

Phase Coexistence in PZT Ceramics

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Abstract

In lead zirconate titanate ceramics, the low temperature tetragonal and rhombohedral ferroelectric phases coexist for compositions near the morphotropic phase boundary (MPB), and the explanation of this fact remains a controversial issue. A model of a statistical distribution of the phases can describe the coexistence of the phases, assuming that it results from the thermal fluctuation quenching during the cooling from the paraelectric to the ferroelectric phases. In this model the width of the phase coexistence region (Δx) is related to the grain size, G , and it should be observed that $\Delta x \propto G^{-3}$. In this work we checked the applicability of this relation on PZT powders and ceramics. Chemical equilibrium is not attained in calcined powders at 900, 1000 and 1100 °C, even after long time heat treatments, and therefore we considered the results from sintered samples. In these samples, instead of the $\Delta x \propto G^{-3}$ predicted relation, we found that $\Delta x \propto G^{-3/2}$. To explain this relation, we assumed that the elementary volume in the model is the ferroelectric domain instead of the grain of the material, based in a parabolic relation between the domain size and the grain size. Calculation of the elementary volumes using thermodynamic data is in good agreement with the volumes of the domains. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Lead zirconate titanate (PZT) ceramics, with general chemical formula $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, are commercially interesting materials due to their good dielectric, ferroelectric, and piezoelectric properties. At room temperature, the complete solid

solution between lead titanate, PbTiO_3 , or PT, and lead zirconate, PbZrO_3 , or PZ, presents two ferroelectric phases, a tetragonal phase in the titanium rich side of the binary system, and a rhombohedral one in the zirconium rich side. The boundary between these phases is normally called morphotropic phase boundary (MPB), and enhanced electrical properties are observed for compositions around this phase transition.¹ In ceramics, both low temperature phases coexist for compositions near this transition and this is often attributed to chemical fluctuations.^{2–4} Isupov^{3,4} assumed that, even in experimental equilibrium conditions, chemical fluctuations inside the material can be frozen in during cooling of the samples. Wersing *et al.*,⁵ studying the phase coexistence in PZT prepared from spray dried salt solutions, showed that, even in these ‘microscopically homogeneous ceramics’, the phase coexistence is still present in a finite compositional range. The authors agreed that compositional fluctuations could stabilise the coexistence of the two phases around the morphotropic transition, although it was not a necessary condition for its occurrence. Emphasis was put on the physical causes for the phase coexistence, namely the reduction of the elastic and the depolarisation energies. Kala⁶ and Isupov⁴ also recognised that internal stress could favour the coexistence of tetragonal and rhombohedral phases around the MPB. Ary-Gur and Benguigui⁷ and Barbulescu *et al.*⁸ justified the phase coexistence by a solubility gap in the PZ–PT binary system. It should be remembered that both the rhombohedral and the tetragonal phases change to a paraelectric cubic phase at ≈ 380 °C, and that above this temperature there is a complete solid solution in the system.^{9,10} If there is a solubility gap below this temperature, samples with a composition inside this gap cooled through the paraelectric-ferroelectric phase transition, should suffer local diffusion of the Zr and Ti ions in order to generate the two ferroelectric phases. However, the temperature at which this should happen seems to be too low for such a diffusion process to occur.^{11,12}

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Since no miscibility gap is expected, Cao and Cross^{11,12} suggested a phase mixing of the two phases having the same chemical composition around the morphotropic transition. Assuming that the paraelectric-ferroelectric transition in the MPB is a second order transition, the authors proposed that a thermal fluctuation quenching originates a statistical distribution of the two ferroelectric phases below that temperature. From this model, the coexistence phase width, (Δx), was found to depend on how much the free energy difference of the two low temperature phases changes with composition, α_1 , and on the volume of the monophasic element, v . The relation between Δx and v is:

$$\Delta x = \frac{2kT_c \ln 3}{\alpha_1 v} \quad (1)$$

Here, besides the already defined parameters, k is the Boltzman's constant, and T_c is the Curie point of the morphotropic phase composition. α_1 is

$$\alpha_1 = \frac{\partial}{\partial x} (g_T - g_R) |_{T,P} \quad (2)$$

where g_T and g_R are the free energy densities of the tetragonal and the rhombohedral phases, respectively, and x is the PbTiO_3 molar fraction that defines the composition of the solid solution, T is the temperature and P is the pressure. α_1 can be considered constant near the MPB composition.

