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Phase coexistence region and dielectric properties of PZT ceramics

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Abstract

In PZT ceramics it is commonly observed that the tetragonal and the rhombohedral phases may coexist around the morphotropic phase boundary (MPB). Some controversy still exists concerning the causes of the real occurrence of the phase coexistence, the distribution of the coexisting phases and their chemical and structural properties. In a previous work we found a relation between the width of the coexistence region and the grain size of the ceramic that could be explained by the statistical distribution model, as long as the elementary phase volumes were considered as the ferroelectric domains inside the grain. In the present work the structural parameters of the phases and the dielectric permittivity of PZT in a compositional range covering the phase coexistence region are determined and analysed. It is observed that in both tetragonal and rhombohedral phases the permittivity increases as the lattice distortion relative to the cubic symmetry decreases. The dielectric permittivities of PZT inside the phase coexistence region were calculated considering that the phase coexistence corresponds to a statistical distribution of phases with the same composition. This model provides dielectric results consistent with the experimental ones. It was also shown that the maximum of the dielectric properties in the MPB does not result from the phase coexistence, but it is a consequence of the approach to a minimum structure distortion. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Phase equilibria; PZT

1. Introduction

Since their discovery in the early 50's, Pb($Zr_{1-x}Ti_x$)O_3, or PZT ceramics are recognised as excellent piezoelectric materials. At room temperature, the solid solution between lead titanate, $PbTiO_3$ (PT), and lead zirconate, $PbZrO_3$ (PZ), presents two ferroelectric phases, a tetragonal phase in the titanium rich side of the pseudobinary system, and a rhombohedral one in the zirconium rich side. Dielectric and piezoelectric maxima properties can be found in ceramics with compositions near Pb($Zr_{0.53}Ti_{0.47}$)O_3, which corresponds to the tetragonal-rhombohedral phase transition composition. This transition is usually classified as morphotropic because it corresponds to a structural change with the variation in composition.[1]

The important properties observed in PZT materials near this phase transition justify the large interest devoted to this region of the phase diagram. Although this transition is represented by a line in the phase diagram,[1] it is commonly observed that the tetragonal and the rhombohedral phases may coexist in a finite range of compositions around the morphotropic phase boundary (MPB) in ceramics.[2–8] For some authors, the maximum in the dielectric and piezoelectric properties observed around the MPB are due to the phase coexistence itself, since it multiplies the number of possible spontaneous polarisation directions.[3,9–11] Some controversy still exists concerning the causes of the occurrence of the phase coexistence in ceramics, the distribution of the coexisting phases, and their chemical and structural properties. Benguigui et al.[7,12,13] and Barbulescu et al.,[8] used the classical thermodynamic theory of solutions to justify the existence of both phases. In their opinion, the two-phases region observed around the MPB of PZT ceramics is a solubility gap. From this model, inside the insolubility interval, only the relative amount of each phase is expected to change according to the lever law, while the chemical composition, the lattice parameters and the physical properties (dielectric susceptibility, piezoelectric constants) of each phase should remain

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constant.[14] Among the research work devoted to this subject, Isupov's contribution is one of the most comprehensive. He formerly considered that the coexistence of the two ferroelectric phases is thermodynamically predictable, and tried to state the conditions for that occurrence.[15–17] He then suggested that the tetragonal phase is a stable phase in the composition range from $x = x_T$ to $x = 1$, while the rhombohedral phase is stable in the $0.08 \leqslant x \leqslant x_R$ range (with $x_T < x_R$). The phase coexistence interval would range from x_T to x_R, with

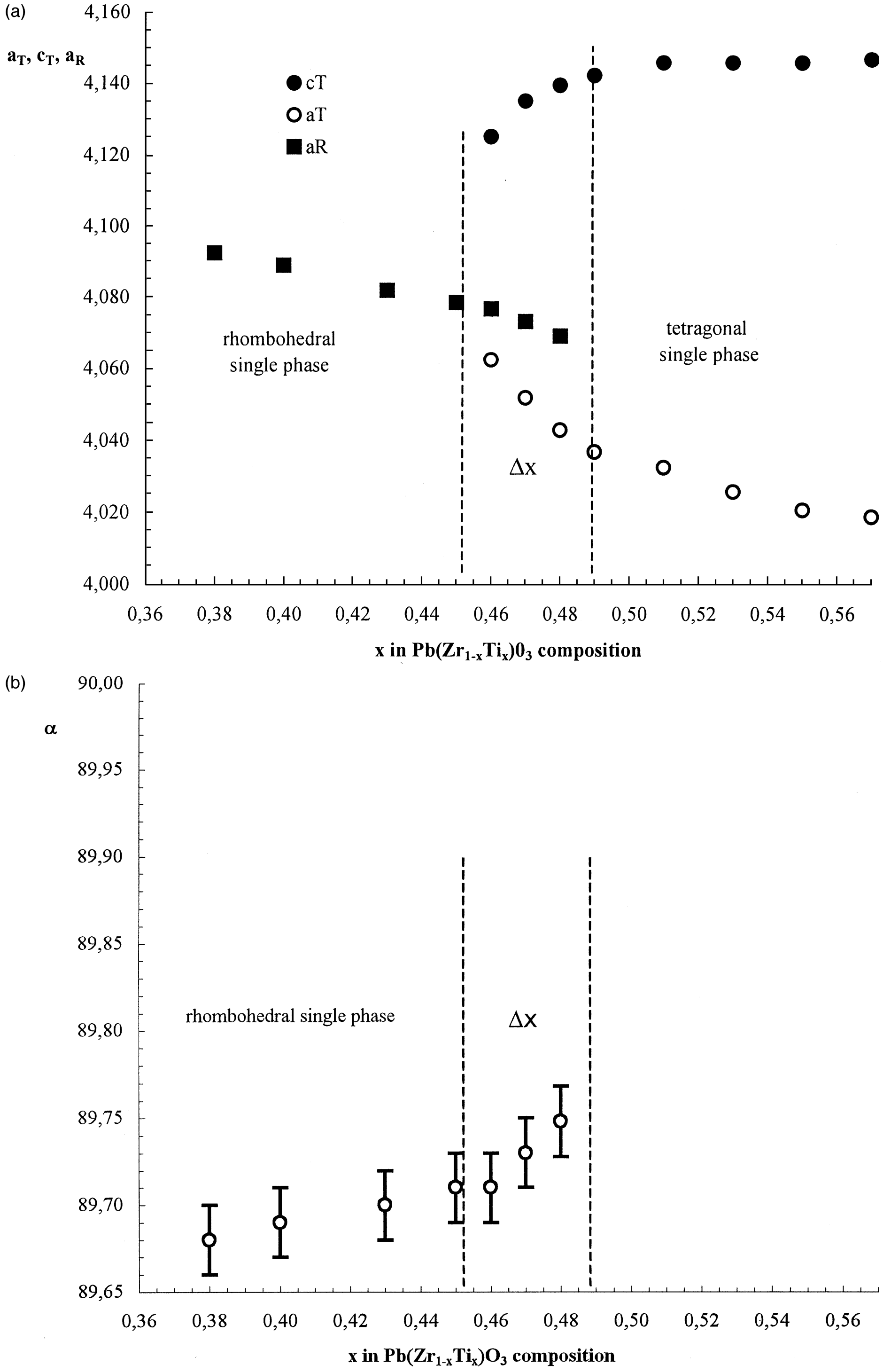

Fig. 1. Evolution of the lattice parameters of crystalline phases with the composition of the PZT sintered at 1250 °C for 2 h: (a) tetragonal phase parameters, a_T and c_T, and rhombohedral phase parameter, a_R; (b) rhombohedral angle distortion, α.

