Octahedral tilting, monoclinic phase and the phase diagram of PZT

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Abstract
Anelastic and dielectric spectroscopy measurements on PbZr1−xTiO3 (PZT) close to the morphotropic (MPB) and antiferroelectric boundaries provide new insight into some controversial aspects of its phase diagram. No evidence is found of a border separating monoclinic (M) from rhombohedral (R) phases, in agreement with recent structural studies supporting a coexistence of the two phases over a broad composition range x < 0.5, with the fraction of M increasing toward the MPB. It is also discussed why the observed maximum of elastic compliance appears to be due to a rotational instability of the polarization linearly coupled to shear strain. Therefore it cannot be explained by extrinsic softening from finely twinned R phase alone, but indicates the presence also of M phase, not necessarily homogeneous.

A new diffuse transition is found within the ferroelectric phase near x ∼ 0.1, at a temperature T_{IT} higher than the well established boundary T_T to the phase with tilted octahedra. It is proposed that around T_{IT} the octahedra start rotating in a disordered manner and finally become ordered below T_T. In this interpretation, the onset temperature for octahedral tilting monotonically increases up to the antiferroelectric transition of PbZrO3, and the depression of T_T(x) below x = 0.18 would be a consequence of the partial relief of the mismatch between the average cation radii with the initial stage of tilting below T_{IT}.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
In spite of a prolonged and intensive research activity on the ferroelectric perovskite PbZr1−xTiO3 (also called PZT 100(1 − x)/100x) and related compounds, unsettled issues remain on its phase diagram and on the microscopic mechanisms that make it the most used piezoceramic material in many applications. The highest electromechanical coupling is obtained at compositions x ≲ 0.5, near the morphotropic phase boundary (MPB), which separates the rhombohedral (R) from the tetragonal (T) region in the x–T phase diagram [1, 2]. For decades such a high electromechanical coupling had been attributed to a coexistence of R and T domains near the MPB, with consequent ease for polarization to change direction through domain switching or domain wall motion. In 1999 Noheda et al [3] found that below the MPB of PZT 52/48 the structure is monoclinic (M), intermediate between R and T. This discovery stimulated extensive investigations to better characterize such an intermediate phase, where the direction of the polarization can in principle rotate continuously between the T(001) and R(111) directions; this provides an appealing explanation for the enhanced ease for polarization to change direction under an external stress or electric field at the MPB. Yet, there is no consensus on the nature or even existence of the M phase, but a range of alternatives from its existence as uniform phase in a narrow composition range, its coexistence with the R phase in a broader range, or actually a fine mixture of R and T domains or finely twinned R domains behaving on the average as monoclinic. The debate has been recently reviewed [4–6].
and involves the mechanisms of rotation and switching of the polarization.

The situation is confused also on the Zr-rich end of the phase diagram, where the ferroelectric R phase approaches the antiferroelectric orthorhombic one. Here electron, but not neutron or x-ray, diffraction experiments reveal superlattice peaks incompatible with the R structure, variously attributed to rotations of the O octahedra [7, 8] or to antiferroelectric-like cation displacements away from the average (111) direction [9, 10].

Structural studies in these critical composition ranges face the problem of analyzing structures of domains with very short coherence lengths and possibly of different coexisting phases, so that information from other techniques, although not providing direct information on the cell symmetry, may prove useful in clarifying some issues. We present anelastic and dielectric spectroscopy measurements, which provide new insight into these debates, and we attempt to rationalize the phase diagram of PZT regarding the tendency of the O octahedra to tilt.

2. Experimental and results

The ceramic samples of PbZr$_{1-x}$Ti$_x$O$_3$, with Ti fractions $x = 0.11, 0.14, 0.17, 0.42, 0.45, 0.452$, were prepared similarly to a previous study [11] with higher values of $x$ (0.455, 0.465, 0.48 and 0.53), with the mixed-oxide method. The starting oxide powders were calcined at 800 °C for 4 h (700°C for $x = 0.1$), pressed into bars and sintered at 1250°C for 2 h, packed with PbZrO$_3$ + 5 wt% excess ZrO$_2$ in order to maintain a constant PbO activity during sintering. The powder x-ray diffractograms did not show any trace of impurity phases and the densities were about 95% of the theoretical ones. The sintered blocks were cut into thin bars 4 cm long and 0.6 mm thick, whose major surfaces were made conducting with Ag paint.