Particles in powders or grains in ceramics were proposed to be the monophasic element.^{11,12} Taking the volume of the particles or the grains as a function of G^3 , where G is the mean particle or grain size, then it should be observed from eqn (1) that,

$$\Delta x \propto G^{-3} \quad (3)$$

As far as we know, this relation has not yet been experimentally verified and it is our purpose in this work to check its applicability on powders and ceramics of PZT materials.

2 Experimental

$\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ powders, in a compositional range from $x = 0.38$ to $x = 0.55$, were prepared by wet mixing PbCO_3 , TiO_2 and ZrO_2 , followed by calcination in the presence of PbZrO_3 (PZ) packing powder at 900, 1000 and 1100 °C for 25, 15 and 5 h, respectively. Powders calcined at 900 °C during 1 h were used to prepare sintered samples. They were wet milled for 15 h, dried, and sieved ($< 44 \mu\text{m}$) and then uniaxially pressed at 590 MPa. The disk shaped compacts were sintered at 1150 and 1250 °C

during 2 and 16 h, with a flux of O_2 and in the presence of PZ packing powder. The weight losses were controlled after calcination and after sintering, and the subsequent results presented in this work were obtained on samples with weight losses $< 3\%$. Since no zirconia precipitation was detected by X-ray diffraction or by SEM observations, it is considered that only PZT phases are present, and that no deviation from Zr/Ti ratio occurs in the final PZT phases due to the appearance of second phases.

X-ray diffraction analysis (Rigaku GeigerFlex) was performed on calcined powders and on sintered samples previously reduced to powders, in the $2\theta = 20$ to 60° angular range, in a step scanning mode, following a step of 0.01° at a speed of $0.5^\circ \text{min}^{-1}$. Since the diffractometer used is not equipped with an incident-beam focusing monochromator, the subtraction of the $K_{\alpha 2}$ and the background contributions was performed on the diffraction pattern by usual analytical methods.¹³

The microstructures of the sintered bodies, after being polished and chemically etched, were analysed by SEM and the mean grain size was determined by the linear intercept method.¹⁴

3 Results and Discussion

In the case of PZT materials that contain both tetragonal and rhombohedral ferroelectric phases, the X-ray diffractograms show the overlapping of the peaks belonging to the two different phases. The deconvolution of the ensembles of the peaks was performed by the adjustment of pseudo-Voigt functions, used to simulate the individual peaks, to the diffraction pattern.¹⁵ This analysis allows the determination of the angular positions, and the integrated intensities of each phase peak.

3.1 Calcined powders analysis

Direct observation of chemical homogeneity in PZT materials by EDS or WDS is not possible, because the spatial resolution of these analytic tools is larger than the magnitude of the component concentration gradients. Therefore, the chemical equilibrium state of the powders and of the sintered materials was indirectly analysed by the change of the lattice parameters of the phases with the thermal treatment time.¹⁶ Calculation of the lattice parameters was done by the minimum square method, using the angular positions of the peaks determined for the two phases. Figure 1 shows the lattice parameter ' a ' of the rhombohedral phase in one of the compositions, $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$, as a function of the calcination or sintering time. This behaviour is similar to the