one of the phases metastable in relation to the other, in one of the sides of the coexistence interval, and vice versa in the other side. The presence of the metastable phases resulted from a composition hysteresis around the MPB,[18] composition that corresponds to the phase transition considered as a first order phase transition.[13] In this case, inside the phase coexistence interval, the dependence of the lattice parameters of each phase on the composition should be the same as in the single phase regions, which was not experimentally observed. Later, Isupov proposed that the coexistence phase interval depends on the degree of chemical equilibrium of the ceramic and tried to justify the phase coexistence by the presence of chemical heterogeneities in the system.[4,18,19] Due to those heterogeneities, associated with composition fluctuations, the coexistence of the tetragonal and the rhombohedral phases is possible in the same grain. Taking a normal distribution of the local Ti:Zr ratio around the mean average composition, $\bar{x}$, the lattice parameters and the dielectric properties can be related to the mean composition of the coexistence phases, $\bar{x}_T$ and $\bar{x}_R$, which change slower with the composition than in the monophasic solid solutions.[14] This is different from the phase structure behaviour predicted by the solubility gap and by the composition hysterisis in the first order transition models.

Beyond chemical fluctuations, other factors seem to contribute to the phase coexistence phenomena in ceramics.[5,6] Wersing et al.[5] showed, that, even in microscopically homogeneous ceramics, the phase coexistence is still present in a finite compositional range. Emphasis was put on the coexistence contribution to the reduction of the elastic and the depolarisation energies.[5] Experimentally, the coexistence of phases with different composition is not detected above the Curie point,[20] and so, it must be considered that above this temperature there is no limited range for the solid solution in PZT system. Therefore, it seems unlikely that upon cooling through the Curie point, the homogeneous solid solution splits into two solid solutions with different compositions.[21,22] The temperature is too low to permit the required diffusion of the cations. Based on this fact, Cao and Cross developed a statistical distribution model to describe the molar fraction change in the region where both phases coexist.[21–23] This model assumes that the two phases occur due to thermal fluctuation quenching during the cooling from the paraelectric to the ferroelectric states. While the solubility gap model reflects the law of mass conservation,

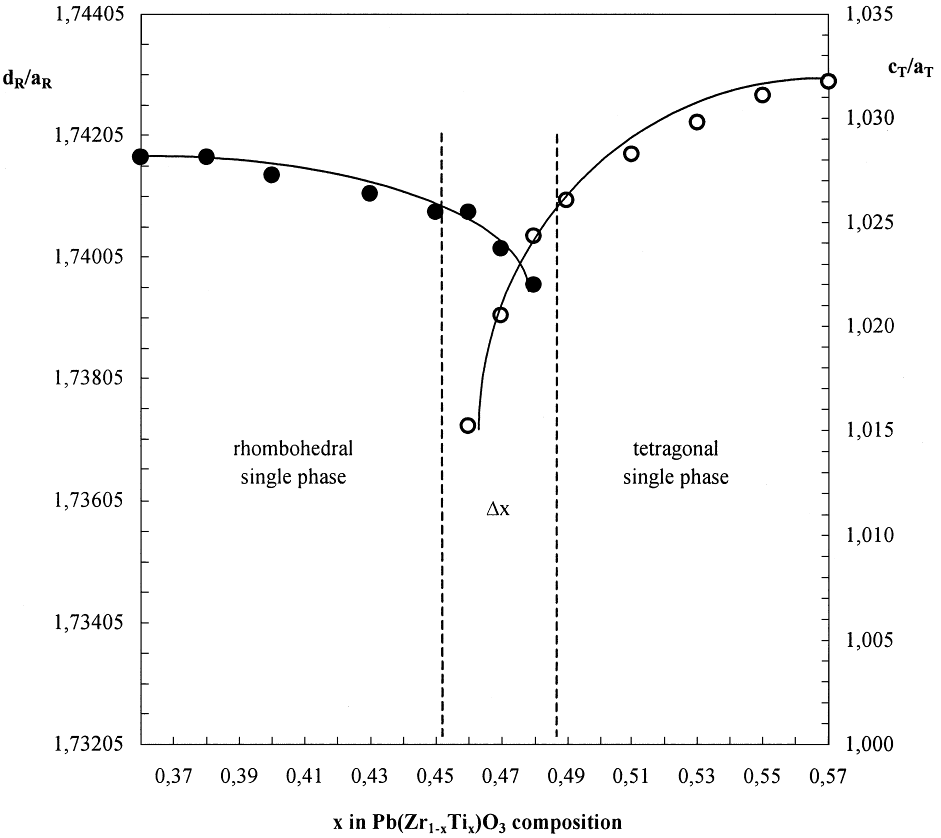

Fig. 2. Evolution of the unit cells distortions of the rhombohedral phase, d_R/a_R, and of tetragonal phase, c_T/a_T, with the composition of the PZT ceramics sintered at 1250 °C for 2 h.

this one considers that the phase coexistence region is a statistical distribution of the two phases, where only the MPB is well defined. The former implies a mixing of phases with different chemical compositions, while the later postulates the mixture of phases with the same chemical composition but with distinct structures.

In a previous work,[24] we showed, based on XRD results, that the chemical equilibrium in PZT materials prepared by a conventional ceramic processing is only attained at the sintering temperatures, and, even in this equilibrium state, the system presents a phase coexistence region. This could still be interpreted by the chemical fluctuation model, assuming that the low rate of diffusion at low temperatures, i.e. in the ferroelectric state, prevents the redistribution of the components throughout the samples.[4,18,19]

However, if this would be the case, there would be no reason to observe two different coexistence phase regions, Δx, for samples sintered at the same temperature (1250 °C) but at different times (2 and 16 h), since it was observed that both samples are in chemical equilibrium state. The main difference between these two sets of samples was the mean grain size, 7 and 17 μm, respectively, and this could explain the different Δx values if it is assumed that $\Delta x \propto G^{-3}$, which is predictable by the statistical model considering that grains are the monophasic basic elements.[21] We found that this model works nicely but with a relation of the type $\Delta x \propto G^{-3/2}$, which lead us to conclude that the basic elements giving origin to the coexistence range are the ferroelectric domains, tetragonal and rhombohedral, coexisting in the same grain.[24] In the present work, we further look inside this possibility analysing the dielectric properties of the samples. Care is also put on the analysis of the XRD data, because this may give a clue to understand the maximum phenomenon observed in the system.