The dielectric susceptibility $\chi(\omega, T) = \chi' - i\chi''$ was measured with an HP 4194 A impedance bridge with a four wire probe and an excitation of 0.5 V mm$^{-1}$, between 0.2 and 500 kHz. The heating and cooling runs were made at 0.5–1.5 K min$^{-1}$ between room temperature and 540 K in a Delta climatic chamber.

The mechanical analogue of the dielectric susceptibility is the elastic compliance $s = s' - is''$, which was obtained as the reciprocal of the dynamic Young’s modulus $E(\omega, T) = E' + iE'' = s^{-1}$. It was measured between 100 and 750 K by electrostatically exciting the flexural modes of the bars suspended in vacuum on thin thermocouple wires [12]. During the same run the first three odd flexural vibrations could be tested, whose frequencies are in the ratios 1.5:4:13.2. The angular frequency of the fundamental resonance is $\omega \propto \sqrt{E}$, and the temperature variation of the real part of the compliance is given by $s(T)/s_0 \propto \omega_0^2/\omega^2(T)$, where $\omega_0$ is chosen so that $s_0$ represents the compliance in the paraelectric phase. The imaginary parts of the susceptibilities contribute to the losses, which are presented as $Q^{-1} = s/\dot{s}$ for the mechanical case and $\tan\delta = \chi''/\chi'$ for the dielectric one.

![Figure 1. Anelastic spectrum of PZT 90/10 measured at 1.8 kHz during heating and cooling.](image)

Figure 1 presents the anelastic spectrum of PZT 90/10. The peak in both the real and imaginary parts of the compliance at $T_C = 532.7$ K, with 1.6 K hysteresis between heating and cooling, signals the transition between cubic paraelectric and ferroelectric phases, while the anomaly at $T_T = 368$ K with a hysteresis of 1 K corresponds to the transition from the high-temperature rhombohedral $R3m$ (R) to the low-temperature tilted $R3c$ ($R_L$) phase, often labeled as $R_{11}$ and $R_3$ respectively. These temperatures fall exactly on the well known phase diagram of PZT, as shown in figure 7 below. There is, however, an additional broad step in $\dot{s}$ , without any counterpart in $Q^{-1}$, at the temperature $T_{IT} \approx 477$ K, which we identify as the onset of an intermediate tilt pattern of the octahedra, before the final tilt pattern develops below $T_T$.

A signature of this new transition is present also in the dielectric susceptibility as a broad step in tan$\delta$ and a hardly discernible hump in $\chi'$. This is shown in figure 2, together with the anomalies at $T_C$ and $T_T$. The dashed arrows in figure 2 are the transition temperatures deduced from the anelastic spectra in figure 1. The elastic compliance is peaked at a somewhat lower temperature than the dielectric susceptibility at the ferroelectric transition, as already observed [14], and the same is true for the tilt transition, but it should be noted that since the two susceptibilities are differently coupled to the order parameter, the shapes of their anomalies have to be different from each other.

In order to check that there is indeed a structural transformation at $T_{IT}$, we verified that the step in $s(\omega, T)$ is independent of the measuring frequency $\omega/2\pi$, temperature
rate and polarization state. In fact, the susceptibility curves may be affected by various processes, especially in the presence of strong domain wall relaxations, as is the case below the ferroelectric transition. When the temperature rate is such that the domain configuration is kept far from equilibrium, the susceptibility curve generally drops when the temperature rate is decreased and partial aging proceeds. This occurs also in certain temperature and composition ranges of PZT, where marked irregularities may be induced in the $s(\omega, T)$ curves by varying the temperature rate. We will not discuss such phenomena, and only mention that they can be reduced by keeping the temperature rate as constant and low as possible, and their amplitude is larger at lower measuring frequency.