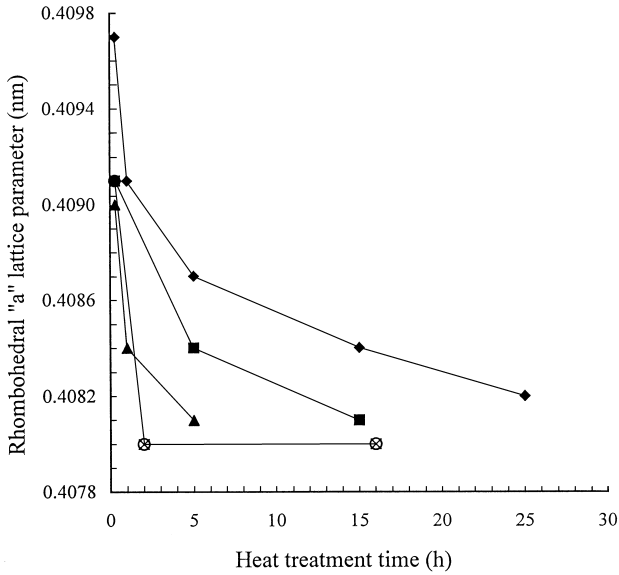


Fig. 1. Evolution of the 'a' lattice parameter of the rhombohedral phase in $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$ with the heat treatment time in calcined powders at 900°C (◆), 1000°C (■), and 1100°C (▲), and in sintered ceramics at 1150°C (○) and 1250°C (x).

other compositions under study. It clearly shows that the lower the heat treatment temperature, the longer the time required to achieve the final 'a' value, as one would expect for a solid state reaction process. It can be seen that the equilibrium state is not attained in the calcined powders, even for long time heat treatments. This fact is responsible for the observation of an enlarged phase coexistence region, as already pointed by Isupov,⁴ and therefore our attention will be concentrated in the results given by the sintered samples.

3.2 Sintered samples analysis

In PZT compounds, X-ray diffraction direct comparison method can be applied to the quantification of the phase concentrations.^{7,11} In this method, the integrated intensity of a (hkl) plane family, $I_{i(hkl)}$, of a phase in a powder mixture, with no preferred orientations, is related to the volume fraction of that phase, V_i , by the expression¹⁷

$$I_{i(hkl)} = C \cdot \|F\|^2 \cdot L \cdot P \cdot A \cdot F_T \cdot \rho \cdot V_i / v^2 \quad (4)$$

where C is a constant, F , L , P , A , F_T and ρ , are the structure, Lorentz, polarisation, absorption, temperature, and multiplicity factors, respectively, and v is the unit cell volume.

The integrated intensities of the (200) and (002) group peaks of both PZT phases were chosen for phase quantification, because, when coexistence occurs, a triplet around $2\theta = 44^\circ$ is observed. In this triplet, the two extreme peaks correspond to the (002) and (200) reflections of the tetragonal phase, and the central one to the rhombohedral (200) reflection.

The quantification of the molar fractions of tetragonal (f_T) and rhombohedral (f_R) phases was simplified using tetragonal and rhombohedral (200) and (002) reflections, which holds, for the tetragonal case,

$$\frac{f_T}{(f_T + f_R)} \approx \frac{V_T}{(V_R + V_T)} \approx \frac{(I_{T(200)} + I_{T(002)})}{(I_{R(200)} + I_{T(200)} + I_{T(002)})} \quad (5)$$

This was done considering that: (a) the two peaks involved differ less than 1° in 2θ ; (b) the compositions and the unit cell volumes are very close to each other; and (c) the structures are also close to each other (both structures can be considered as one cubic with small distortions, with the atoms lying approximately in the same positions).

In the statistical model, f_T and f_R are related to the phase coexistence composition width, Δx , and to the x_0 value, which is the PT molar fraction in PZT at the MPB, i.e. when $f_R/f_T = 3/2$,^{11,12} by

$$f_T = \begin{cases} \frac{6}{\pi} \arcsin \left[\frac{\sqrt{3}[2(1-\delta)] - \sqrt{3}}{2(1-\delta)^2 + [\sqrt{3} - (1-\delta)]^2} \right], & 1 - \sqrt{3} \langle \delta \rangle \left(1 - \frac{2}{\sqrt{3}} \right) \\ \frac{6}{\pi} \arcsin \left[\frac{[\sqrt{3}(1-\delta) - 1]^2}{2 + [\sqrt{3}(1-\delta) - 1]^2} \right], & 1 - \frac{2}{\sqrt{3}} \langle \delta \rangle \left(1 - \frac{1}{\sqrt{3}} \right) \end{cases}$$

$$f_R = 1 - f_T \quad (6)$$

with

$$\delta = 1 - \exp \left[\frac{(x - x_0) \ln(3)}{\Delta x} \right] \quad (7)$$

The definition of the parameter δ in eqn (7) is only valid in a compositional range around the MPB, where a linear dependence of the difference in the free energies densities $|g_R - g_T|$ on composition can be assumed [eqn (2)]. We considered that, at room temperature, the linear dependence is still valid for $0.38 < x < 0.55$, and an $\alpha_1 = 5 \times 10^7 \text{ J m}^{-3}$ value was estimated from reported data.^{18,19}