2. Experimental

PZT samples were prepared in the way described before.[24] $Pb(Zr_{1-x}Ti_x)O_3$ powders, ($x = 0.36$ to $x = 0.57$), were prepared by wet mixing $PbCO_3$, TiO_2 and ZrO_2, followed by calcination at 900 °C. Disk shaped compacts were sintered at 1250°C during 2 and 16 h, with a flux of O_2 and in the presence of $PbZrO_3$ packing powder. 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 sintered samples previously reduced to

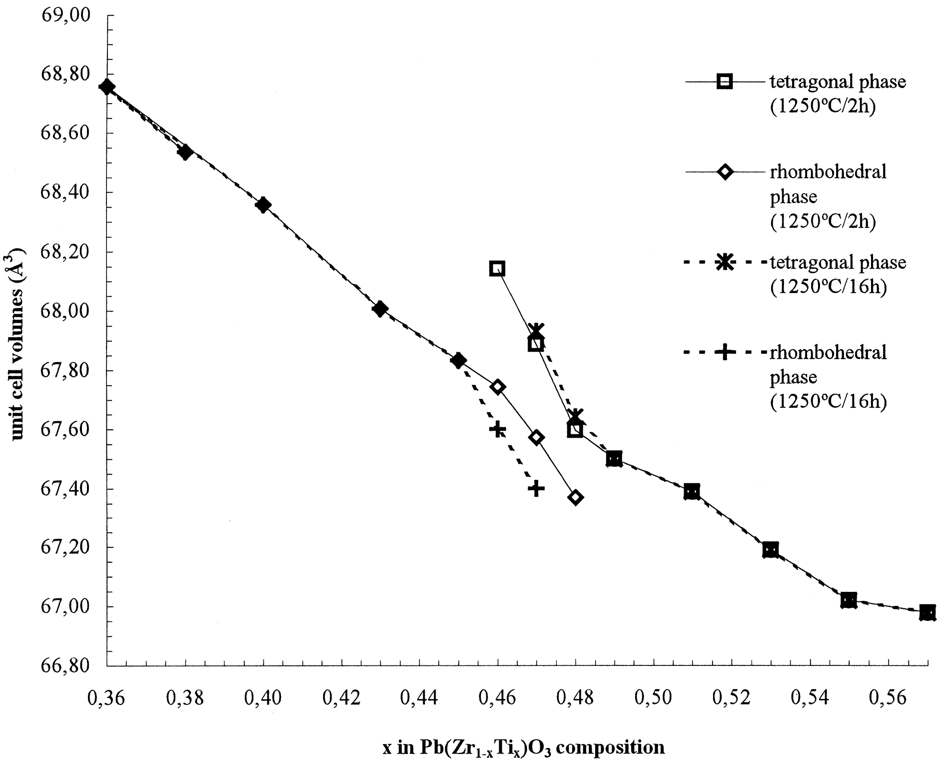

Fig. 3. Volume of the rhombohedral and of the tetragonal phase unit cells in function of the composition, in PZT sintered at 1250 °C for 2 and 16 h. Lines are used for eye guidance only.

powder, in the $2\theta = 20-60°$ angular range, in a step scanning mode, following a step of 0.01° at a speed of 0.5°/min. Since the diffractometer used is not equipped with an incident-beam focusing monochromator (it only has a graphite monochromator), the subtractions of the K_{α_2} and the background contributions were performed by usual analytical methods.[25] The calculation of the lattice parameters was done by the minimum square

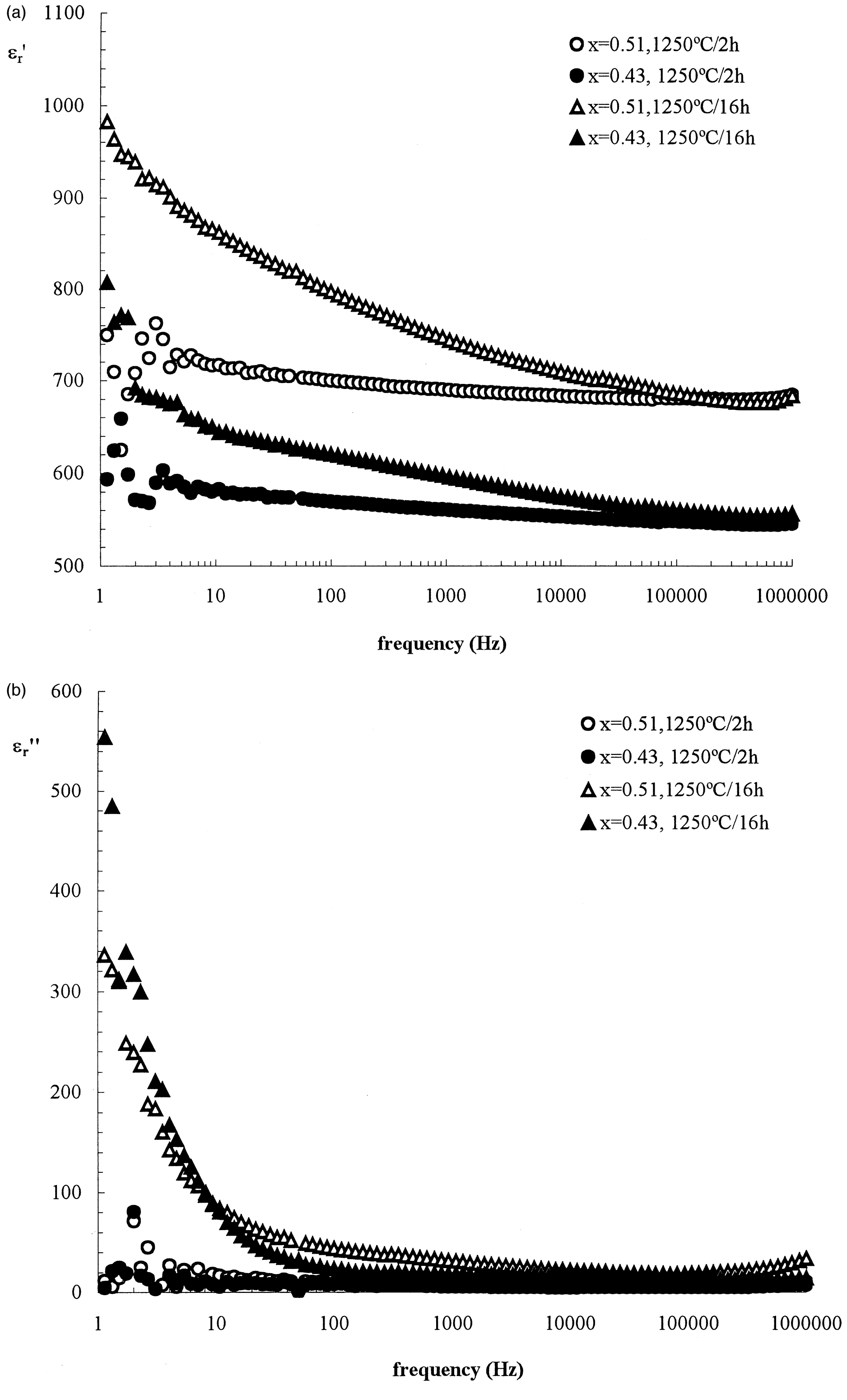

Fig. 4. Dependence of the dielectric permittivity with the frequency, at room temperature in tetragonal and rhombohedral PZT ceramics sintered at 1250 °C for 2 and 16 h: (a) real part of permittivity, ε_r'; (b) imaginary part of permittivity, e_r''.