Figure 3 shows that the anomaly at $T_{IT}$ is instead perfectly reproducible and independent of all these variables. Curve 1 (dashed) was measured in the initially polarized state of the sample, obtained by application of 3 kV mm$^{-1}$ at 120°C for 40 min. The temperature rate was $+1.3$ K min$^{-1}$, except near $T_T$, where it was lowered to 0.8 K min$^{-1}$ in order to get enough accurate and closely spaced data points; the run was extended up to 580 K, hence losing the polarization. Curve 2 (solid) is the subsequent heating run at $3 \pm 1$ K min$^{-1}$. The imaginary part is always above the previous run both because of the higher density of relaxing domain walls in the unpoled state, and because at the higher temperature rate such walls are more out of equilibrium. Yet, the real parts are practically coincident until $\sim 430$ K, where they start slowly departing from each other due to the increasing influence of the ferroelectric domain wall relaxation. The other three curves (empty circles) were measured during the third heating run at 2–3 K min$^{-1}$ until $\sim 430$ K and 0.13 K min$^{-1}$ above that temperature; the frequencies were $f_1 = 1.8$ kHz, $f_2 = 9.7$ kHz and $f_3 = 24$ kHz. The important point is that both steps at $T_T$ and $T_{IT}$ are practically the same in all the $s'$ curves. This is true also for the peak in $Q^{-1}$ at $T_T$, while the differences in the $Q^{-1}(\omega, T)$ curves at higher temperature and particularly the drop when the rate is lowered to 0.13 K min$^{-1}$ have to be attributed to the tail of the domain wall relaxations below $T_C$. There is an additional peak or kink around 455/460 K in the $Q^{-1}(\omega, T)$ curves, which does not appear to be connected with anomalies in the real part and will be ignored. The lack of a peak in $Q^{-1}$ at $T_{IT}$ and the independence on frequency of the step in $s'$ also exclude that the anomaly is caused by relaxation of any type of defect. Figure 3 therefore demonstrates that at the origin of the anomaly at $T_{IT}$ there is a somewhat broadened but otherwise well behaved phase transformation. We will consider $T_{IT}$ as the temperature of the upper edge of the rounded step in $s'(T)$, analogously to $T_T$, where the assignment is corroborated by the peak in $Q^{-1}(T)$.

In order to draw a $T_{IT}$ line in the phase diagram, we also measured the two concentrations $x = 0.14$ and 0.17, whose compliances are plotted together with that of $x = 0.10$ in figure 4. The step at $T_T$ shifts to higher temperature according to the usual phase diagram, though it acquires a peaked component, particularly evident at $x = 0.14$, while the broader step at $T_{IT}$ shifts to lower temperature merging with $T_T$. That an anomaly exists for $x = 0.14$ around 430 K is evident by comparing with the curve of $x = 0.17$. Both curves are practically coincident above 470 K and run parallel to each other below the step at $T_T$, but the $x = 0.14$ curve has a clear
Figure 4. Anelastic spectra of PbZr$_{1-x}$Ti$_x$O$_3$ with $0.10 \leq x \leq 0.17$ measured at 1.8 kHz during heating.

bump indicated by the arrow, whose precise shape is, however, difficult to evaluate. An even more attenuated anomaly might exist also for $x = 0.17$, even closer to $T_T$, but it is not actually distinguishable.

2.2. Compositions near the MPB

The measurements on the samples at higher Ti content are similar to those already published [11] and a selection of them, including some from [11], is presented in figure 5. With increasing $x$, the anomaly at $T_T$, marked by vertical lines, becomes more diffuse and the spike in $Q^{-1}$ gradually transforms into a step of increasing amplitude, at least until it occurs in the R/M phase, when $x < 0.5$. This is consistent with the observation of a diffuse tilt transition by neutron diffraction in PZT 60/40 [15, 16]. The step in $s'$, instead, decreases its amplitude and becomes hardly visible due to the peak at $T_{MPB}$. The latter has been attributed to the ability of the polarization to continuously rotate in the M phase between the T and R directions [11]. The analysis of the anomaly at $T_T$ is also hindered by a broad peak in the losses around 200–350 K, labeled $R_2$ in [11], and whose frequency dispersion indicates a relaxational origin rather than a phase transformation. It appears also as a frequency-dependent hump in $s'$ and is indicated by arrows in figure 5 (the dependence on frequency is not shown). Except for the amplitude of the $s'(T_{MPB})$ peak, the curves with $x = 0.45, 0.452, 0.455$ and 0.465 are very similar to each other, with $T_T$ signaled by a weak step in $s'(T)$ and a small cusp in $Q^{-1}(T)$, which at first appear as qualitatively different from the clear step in $Q^{-1}$ at $x = 0.48$. The difference in the $Q^{-1}(T)$ curves, however, may be less important than it appears, because one must take into account the maximum $R_2$, which loses importance with respect to the spike/peak at $T_T$ on approaching the MPB. It is therefore possible that, if one were able to decompose the curves into the two contributions, $R_2$ and the anomaly at $T_T$, the latter would result as a broadened step already at $x \simeq 0.46$.