Δx is related to the volume of the elementary phase, v , [eqn (1)], or to the mean grain size [eqn (3)], assuming that the elementary volume is the grain volume. So, in the above determination of Δx , we must have the results of f_T and f_R of samples with the same mean grain size. The grain size (G), was measured in the solid state reacted PZT sintered for several temperatures and times. The sintering time was used to induce grain growth. The microstructures of the sintered samples of the composition $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$, at 1250°C for 2 h and 16 h (Fig. 2) give an illustrative example of the grain size variation obtained in PZT samples with different sintering times. Figure 3 shows that the

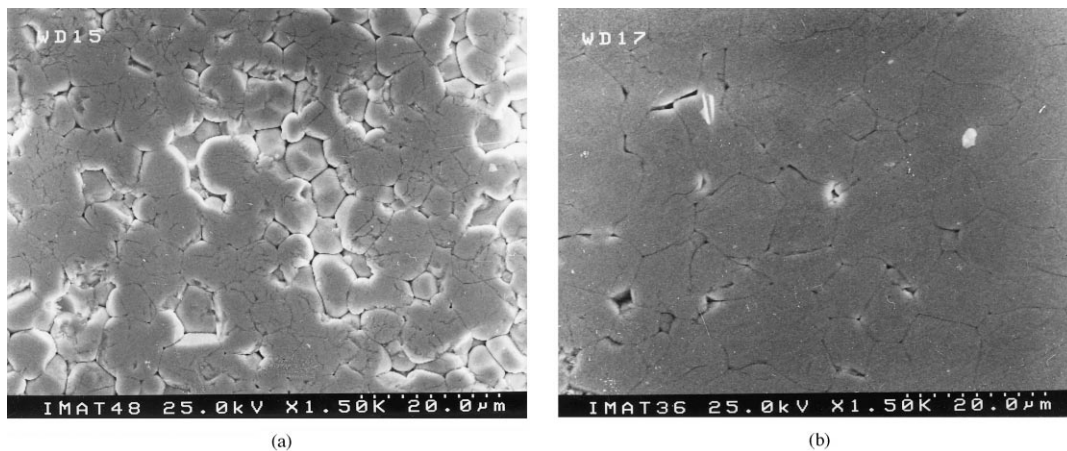


Fig. 2. SEM microstructures of the sintered samples of $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$ composition at 1250°C for (a) 2 h and (b) 16 h.

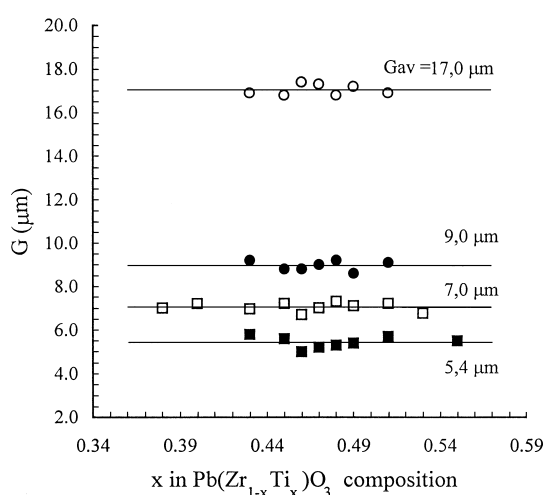


Fig. 3. Dependence of the mean grain size on the composition of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ solid solutions in sintered ceramics at 1150°C for 2 h (■) and 16 h (●), and at 1250°C for 2 h (□) and 16 h (○). The lines correspond to the average of the mean grain size (G_{av}) for each sintering temperature/time run.

composition, for $0.38 \leq x \leq 0.55$, has a negligible effect on the mean grain size for samples prepared under the same sintering conditions. To do that, we used the average of the mean grain size (G_{av}) for each sintering temperature/time run, which is also shown in Fig. 3. Therefore, Δx could be determined for four cases: two different temperatures and two different sintering times. The procedure now involves the fitting of eqns (6) and (7) to the experimental f_T and f_R values. Figure 4 shows those fittings from where we took the Δx and x_0 values listed in Table 1.