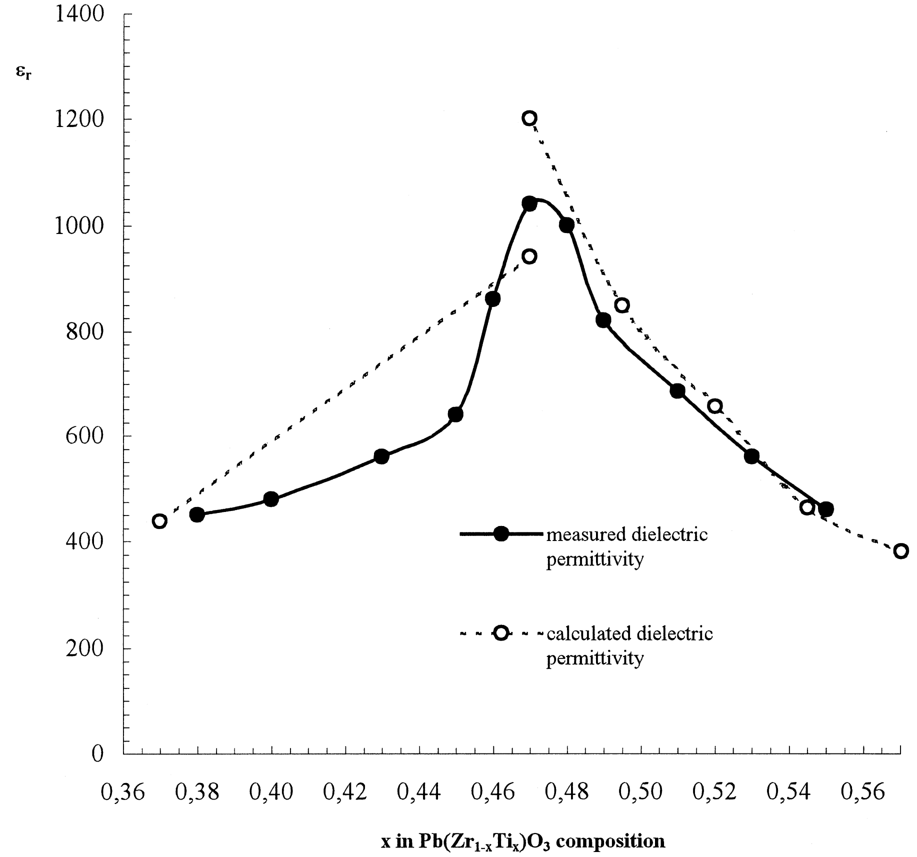

Fig. 5. Dielectric permittivities of PZT ceramics sintered at 1250°C for 16 h and thermodynamical calculated values for monocrystalline, monodomain and monophasic materials.[28]

method, using the angular position of the peaks determined for the two phases.

For the dielectric measurements, the PZT discs were lapped to 1 mm thick, cleaned, and annealed at 600 °C to release hypothetical superficial stresses resultant from polishing and residual cleaning fluids, before the sputtering of Au electrodes. The dielectric permittivity was calculated from impedance data (Solartron 1260 Impedance/Gain-Phase Analyser) obtained at room temperature, using an ac signal of 1V, in a frequency range from 1 Hz to 1 MHz. The calculations were done considering that, at this temperature, the materials can be described by a parallel RC electric circuit. The results that will be presented are the mean values of the measurements performed on five samples and show a standard deviation inferior to 3%.

3. Results and discussion

3.1. XRD analysis

In the case of PZT materials containing both the tetragonal and the rhombohedral ferroelectric phases, the X-ray diffractograms show a partial overlapping of the peaks belonging to the two different phases. The deconvolution of the ensembles of the peaks is necessary to determine the angular positions and the integrated intensities of each phase peaks. This was performed by fitting the parameters of the pseudo-Voigt functions, used to simulate the individual peaks to the diffraction patterns.[26] The basis for the deconvolution of the PZT diffractograms procedure is exposed in detail in Appendix A.

Fig. 1(a) shows the lattice parameters of the tetragonal phase, a_T and c_T, and the a_R parameter of the rhombohedral one, as a function of the concentration of Ti, x, and Fig. 1(b) shows the variation of the rhombohedral lattice distortion angle, α, with x for the 2 h sintered samples. In the $0.451 < x < 0.488$ range both phases are present, denoted by the Δx interval,[24] and it can be noted that in this region all the structural parameters presents a stronger change than outside of it. This is completely opposite to the constant dependence observed by Hanh et al.,[14] and shows that the solubility gap model can be ruled out because structurally the phases parameters change inside the region. Wersing et al.[5] were the first to report results on the lattice parameters change with PZT composition by X-ray diffraction analysis with K_α radiation of a Cu tube with a primary beam monochromator. Their conclusions on the lattice parameters change are similar to ours. In all the composition range where the tetragonal phase is present, c_T and a_T are closing together with the decrease of Ti content, particularly inside the coexistence region, meaning that the structure is approaching the cubic geometry. The same is true for the rhombohedral phase, where α is smoothly changing to $\alpha = 90°$, the limit case where it should be cubic, with an increase of x. Fig. 2 depicts this observation, where the tetragonal lattice distortion, c_T/a_T, is decreasing down to $c_T/a_T = 1$ (the cubic phase), and the rhombohedral lattice distortion, d_R/a_R, where d_R is the diagonal of the rhombohedro, is decreasing down to $d_R/a_R = \sqrt{3}$ (the cubic phase), and both decreasing behaviours are more pronounced inside the coexistence region. It seems, therefore, that the phase transition is realised through very similar crystal structures, supporting the model of the thermal fluctuation quenching through the Curie point and the subsequent statistical distribution of the phases proposed by Cao and Cross. A final step to be analysed is the order of the phase transition. Fig. 3 shows the change of the volume cells of both the tetragonal and the rhombohedral phases with the composition. It can be observed, by this parameter, that the transition is a first order phase transition, although in a very smooth way. Both cells inside the coexistence region are very similar in volume and a good matching between the two is expected, i.e. mismatch stresses are probably not very important in this region. This means that the difference in the free energy of both phases inside the coexistence region must be very small, which further supports the statistical distribution principles. In the case of the 16 h samples, the structural behaviour is similar to the one observed in the 2 h sintered samples.

Our previous observation was that the grains are composed by ferroelectric domains of each phase, probably in a sequence of the type tetragonal–rhombohedral–tetragonal–. . .,[27] because the width of the coexistence region, Δx, is proportional to $(G^{-3/2})$.[24] In view of the above results, it is now important to check the applicability of this coexistence phase model to the dielectric results.

3.2. Dielectric results

At room temperature, the real and the imaginary parts of the dielectric permittivity show a relaxation phenomenon at frequencies below 1 kHz, which frequency is independent of the composition and of the sintering time [Fig. 4(a) and (b)]. Only the intensity of the relaxation peak depends on the time and the composition of the PZT solid solution. Above 1 kHz the permittivity has an almost constant value. Taking the dielectric permittivities values measured at 100 kHz for the tetragonal single phase compositions, it is observed that they