Figure 5. Anelastic spectra of PbZr$_{1-x}$Ti$_x$O$_3$ with $x = 0.1, 0.42, 0.455, 0.48$ and 0.53 measured at 1–1.8 kHz. The vertical lines mark $T_T$, while the arrows mark the relaxation $R_2$ (the three highest $x$ are from [11]).

Figure 6. Elastic compliance of PbZr$_{1-x}$Ti$_x$O$_3$ with $x = 0.42, 0.45, 0.452, 0.455, 0.465$ and 0.53 measured at 1–1.8 kHz.

The main feature of the spectra near the MPB, however, is the $s'(T_{MPB})$ peak, which becomes extremely high and sharp in the narrow composition range $0.455 < x < 0.48$. This had already been discussed [11] but appears even more outstanding when the spectra at the new compositions are added, as in figure 6.
Figure 7. Phase diagram of PZT with the following phases: C paraelectric cubic Pm\̅3m, O antiferroelectric orthorhombic Pbmm, all the other phases are ferroelectric: T tetragonal P4mm, R + M mixed rhombohedral R3m + monoclinic Cm, (R + M)\(_L\) mixed tilted rhombohedral R3c + monoclinic Cm, (R + M)\(_T\) rhombohedral + monoclinic with intermediate tilt. The filled circles are the transition temperatures deduced from our measurements here and in [11]. The dashed lines are proposed here and the hatched region is that where the anisotropy of the free energy has its minimum, as deduced from the amplitude of the \(s'\) (\(T\_MPB\)) peak.

3. Discussion

Figure 7 presents the commonly accepted phase diagram of PZT [1, 17] (solid lines) together with the points deduced from our anelastic spectra, including those of [11]; the dashed lines pass through our data and are drawn as explained in the following paragraphs, but further measurements are necessary in order to confirm their exact shape. The new anelastic and dielectric experiments presented here contain essentially two results: the existence of a novel phase transformation at \(T\_TT\) below \(x \approx 0.17\) and the confirmation that there is a perfect continuity of the \(T\_T(x)\) line of the onset of octahedral tilting up to the MPB, while \(T\_T\) in the T phase is lower than the extrapolation from the MPB.

The phases are the following: C is paraelectric cubic Pm\̅3m, O is antiferroelectric (AFE) orthorhombic Pbmm with the octahedra rotated by the same angle in anti-phase along the pseudocubic directions [100] and [010] (\(a^-a^-c^0\) in Glazer’s notation [18]) and antiferroelectric shifts of the cations along [110] [10, 19]. All the other phases are ferroelectric (FE), those just below the Curie temperature \(T\_C\) having unrotated octahedra: T is tetragonal P4mm with polarization along [001], R is rhombohedral R3m with polarization along [111], M is monoclinic Cm with the polarization along a direction intermediate between T and R. Below the \(T\_T\) border the octahedra rotate giving rise to R\(_L\) rhombohedral R3c (\(a^-a^-c^-\)), T\(_L\) tetragonal P4cm with tilt pattern \(a^0a^0c^-\), as predicted by first-principle calculations [20] and recently verified by neutron diffraction at 5 K [21]. The presence of a low-temperature monoclinic Cc phase [22] with tilt pattern \(a^-a^-b^-\) intermediate between R\(_L\) and T\(_L\) has been excluded by a recent neutron diffraction experiment on single crystals [23]. According to this study below \(T\_T\) there is coexistence of tilted R3c and untilted Cm phases. Our techniques cannot distinguish between R3c+Cc and R3c+Cm and therefore we simply label this as (R + M)\(_L\). The nature of the monoclinic phases, highly debated, and of the new intermediate phase (R + M)\(_T\) are discussed next.

3.1. MPB and search for the R/M border

The phase diagram proposed by Noheda et al [17, 24], and since then commonly adopted and reproduced with first-principle calculations [20], contains an almost vertical border between the R and M phases within the MPB range at \(x_{R,M} \approx 0.455\), but the presence of this border is contradicted by recent neutron diffraction experiments. The results of one of them [16] are much better refined in terms of monoclinic Cm rather than R structure at \(x = 0.4\), well within the supposed R region. In the other experiment [6] it is established that in ceramic samples the R and M phases coexist over the whole composition range from the orthorhombic (O) phase to the MPB, with the fraction of M phase increasing toward the MPB. The actual relative fraction of the two phases, and some details of the atomic displacements depend on the preparation technique and a pure R phase can be obtained in single crystals with \(x \leq 0.1\) [6, 25, 26] or slightly exceeding 0.3 but only in the untilted phase [23]. In addition, there is considerable debate about the role of the short length scale of the T, R and M domains near the MPB [27] and of the high density of domain boundaries or microtwinnings of the R domains, that may constitute an adaptive phase with the average properties attributed to the M phase [21, 28–32]. First-principle calculations do not solve the issue, since in some studies a stable monoclinic ground state is found [33] but in other cases is excluded [34, 35].