Table 1 shows that Δx depends on the sintering temperature and time, a similar result to those reported by Kakegawa *et al.*¹⁰ and Mabud,²⁰ and that there is a relation between Δx and the average grain size. This relation is shown in Fig. 5, where a log–log scale of Δx -versus- G reveals that Δx depends on $G^{-3/2}$, instead of G^{-3} as one would expect considering that the elementary volume, v ,

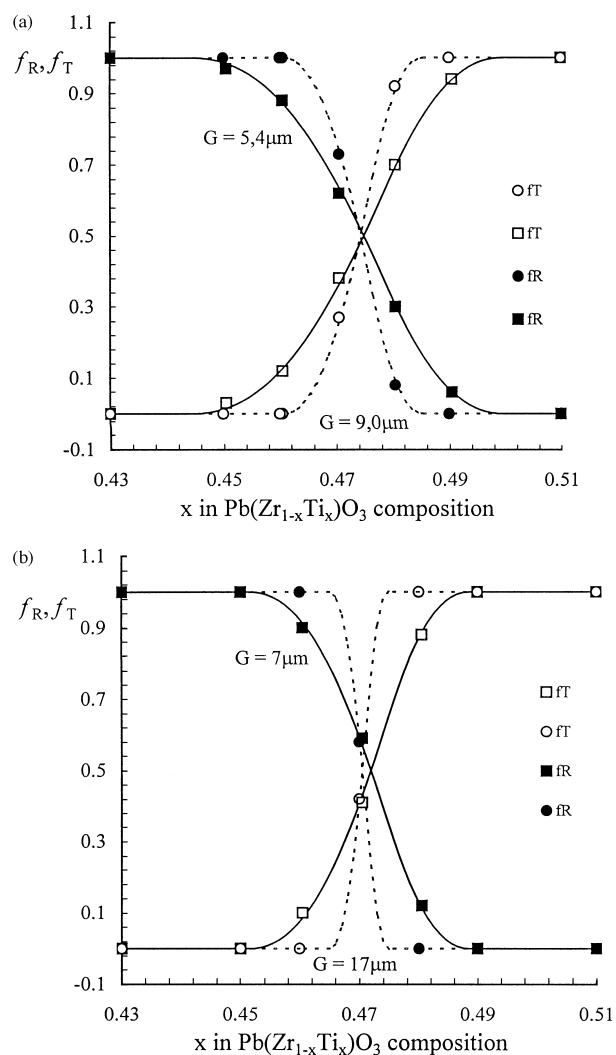


Fig. 4. Molar fractions of the rhombohedral and the tetragonal phases, f_R and f_T , respectively, in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ solid solutions. The points correspond to experimental results of the present work and the curves are fittings using the statistical model: (a) sintered ceramics at 1150°C for 2 h (■, □) and 16 h (●, ○), and (b) sintered ceramics at 1250°C for 2 h (■, □) and 16 h (●, ○).

corresponds to the volume of the grains [eqn (3)]. However, the good relation observed in Fig. 5, lead us to assume that the statistical model is still

applicable to this system, providing the elementary volume is an entity other than the volume of the grain.