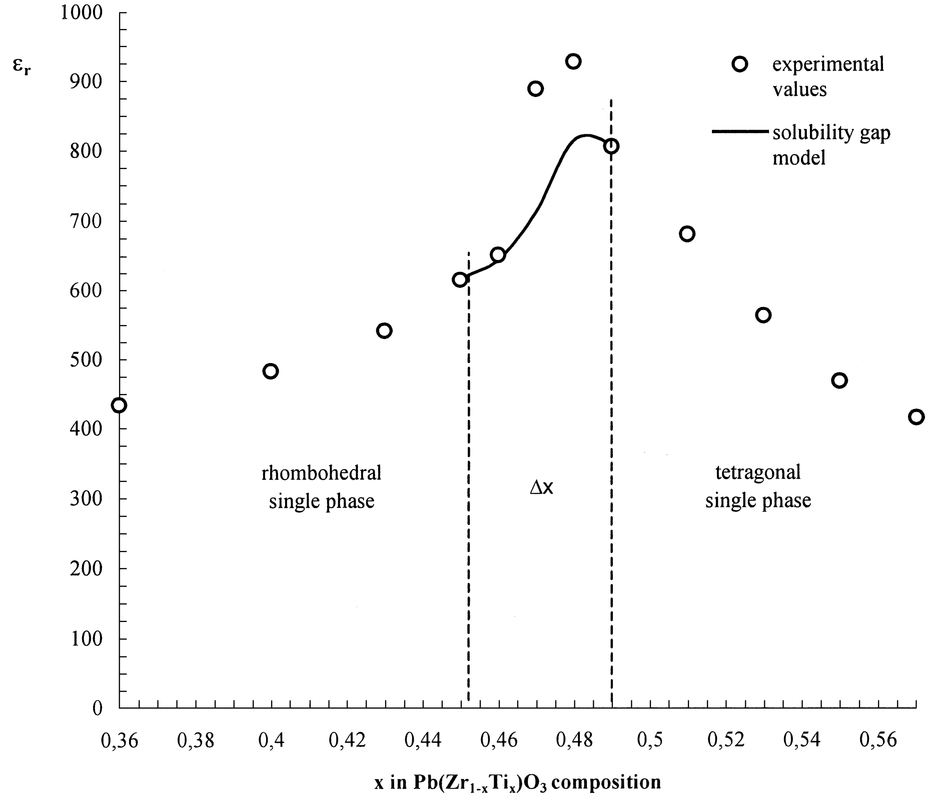

Fig. 6. Dielectric permittivity of PZT ceramics sintered at 1250°C/2 h (measured at 100 kHz, at room temperature) and predicted considering that the phase coexistence region is a solubility gap.

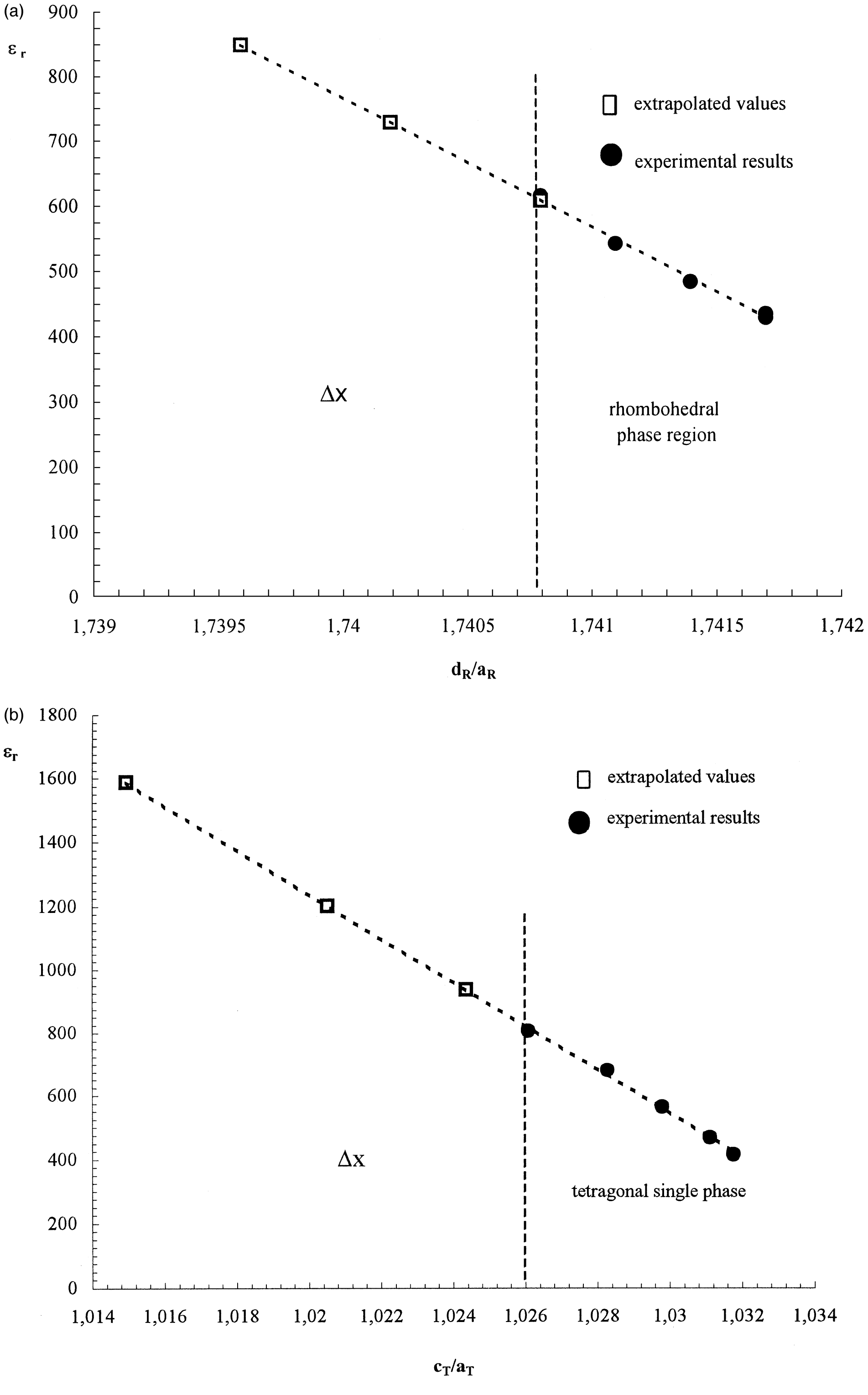

Fig. 7. Relation between the dielectric permittivity and the lattice distortion of single phase PZT: (a) rhombohedral phase; (b) tetragonal phase.

are very close to those permittivities values proposed by Haun et al.[28] from thermodynamic calculations, who considered that the materials are single-domain compounds (Fig. 5). The authors recognised that their theory has some quantitative limitations in the calculation of the low temperature dielectric permittivities of the rhombohedral phase compositions, due to the lack of tilt angle data that should be included in the Gibbs free energy function. In spite of these limitations, they are also in good agreement with our results (Fig. 5).

In the coexistence phase region, the dielectric permittivity of the material results from the contribution of the

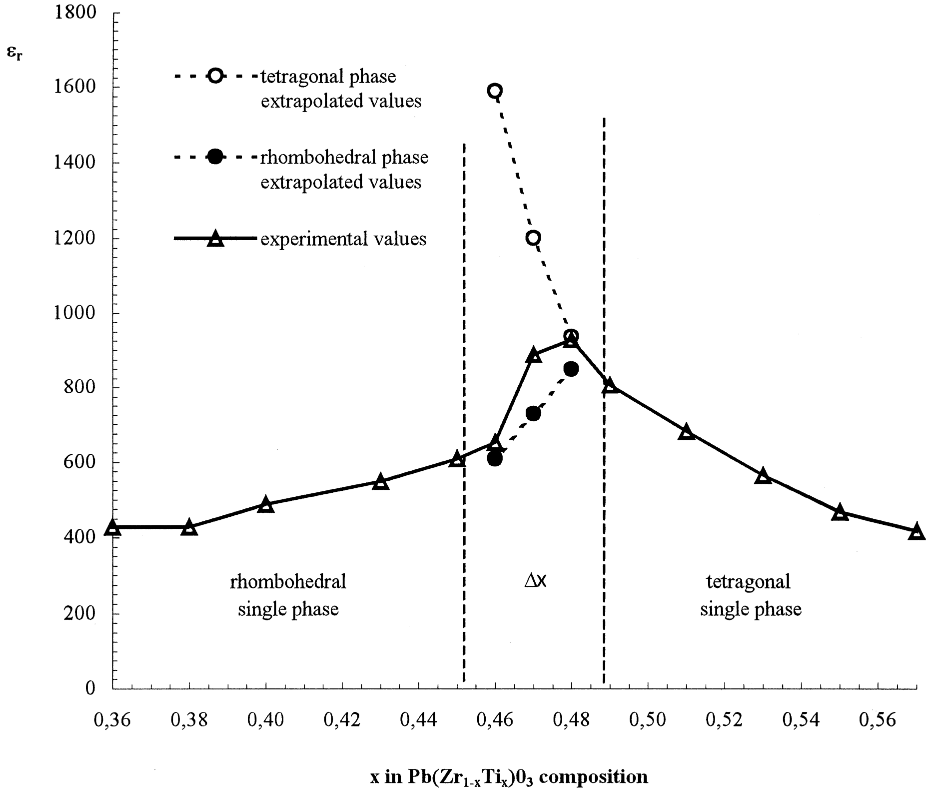

Fig. 8. Dielectric permittivity (measured at 100 kHz, at room temperature) of PZT ceramics sintered at 1250°C/2 h and extrapolated for the tetragonal and rhombohedral in the phase coexistence region.