In our data there is no sign of an R/M border, at least within the interval 0.42 < \(x < 0.48\). In fact, the \(T\_T(x)\) line is perfectly continuous within that interval, and the anelastic spectra exhibit a smooth evolution from \(x = 0.42\) to 0.465 and probably also 0.48, as discussed in the explanation of figure 5. Moreover, the anelastic spectra do not have any sign of an additional M/R phase transition, expected if the M/R border existed for \(x > 0.42\) and were not vertical, as in the theoretical phase diagram obtained from first-principle calculations [20]. Of course, the absence of an M/R boundary is natural in the hypothesis that the M phase is actually the average of an adaptive microtwinned R phase.

3.2. M versus R/T adaptive phase and the role of anisotropy and size

The different conclusions of the various analyses based on thermodynamic approaches and first-principle calculations reflect the different choices for carrying out the calculations, like to which power order to stop the free energy expansion or which point symmetries to include in the ground state calculations, but they also probably reflect the fact that the
border between a true M phase and an adaptive one is indeed vague. The MPB is the locus in the phase diagram where the anisotropy of the free energy changes over from stabilizing the R phase to the T phase. The main anisotropic term in the Landau expansion in terms of powers of the polarization $\mathbf{P}$ is $\propto (P_4^+ + P_4^- + P_4^0)$ or its complement $(P_4^4 + P_4^2P_2^2 + P_2^4)$, with extrema in the $(100)$ or $(111)$ directions, depending on the sign, which stabilize the R or T phase. Including terms of the sixth order, the anisotropy acquires extrema also along directions stabilizing the O phase, while it is necessary to include eighth order terms in order to stabilize the M phase [36], and the most general treatment requires terms up to the twelfth order [37].

At the MPB the anisotropic term of fourth order changes sign and therefore vanishes [38, 39]: the material is isotropic with respect to polarization, at least up to the fourth order in $\mathbf{P}$, and one has a transverse or rotational instability of $\mathbf{P}$ [40] accompanied by divergence of the transverse dielectric susceptibility and some enhancement of the corresponding shear compliance $s_{44}$ [41]. A divergence of the compliance needs the more stringent condition for the transition between the T and O phases, including the sixth order terms [41], but this is not the case for PZT, which does not have an O phase at the T and O phases, including the sixth order terms [41], but needs the more stringent condition for the transition between the M phase [36], and the most general treatment requires terms up to the twelfth order [37].

The theoretical expressions of the compliances from an expansion of the free energy up to the eighth order are certainly cumbersome, but it is not necessary to work them out in order to establish that a divergence of $s_{44}$ is expected also at the T/M border. In fact, we provided a simple geometrical argument [11] that in the case that an M phase exists in which $\mathbf{P}$ can continuously tilt from the T to the R directions with little change of the magnitude, the rotation angle from the original T direction, or equivalently the transverse polarization, acts as an order parameter [42] and is almost linearly coupled to the strains of symmetry $\Gamma_{5-} (\epsilon_{33}, \epsilon_{55} \text{ and } \epsilon_{65} \text{ in Voigt notation})$, thereby causing a divergence in the respective compliance $s_{44}$ [43, 44]. Accordingly, we interpreted the maximum in the compliance at the MPB, particularly pronounced at $x = 0.465$, as due to this rotational instability in the M phase [11]. The conditions for a divergence or peak in the elastic compliances $s$ [41] are more stringent than those for the dielectric susceptibilities [45] or piezoelectric constants [37] and therefore the amplitude of the $s$ (T$_{\text{MPB}}$) peak can be considered as a good indication of the degree of isotropy of the free energy. From figure 6 it appears that the rotational or transverse instability is maximum within the range $0.455 < x < 0.48$ and $300 \text{ K} < T < 400 \text{ K}$, and this region is hatched in the phase diagram of PZT in figure 7 as the locus where the anisotropy of the free energy has its minimum.