The nature of the elementary phases in PZT ceramics, when both phases are present, is still a controversial question. Some authors admit that each grain should be monophasic,^{11,12} while others suggest that the phases can coexist inside the same grain, with one of the two phases metastable in relation to the other.^{3,11,21} Lucuta²² explained the electron diffraction spot triplet splitting, by the coexistence of both phases in the same grain in a ferroelectric-domain level. A twin related tetragonal–rhombohedral (T–R–T...) adjacent ferroelectric domain distribution, was proposed in the case of compositions around the MPB, since it requires a smaller energy for the rotation of the polarisation vector comparing to other domain configurations. This type of phase distribution is further supported by the calculation of the elastic stored energy in domain walls, when different adjacent domain wall possibilities are considered.²² If the grains are composed by domains of different phases, then the elementary volume in the statistical model should be taken from domain size, d , rather than from the grain size. Since Δx depends

on $G^{-3/2}$ (Fig. 3), then the above statement should only be observed if G depends on $d^{1/2}$. In fact, Cao and Randall^{23,24} obtained such a relation for samples with mean grain size in the 3 to 10 μm range. Taking their relation and extrapolating it up to 17 μm , the larger average grain size obtained in this work, one can calculate the volume of the elementary phases, v_1 , assuming that $v_1 = d^3$. Then, we can compare these volumes with those calculated from eqn (1), v_2 , taking Δx from the fittings in Fig. 4, and $\alpha_1 = 5 \times 10^7 \text{ J m}^{-3}$ from thermodynamic data.^{18,19} Both results are shown in Table 2 and in Fig. 6. There is a good proportionality between the two volumes, although one must be careful in its analysis. We do not know the exact relation between v_1 and d^3 , i.e. the geometric factor k in $v = kd^3$, but it seems reasonable that $k > 1$ because the domains have not a cubic configuration.²⁵ Fig. 6 shows us that $v_1 > v_2$, meaning that even the simplest assumed configuration for the domain volume, a cube, give origin to $k < 1$. This discrepancy, can result from the α_1 value considered in the calculation of the elementary volume by eqn (1). Identical volume values from both simulations, with $k > 1$, would be obtained for smaller values of the α_1 constant. It should be remembered that a

Table 1. Sintering conditions for $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ compositions in the range $0.38 \leq x \leq 0.55$. For each sintering condition, the width of the tetragonal and rhombohedral phases coexistence region, Δx , the MPB composition, x_0 , and the average grain size, G_{av} , are presented

Temperature ($^{\circ}\text{C}$)	Time (h)	Δx	x_0 (in PbTiO_3 molar fraction)	G_{av} (μm)
1150	2	0.055	0.472	5.4
1150	16	0.025	0.473	9.0
1250	2	0.037	0.470	7.0
1250	16	0.010	0.470	17.0

Table 2. The width of the tetragonal and rhombohedral phases coexistence region, Δx , the average grain size, G_{av} , the calculated domain size, d , and the elementary volume calculated from the domain size, v_1 , and from the statistical model, v_2

Δx	G_{av} (μm)	d (\AA)	$v_1 = d^3$ ($\times 10^9 \text{ \AA}^3$)	v_2 ($\times 10^9 \text{ \AA}^3$)
0.055	5.4	920	0.8	0.2
0.037	7.0	1050	1.2	0.3
0.025	9.0	1200	1.7	0.4
0.010	17.0	1650	4.5	1.0

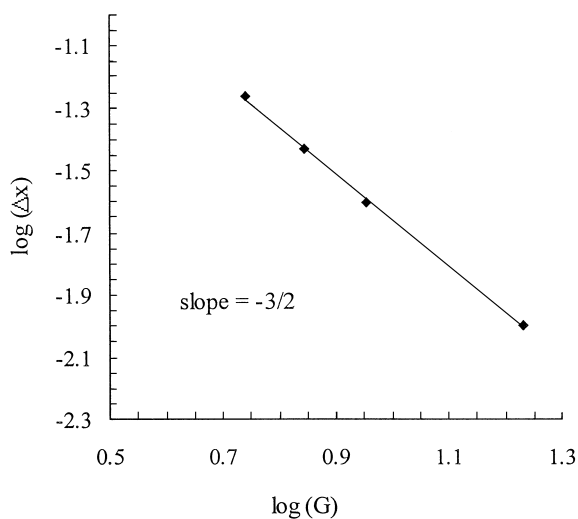


Fig. 5. Log–log curve of the width of coexistence phase region, Δx , versus the average grain size of PZT ceramics, G_{av} .