two phases. Although the structural evolution of the phases shows that the phase coexistence region is not a solubility gap, we can test if it applies to the dielectric results. The phases that coexist around the MPB must have the same composition as those corresponding to the extremes of the gap, e.g. for the ceramics sintered at 1250°C during 2 h, we have the $x=0.451$ and $x=0.488$ extremes. In this case, the structure and the dielectric permittivities of each phase, are considered to be constant for all the compositions in the interval. Inside the gap, the dielectric permittivities of the ceramic were calculated using the following equation[29]

$$\varepsilon = \exp\left[\frac{\ln\left\{V_T\varepsilon_T^{(V_T-0.65)} + V_T\varepsilon_R^{(V_T-0.65)}\right\}}{V_T - 0.65}\right] \tag{1}$$

where ε is the permittivity of the compound with the two phases, V_T is the volume fraction of the tetragonal phase, ε_T its permittivity, and ε_R is the rhombohedral phase permittivity. We used this equation, deduced from Monte Carlo and finite element method, to predict the dielectric permittivity of the PZT ceramics composed by the two phases because it is applicable to compounds consisting of two different non aspect phases and it takes into account the effect of the dielectric polarisation and the infringing of the electric flux at the boundary region of the two different materials.[29] The volume fractions of the phases that coexist in a PZT ceramic can be directly determined by X-ray diffraction results and their calculation and results were presented in a previous work.[24] The results calculated with Eq. (1) are presented in Fig. 6 together with the experimental values. It can be seen that the agreement between the calculated and the experimental results is poor. Other equations[29] besides Eq. (1) can be used to calculate the dielectric permittivity of the materials with the two phases, but do not provide a better fitting of the experimental results. It can be concluded again that the solubility gap model can not be applied to the system.

Our next step is to analyse the applicability of the statistical model to the dielectric results. For each of the compositions inside the coexistence range, we already know the volume fraction of tetragonal phase, V_T, in Eq. (1), but we do not know the permittivity values, ε_T and ε_R. As a first approach, we could use the permittivitty values determined by the thermodynamic calculations,[28] but these were calculated considering that the material is a monophase and a monodomain system, and here we are assuming that each grain is composed by domains of the two different crystal structures. Another possibility to overcome this problem, is to find any relation between the crystal structure and the dielectric permittivity outside the coexistence range, and then to extrapolate this relation to the inside interval, because crystal structures are the only parameters that are well defined in this range. Such a relation is observed between the lattice distortions, c_T/a_R or d_R/a_R, and the dielectric permittivities measured in the monophasic tetragonal or rhombohedral compositions. These relations are evident in the plots of Figs. 7(a) and (b), respectively. It is possible to observe that the dielectric permittivity of the ceramic increases as the lattice distortion decreases, i.e. when approaching the cubic structure in both cases. Figs. 7(a)

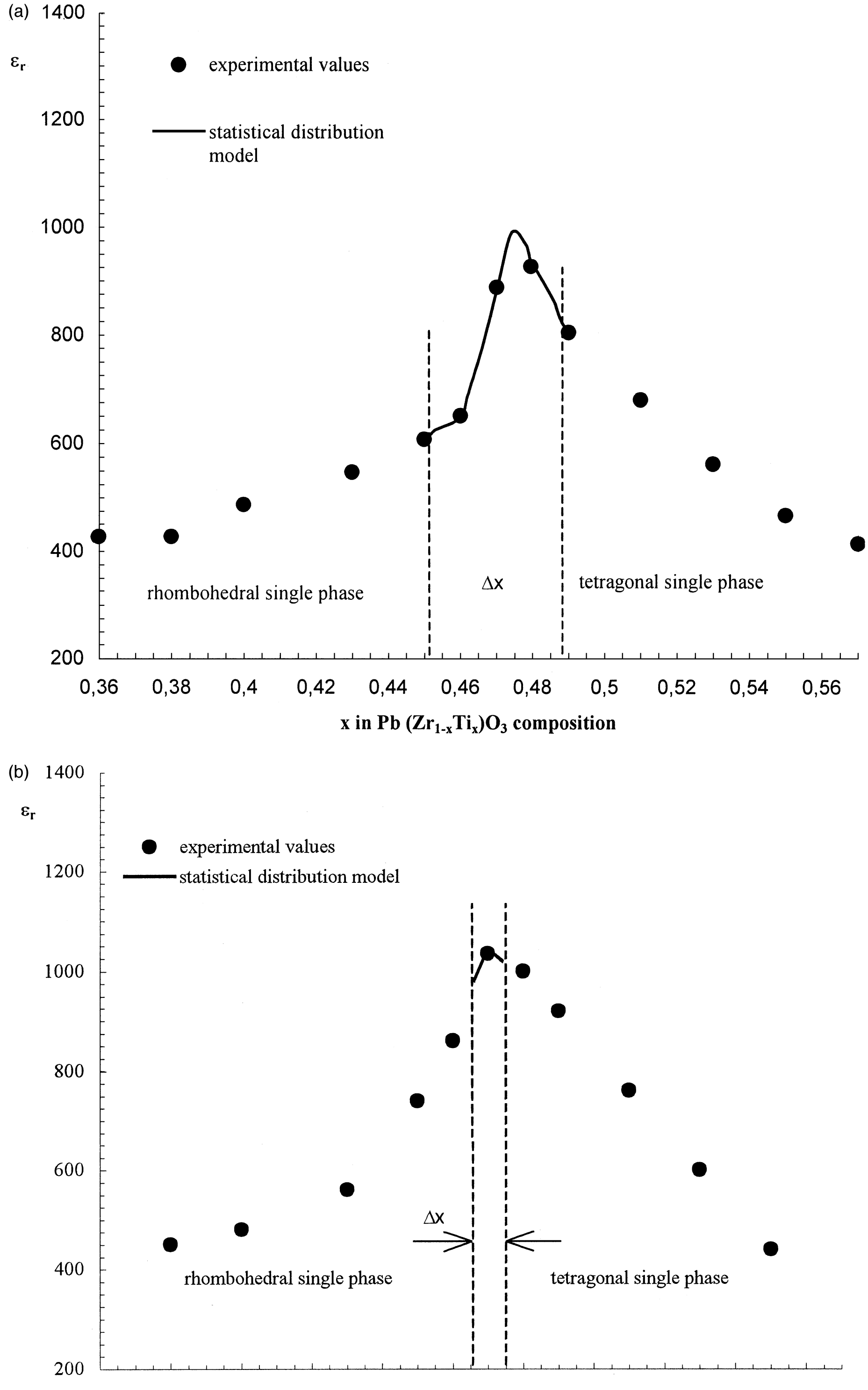

Fig. 9. Dielectric permittivity of PZT, measured at 100 kHz at room temperature and, calculated values supposing that both phases have the same composition, but different structures inside the phase coexistence interval:[21–24] (a) ceramics sintered at 1250°C/2 h; (b) ceramics sintered at 1250°C/16 h.

