hr	0.98	0.82	0.037	26	9.5	Hot pressed
1000°C/4 hr	2.4	2.2	0.12	49	20	Conventional
1200°C/4 hr	5.9	—	0.19	66	10	Conventional
1300°C/50 hr	14.3	12.5	0.59	82	13	Conventional

\* Commercial soft PZT, † Grain size determined from line intercept

fine grain thin film ferroelectrics [19]. The departure to higher domain densities in submicron grains may be associated with the inhomogeneous strain fields, which also have been found to increase the domain densities in highly defective coelastic crystals [4]. With higher domain densities, one might expect a larger extrinsic contribution to elastodielectric properties, but this is found not to be the case in both PZT fine grain bulk ceramics and thin film studies [20,21]. One possible reason for this is a decrease in the domain mobility and the number of variants in each grain as the grain size decreases. In the case of grain sizes larger than  $10\ \mu\text{m}$  our data are limited to one composition and one grain size but it is noted that this point also departs from the parabolic relation in a manner consistent with the coarsened grain BaTiO<sub>3</sub> ceramics [see the upper curve in Fig. 6 (b)], i.e. domain density becomes higher than the  $m = 1/2$  relation.

The domain structures observed in the poled PZT ceramics are shown to be strongly influenced by the domain structures in neighboring grains, both with regard to domain wall spacing and orientations. Figure 2 (a) and (b) clearly shows a transgranular elastic coupling, which can only be explained through cooperative intra- and trans-granular domain switching. Figure 2 (a) shows grain #3 with two sets of periodic ferroelastic twins, DW<sup>x</sup> and DW<sup>y</sup>, which couple, respectively, to domain configurations in the adjacent grains labeled #1 and #2, respectively. Figure 2 (b) also shows transgranular coupling of poled domain structures. This micrograph shows that the grain boundary between grains #2 and #3 perturbs the periodicity of domain structure in grain #1. Transgranular coupling is also of practical importance for fine grained thin film piezoelectric materials for devices such as micromotors. Grain boundary phases must be kept at a minimum to maximize the transgranular coupling. The transgranular coupling and their relation to elastodielectric properties will be the focus of future investigations in the domain structures of PZT ceramics.

## CONCLUSIONS

With the semi-infinite medium approximation, one can derive the exponent in eqn (1) to be  $1/2$ . However, experimental data supporting the parabolic relationship are scarce in the literature. The main reason for this is due to the strong influence of boundary conditions during the formation of domains. We have roughly estimated a situation of limited deformable medium with one side fixed and found that the exponent becomes  $1/3$  [22]. Through the experimental results reported here we show that in hard and soft PZT systems the parabolic relation ( $m = 1/2$ ) is

roughly obeyed only for grain size between  $1.0$  and  $10\ \mu\text{m}$ . For grain size  $> 10\ \mu\text{m}$  and  $< 1\ \mu\text{m}$ , deviation is found from the parabolic relation to higher domain densities. Because the problem is very complex for the ceramic system with a finite size, there is no sound theory with proper treatment of the boundary conditions to account for the domain size grain size relation at this point. We are currently pursuing numerical analysis using finite element method and hopefully will resolve some of the key issues in the near future.

One of the important contributions from our experimental works is the confirmation of the TEM technique as a valid method for domain size assessment in bulk ceramics. Using poled samples and heating cycles, we conclude that the domain size obtained in the TEM reflects that of the bulk ceramic if the samples were prepared at temperatures much below the transition temperature. Domain redistribution reflecting the new boundary conditions of the thin foil was found only after the samples were heated to temperatures near  $T_c$ .

Additionally, it was noted that fine grain ferroelectrics ( $< 1\ \mu\text{m}$ ) often contain one or two sets of simple twin bands, while larger grains can have many cross hatching twin band structures. The result of fine grains having simple domain structures implies a reduction in the degrees of freedom a fine grain can readily deform while the system is undergoing the paraelectric-ferroelectric phase transition. The reduced variants combined with the surface pinning of the domain walls may be the cause for the reduction of domain wall mobility and hence the associated extrinsic elasto-dielectric properties for fine grain PZT ceramics and thin films.

The poled ceramic samples reveal direct evidence of the domain switching process involving both intra-granular and trans-granular cooperation. The trans-granular switching indicates that the non- $180^\circ$  domains have strong semi-coherent elastic coupling across grain boundaries which in turn complicates the measure of effective grain size in the calculation of domain size.

*Acknowledgements*—We wish to thank Drs T. R. Shrout and N. Kim for the supplying of the ceramic samples in the TEM studies. The authors are also wish to acknowledge many insightful conversations with Drs L. E. Cross, R. E. Newham, and T. R. Shrout. This research is supported by the National Science Foundation under Grant MRG DMR-92-23847.

## REFERENCES

1. Fousek J. and Janovec V., *J. Appl. Phys.* **40**, 135 (1969).
2. Sapriel J., *Phy. Rev.* **B12**, 5182 (1975).
3. Khachatryan A. G., *Theory of Structural Transformations in Solids*. John Wiley, New York (1983).

4. Salje E., *Phase Transitions in Ferroelastic and Coelastic Crystals*. Cambridge University Press (1990).
5. Kittel C., *Phy. Rev.* **70**, 965 (1946).
6. Mitsui T. and Furuichi J., *Phy. Rev.* **90**, 193 (1953).
7. Arlt G., *Ferroelectrics* **104**, 217 (1990).
8. Chenskii E. V., *Sov. Phy. Solid-State* **14**, 1940 (1973).
9. Buessem W. R., Cross L. E. and Goswami A. K., *J. Am. Ceram. Soc* **49**, 33 (1966).
10. Swartz S. L., *IEEE Trans. Elect. Insulator* **25**, 935 (1990).
11. Whatmore R. W., Patel A., Shorrocks N. M. and Ainger F. W., *Ferroelectrics* **104**, 269 (1990).
12. Cross L. E. (private communication).
13. Randall C. A., Rossetti G. A. and Cao W., *Ferroelectrics* **150**, 163 (1993).
14. Philippe P., Dougherty J. P. and Shrout T. R., *J. Mater. Res.* **5**, 2901 (1990).
15. Shrout T. R., *Proc. 1st Int. Meeting on Chem. of Electron. Ceram. Mater.* (1990).
16. Jaffe B., Cook W. R. and Jaffe H., *Piezoelectric Ceramics*. Academic Press (1971).
17. Gevers R., Blank H. and Amelinckx S., *Phys. Stat. Sol.* **13**, 449 (1966).
18. Randall C. A., Barber D. J. and Whatmore R. W., *J. Mater. Sci.* **22**, 925 (1987).
19. Tuttle B., Voigt J., Headley T. J., Potter B. G., Dimos D., Schwartz R. W., Duggan M. T., Michael J., Nasby R. D., Garino T. J. and Goodnow D. C., *Ferroelectrics* **151**, 11 (1994).
20. Demartin M., Carry C. and Setter N., *Proc. 4th Int. Conf. on Electron. Ceram. and Applications*, P. 393 (1994).
21. Eatough M., Dimos D. and Tuttle B., *MRS Fall Meeting* (1994).
22. Cao W., *Ferroelectrics*, **172**, 31 (1995).