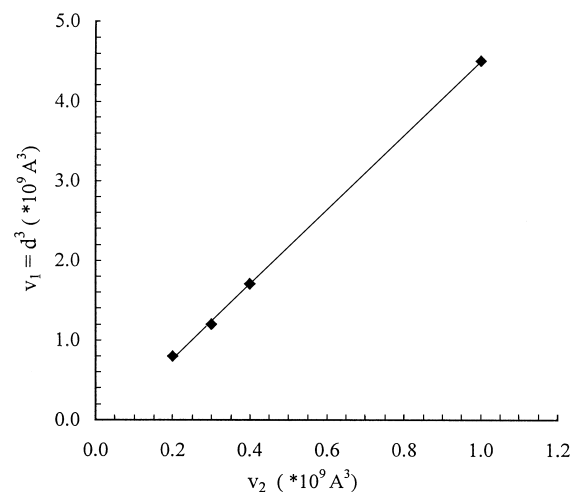


Fig. 6. Relation between the elementary volumes estimated from the grain size model, v_1 , and from the phase coexistence statistical model, v_2 .

smaller α_1 constant corresponds to a slower change of $|g_R - g_T|$ with the composition. The existence of a compositional range where such a small difference between the tetragonal and rhombohedral phases free energies is observed, would better support the assumption that the coexistence of the two phases around the MPB is due to the statistical distribution of the phases in the same grain.^{11,12}

4 Conclusions

In this work, we intended to study the relation between the width of the tetragonal and the rhombohedral phases coexistence around the MPB, Δx , and the particle size of powders or the grain size in ceramics, G , in PZT materials.

The materials were prepared by solid state reaction between PbCO_3 , ZrO_2 and TiO_2 . XRD analyses of calcined powders at 900, 1000 and 1100 °C, showed that the powders are not in an equilibrium state, even for long time heat treatments. Since the lack of chemical homogeneity can be responsible for the enlargement of phase coexistence region, and it may introduce deviations in the analysis of the phase coexistence, attention was concentrated in the sintered samples.

Although, at sintering temperatures, PZT ceramics seem to be in a composition equilibrium state, phase coexistence is still observed.

In the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ compositional range under study, i.e. $0.38 \leq x \leq 0.55$, the sintering process at 1150 and 1250 °C does not seem to be affected by the composition. For each temperature, after the same sintering time, the samples show similar microstructural characteristics with almost the same mean grain size. The statistical distribution model was used to calculate the width of the coexistence of the rhombohedral and tetragonal phases, Δx , for each sintering temperature/time run. The model was used to fit the f_R and f_T experimental results, where f_T and f_R are the molar fraction of the tetragonal and rhombohedral phases, respectively. Having PZT materials in the equivalent microstructural parameters it is possible to relate the values of Δx to those of the average mean grain size, G_{av} . A $\Delta x \propto G^{-3/2}$ relation was found, instead of the $\Delta x \propto G^{-3}$ predicted if the monophasic elements were considered to be the grains of the ceramics. Based on the parabolic relation between domain size and grain size, domains were proposed as possible single phase elements in PZT, within the coexistence region. The statistical model seems to give a good physical description of the phase coexistence region, if these different basic elements are considered to be responsible for the phase coexistence.