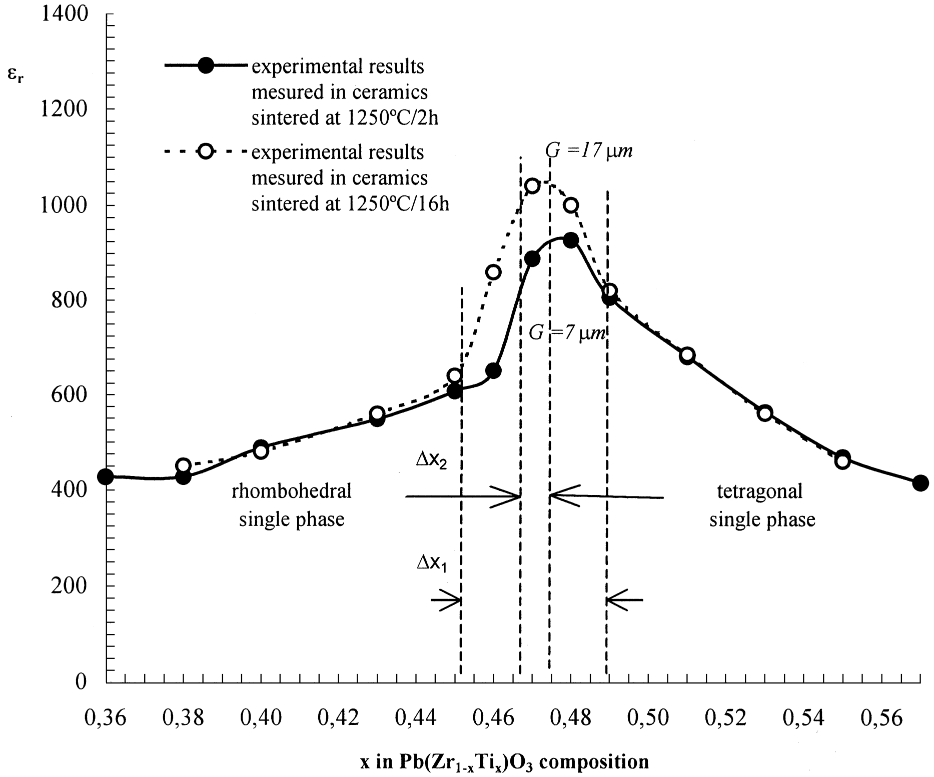

Fig. 10. Dielectric permittivity (measured at 100 kHz, at room temperature) of PZT ceramics sintered at 1250°C for 2 and 16 h. Δx_1 and Δx_2 are the widths of the phase coexistence regions of PZT ceramics sintered at 1250°C for 2 and 16 h, respectively.

and (b) also show the extrapolated values of the permittivities to the coexistence range (open squares). In Fig. 8 the dielectric permittivities of each phase predicted from the structure evolution are plotted as a function of the composition, together with the permittivities measured in the ceramics sintered at 1250 °C during 2 h. Considering that the extrapolated values are in fact the true values of the phases, it comes out from this figure that inside the coexistence region, the dielectric permittivities of the ceramics are inferior to those of hypothetical ceramics strictly composed by the tetragonal phase. It seems that the mixture of the tetragonal and rhombohedral phases does not benefit the properties of the PZT material in the Ti rich side of the MPB neighbourhood. We are now able to calculate the permittivity of the ceramics inside the coexistence range through Eq. (1). Fig. 9(a) and (b) shows that the agreement between these values and the experimental ones is excellent. Although this equation is the one that provides the best fitting of experimental results, other equations[29] used to predict the dielectric permittivity of a multiphase compound also give a good agreement. The good fitting observed in Fig. 9 once again supports the assumption that the statistical phase distribution model gives a good description of the coexistence phase region in these ceramics. Therefore, for ceramic materials in chemical equilibrium, around the MPB, two different structures, tetragonal and rhombohedral, of the same composition may coexist, and these phases probably correspond to ferroelectric domains.[24] A very narrow interval of phase coexistence is expected in PZT ceramics with large grain size, in accordance to the $\Delta x \propto G^{-3/2}$ relation.[24] These conclusions may insert an important technological point: the development of ceramic materials with microstructures composed by large grains, can provide a very narrow coexistence region, or in the limit, its disappearance. The interest of this development depends on whether the maximal dielectric and piezoelectric properties result from the phase coexistence itself, as many authors propose, or on the contrary this coexistence represents a dilution of the maximal attainable properties for the compositions around the MPB. In this work, it was possible to conclude that the dielectric properties of the PZT materials do not show the maximum attainable permittivity, that of the hypothetical tetragonal monophasic materials. This is possible to confirm by the observation that the dielectric permittivities of the ceramics sintered at 1250 °C for 16 h, those that show the narrower phase coexistence width (0.01 molar), are higher than those of the materials sintered at 1250 °C for 2 h (Fig. 10). Since the decrease of the coexistence region width is associated to the increase of the maximum attainable permittivities, it seems reasonable to conclude that the

Table 1
Relative integrated intensities (I_{int}) of the hkl reflections in the powder method X-ray diffraction of PZT tetragonal and rhombohedral phases

	Tetragonal phase			Rhombohedral phase	
hkl	I_{int} (%) Results from the pseudo-Voigt fitting of tetragonal PZT diffractograms	I_{int} (%) Results from the simulation of the tetragonal PZT diffractograms (Powder Cell 1.7)	hkl	I_{int} (%) Results from the pseudo-Voigt fitting of rhombohedral PZT diffractograms	I_{int} (%) Results from the simulation of the rhombohedral PZT diffractograms (Powder Cell 1.7)
001	14	13	100	38	41
100	19	24	110	100	100
101	100	100	$1\bar{1}0$	100	100
110	44	48	111	9	9
111	27	31	$11\bar{1}$	25	28
002	14	16	200	55	59
200	27	28	210	10	11
102	8	7	$2\bar{1}0$	10	11
201	6	6	211	18	20
210	3	6	$21\bar{1}$	37	40
112	21	21			
211	37	39			

coexistence of the phases and the multiplicity of possible polarisation directions do not determine the occurrence of the maximum of the properties. The increase of the dielectric permittivity seems to result from the proximity of the phases structure to the cubic symmetry observed near the MPB. Providing a fine composition control of the ceramics, it comes out that grain growth becomes a main objective when good properties are pursued. The achievement of process conditions that assure a good compromise between grain growth and high densities, avoiding stoichiometric deviation, especially by lead oxide loss, represents an important challenge in these system engineering.