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References

- Jaffe, B., Jaffe, H. and Cook, W. R., *Piezoelectrics Ceramics*. Academic Press, London, 1971.
- Takegawa, K., Arai, K., Sasaki, Y. and Tomizawa, T., Homogeneity and properties of lead zirconate titanate prepared by a combination of thermal spray decomposition method with solid-phase reaction. *J. Am. Ceram. Soc.*, 1988, **71**(1), C49.
- Isupov, V. A., Some aspects of the physics of piezoelectric ceramics. *Ferroelectrics*, 1983, **46**, 217–225.
- Isupov, V. A., Reasons for discrepancies relating to the range of coexistence of phases in lead zirconate-titanate solid solutions. *Sov. Phys. -Sol. State*, 1980, **22**(1), 98–101.
- Wersing, W., Rossner, W., Eckstein, G. and Tomandl, G., The morphotropic phase boundary in PZT ceramics prepared by spray drying of salt solutions and by the mixed oxide method. *Silic. Ind.*, 1985, **3–4**, 41–46.
- Kala, T., Contribution to the study of tetragonal and rhombohedral phase coexistence in the PbZrO_3 – PbTiO_3 system. *Phys. Stat. Sol. (a)*, 1983, **78**, 277–282.
- Ari-Gur, P. and Benguigui, L., X-ray study of the PZT solid solution near the morphotropic phase transition. *Sol. Stat. Commun.*, 1974, **15**, 1077–1079.
- Barbulescu, A., Barbulescu, E. and Barb, D., Phase transitions in PZT solid solutions. *Ferroelectrics*, 1983, **47**, 221–230.
- Cao, W. and Cross, L., The ratio of rhombohedral and tetragonal phases on morphotropic phase boundary in lead zirconate titanate. *Jpn. J. Appl. Phys.*, 1992, **31**(5A), 1399–1402.
- Takegawa, K., Mohri, J., Takahashi, T., Yamamura, H. and Shirasaki, S., A compositional fluctuation and properties of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$. *Sol Stat. Commun.*, 1977, **24**, 769–772.
- Cao, W. and Cross, L., Distribution functions of coexisting phases in a complete solid solution system. *J. Appl. Phys.*, 1993, **73**(7), 3250–3255.
- Cao, W. and Cross, L. E., Theoretical model for the morphotropic phase boundary in lead zirconate–lead titanate solid solution. *Phys. Rev. B*, 1993, **47**(9), 4825–4830.
- Louër, D. and Langford, J. I., Peak shape and resolution in conventional diffractometry with monochromatic X-rays. *J. Appl. Cryst.*, 1978, **21**, 430–437.
- Fullman, R. L., Measurement of particle sizes in opaque bodies. *J. Metals*, 1953, 447–452.
- Langford, J. I., A rapid method for analysing the breadths of diffraction and spectral lines using the Voigt function. *J. Appl. Cryst.*, 1978, **11**, 10–14.
- Vasiliu, F., Lucuta, P. G. and Constantinescu, F., Structure–sintering temperature relationship in PZT solid solutions at the morphotropic phase boundary. *Phys. Stat. Sol. (a)*, 1983, **80**, 637–642.
- Cullity, B. D., *Elements of X-Ray Diffraction*, 2nd edn. Addison-Wesley, New York, 1978, pp. 411–415.
- Haun, M. J., Furman, E., Jang, S. J. and Cross, L. E., Thermodynamic theory of the lead zirconate–titanate solid solution system, Part V: theoretical calculations. *Ferroelectrics*, 1989, **99**, 63–86.
- Haun, M. J., Zhuang, Z. Q., Furman, E., Jang, S. J. and Cross, L. E., Thermodynamic theory of the lead zirconate–titanate solid solution system, Part III: Curie constant and sixth-order polarization interaction dielectric stiffness coefficients. *Ferroelectrics*, 1989, **99**, 45–54.
- Mabud, S., The morphotropic phase boundary in PZT ceramics. *J. Appl. Cryst.*, 1980, **13**, 211–216.

21. Isupov, V. A., Dielectric polarization of PbTiO_3 - PbZrO_3 solid solutions. *Sov. Phys. —Sol. State*, 1970, **12**(5), 1084–1088.
22. Lucuta, P., Ferroelectric-domain structure in piezoelectric ceramics. *J. Am. Ceram. Soc.*, 1989, **72**(6), 933–937.
23. Cao, W. and Randall, C., Grain size and domain size relations in bulk ceramic ferroelectric materials. *J. Phys. Chem. Solids*, 1996, **57**(10), 1499–1505.
24. Randall, C., Kim, N., Kucera, J., Cao, W. and Shrout, T. R., Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate. *J. Am. Ceram. Soc.*, 1998, **81**(3), 677–688.
25. Chung, H. T. and Kim, H. G., Characteristics of domain in tetragonal phase PZT ceramics. *Ferroelectrics*, 1987, **76**, 327–333.