4. Conclusions

The coexistence phase region in PZT ceramics was analysed by XRD and dielectric measurements. Samples were prepared by a conventional ceramic procedure, sintered at 1250°C, for 2 and 16 h. The phase coexistence range, Δx, depends on the sintering time, as previously reported, and it is $\Delta x = 0.037$, and $\Delta x = 0.010$, for 2 and 16 h, respectively. The crystalline structures parameters change with composition, and these changes are more pronounced inside the coexistence phase region. These observations rule out the presence of a solubility gap to explain the coexistence interval. In the monophasic parts of the pseudo-binary PZ-PT system, both the tetragonal and the rhombohedral phases tend to the cubic symmetry when approaching the coexistence region, and this tendency is more pronounced inside this region. The dielectric permittivity values in the monophasic regions follow this tendency, and good relations between the permittivitty values and the tetragonal and rhombohedral lattice distortions relative to the cubic symmetry could be found. Extrapolating these relations to the coexistence range, it was possible to obtain the permittivity values of each phase for the same chemical composition. Using these extrapolated values together with the volume fraction of each phase determined by XRD results, it was possible to completely reproduce the experimental permittivity values inside the coexistence range. In view of this good agreement, one could conclude that the statistical model better describes the dielectric permittivity maximum observed in this system. Therefore, this maximum is not caused by the coexistence of the two phases, as normally proposed. These results, together with the relation $\Delta x \propto G^{-3/2}$, being Δx the width of the coexistence region and G the average grain size, stated in previous work, insert an important technological meaning, pointing to the need of the development of monophasic ceramics of large grain size, when important dielectric properties are pursued.

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Appendix A

The powder X-ray diffractograms of the PZT materials that contain both tetragonal and rhombohedral ferroelectric phases, show the partial overlapping of the peaks belonging to the two phases. The deconvolution of the ensembles of peaks of each phase is necessary to determine the angular positions [$2\theta(\mathrm{i})$] and the integrated intensities of each phase peaks (I_{int}) used to calculate the lattice parameters and the molar fractions of the phases present in the coexistence region.

The deconvolution is performed by the adjustment of the parameters of the pseudo-Voigt function used to simulate the diffraction peaks, after background removal. These parameters are w, equal to FWHM/2 (half of the full width half maximum), x, the angle that corresponds to the difference between each 2θ position and the centre of the peak [$2\theta - 2\theta(\mathrm{i})$], and I_0, the maximum intensity of the peak. This pseudo-Voigt function corresponds to the addition of a fraction, f, of a Lorentz function with a fraction, $1-f$, of a Gaussian function. The intensity is then calculated by

$$I = f\frac{I_0}{\left(1+\frac{1}{w^2}x^2\right)} + (1-f)I_0\exp\left(\frac{-\log 2}{w^2}x^2\right)$$

The first step is the determination of the parameters of the pseudo-Voigt function for each peak of the diffractograms of the monophasic materials. A profile fitting can be performed using the specific program of the Rigaku IBM software of X-ray diffraction quantitative analysis. In this program the parameters are changed by a least square procedure, until the minimisation of the residuals between the pseudo-Voigt profiles and the experimental spectra is achieved. In this work, results were accepted when the function converges to a solution and the parameters change less then 0.1% between two iterations.

In the monophasic PZT ceramics we observed that:

(a) a $f = 0.8$ Lorentzian coefficient is suitable for all the compositions;
(b) the fitting of the peaks can be achieved considering that they are symmetric;
(c) the shape of the peaks, i.e. the parameter w and I_0, depends on the hkl index, for samples of the same composition and changes with the composition of the PZT solid solution; and
(d) the integrated intensity relation between the peaks of each phase determined by this program is in good agreement with the one predicted by the X-ray diffractogram simulation program Powder Cell 1.7., and is independent of the composition of the phases (Table 1).

The evolution of w, I_0 and $2\theta(\mathrm{i})$ parameters with the composition for both tetragonal and rhombohedral phases was analysed and the values of these parameters for compositions inside the coexistence phase region were extrapolated. Those values were taken as a first approach in the fitting of the peaks that partially overlap. The adjustment of the peaks followed a least square routine built specially for this system. The individual peaks described by this mathematical functions were also analysed in order to reflect the relative integrated intensity relations for each phase plan reflections.

References

1. Jaffe, B., Jaffe, H. and Cook, W. R., *Piezoelectrics Ceramics*. Academic Press, London, 1971.
2. Kakegawa, 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.
3. Isupov, V. A., Some aspects of the physics of piezoelectric ceramics. *Ferroelectrics*, 1983, **46**, 217–225.
4. 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.
5. 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.
6. 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.
7. 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.
8. Barbulescu, A., Barbulescu, E. and Barb, D., Phase transitions in PZT solid solutions. *Ferroelectrics*, 1983, **47**, 221–230.
9. Isupov, V. A., Properties of $Pb(Ti,Zr)O_3$ piezoelectric ceramics and nature of their orientational dielectric polarization. *Sov. Phys. -Sol. State*, 1968, **10**(4), 989–991.
10. Isupov, V. A., Dielectric polarization of $PbTiO_3$-$PbZrO_3$ solid solution. *Sov. Phys. -Sol. State*, 1970, **12**(5), 1084–1088.
11. Isupov, V. A., Orientational dielectric polarization and phase composition of polycrystalline $Pb(Ti,Zr)O_3$ and $(Pb,Ba)Nb_2O_6$ in strong fields. *Sov. Phys. Cryst.*, 1977, **22**(3), 369–370.
12. Ari-Gur, P. and Benguigui, L., Direct determination of the coexistence region in the solid solutions $Pb(Zr_xTi_{1-x})O_3$. *J. Phys. D: Appl. Phys.*, 1975, **8**, 1856–1862.
13. Benguigui, L., Thermodynamic theory of the morphotropic phase transition tetragonal-rhombohedral in the peroveskite ferroelectrics. *Sol. Stat. Commun.*, 1972, **11**, 825–828.
14. Hanh, L., Uchino, K. and Nomura, S., On the phenomenon of morphotropic tetragonal-rhombohedral phase boundary in the ferroelectric ceramics. *Jpn. J. Appl. Phys.*, 1978, **17**, 637.
15. Isupov, V. A., Characteristics of coexistence of tetragonal and rhombohedral phases in piezoelectric ceramics based on $PbTiO_3$ and $PbZrO_3$. *Sov. Phys. -Sol. State*, 1976, **18**(4), 529–532.
16. Benguigui, L., On the properties of PZT solid solutions: a reply to a comment. *Sol. Stat. Commun.*, 1976, **19**, 979–981.
17. Isupov, V. A., Thermodynamic analysis of phase transitions in perovskite ferroelectrics. *Sov. Phys. -Sol. State*, 1977, **19**(5), 783–786.
18. Isupov, V. A., Comments on the paper X-ray study of the PZT solid solutions near the morphotropic phase transition. *Sol. Stat. Commun.*, 1975, **17**, 1331–1333.
19. Isupov, V. A., Tetragonal-rhombohedral phase boundaries in a piezoceramic of ZTL type. *Sov. Phys. -Sol. State*, 1975, **16**(7), 1370–1371.
20. Kakegawa, K., Mohri, J., Takahashi, T., Yamamura, H. and Shirasaki, S., A compositional fluctuation and properties of $Pb(Zr, Ti)O_3$. *Sol Stat. Commun.*, 1977, **24**, 769–772.

21. Cao, W. and Cross, L., Distribution functions of coexisting phases in a complete solid solution system. *J. Appl. Phys.*, 1993, **73**(7), 3250–3255.
22. 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.
23. 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.
24. Soares, M. R., Senos, A. M. R. and Mantas, P. Q., Phase coexistence in PZT ceramics, accepted for publication in the *J. Eur. Ceram. Soc.*
25. Louër, D. and Langford, J. I., Peak shape and resolution in conventional diffractometry with monochromatic X-rays. *J. Appl. Cryst.*, 1978, **21**, 430–437.
26. 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.
27. Lucuta, P., Ferroelectric-domain structure in piezoelectric ceramics. *J. Am. Ceram. Soc.*, 1989, **72**(6), 933–937.
28. 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.
29. Wakino, K., A new equation for predicting the dielectric constant of a mixture. *J. Am. Ceram. Soc.*, 1993, **76**(10), 2588.