The main arguments against a true M phase are that it is very unlikely that PZT is so anharmonic as to require terms up to the eighth power of $\mathbf{P}$ in the expansion of the free energy [32, 39]. As a consequence, the real structure should be R, but with fine twinning thanks to the near isotropy at the MPB, which lowers the energy of the domain walls. Such an adaptive phase, analogous to the heavily twinned phases in martensites, would produce diffraction patterns easily confused with a homogeneous M phase and would also cause extrinsic softening [32, 39]. The first part of the argument is certainly convincing for an ideal homogeneous crystal, but PZT has both quenched strain fields from the cation disorder [36] and also internal fields from the domain configuration, which present particularly wavy and strained walls in the R phase [30]. While these microstructural and internal strains may let the diffraction patterns of the R phase appear as a homogeneous M phase, they also modify the local anisotropy, acting as higher order terms in the free energy expansion and stabilizing an M phase [36]. We would therefore expect that there are regions where a real M phase is formed, although with cell parameters and direction of the polarization dependent on the local field. A border between a mixed M + R [6] and a polar glass state [32] is probably impossible to establish, and the balance between the two descriptions may also depend on the sample preparation and microstructure, and whether the sample is bulk ceramic or thinned for electron microscopy. In this respect, we just mention that the density of domain walls depends on the grain size, in the case of thin grains as the square root of their thickness [46, 47], and on doping [48].

### 3.3. M versus adaptive phase and the role of frequency

Here we would like to point out an aspect that distinguishes between M, not necessarily homogeneous, and microtwinned adaptive R phase and is overlooked in the debate: the dynamics. In fact, an adaptive phase with high density of domain walls having vanishing energies causes extrinsic softening [32, 39], but we are not aware of a detailed theory of its frequency and temperature dependence. We would expect an important contribution of relaxational nature, with a consequent dependence on frequency, and possibly also nonlinear response, none of which we observe [11]. Certainly a complicated and fine domain structure exists, and it may well be at the origin of the nonlinear stress–strain response of PZT [32, 49], but the elastic response to low amplitude excitation that we measure is strictly linear and almost frequency independent. Again, the border between extrinsic softening from fine twinning and intrinsic linear softening due to a rotational instability may be vague, since the vanishing of the orientational free energy barrier brings about a crossover from thermally activated, characteristic of domain walls, to almost phonon-like dynamics, but the peak in $s'$ at $T_{\text{MPB}}$ is definitely more characteristic of the latter.

### 3.4. The octahedral tilt transition

From the present experiments we are not able to establish whether the tilting transition affects both M and R domains in the same manner or not, because we are not able yet to interpret the evolution of the shape and amplitude of the anomaly at $T_T$ with varying $x$ (figure 5), whose analysis is also made difficult by the relaxation $R_2$ (figure 5).
We would like to stress the different origin of the hump corresponding to $R_2$ with respect to the anomalies at $T_T$ and $T_{IT}$, since they all appear similar in the $s(T)$ curves, and it may be tempting to identify $R_2$ as another structural transition, for example tilts in the M phase instead of the R phase. A more careful examination, however, indicates that this is not the case. The anomalies at $T_T$ and $T_{IT}$ have all the characteristics of well behaved, though diffuse, structural transformations, as described above and in [11] for $T_T$: they are perfectly reproducible during heating and cooling, and are independent of frequency and temperature rate. Instead, $R_2$ has none of these characteristics: its amplitude is larger at lower frequency and strongly depends on the temperature rate (data not shown here), so that we attribute it to kinetic effects of the rearranging ferroelectric domain walls or adaptive microtwins, rather than to a phase transformation. A final argument against the involvement of octahedral tilts in the relaxation $R_2$ is that it is observed also in the T phase just below $\sim 300$ K (curve $x = 0.53$ in figure 5), where tilting has never been observed.

The tilted tetragonal phase is predicted to have $I4cm$ space group, based on first-principle calculations [20] and neutron diffraction [21] and Raman spectroscopy [70] observations. A cell doubling transition in the T phase, possibly due to an octahedral anti-phase rotation, was proposed by Ragini et al [50], after the observation in PZT 48/52 of superlattice peaks below 189 K and anomalies in the dielectric $\chi$ and resonance frequency, but the temperature of such anomalies is definitely higher than the $T_T$ we found at the same composition [11]. We cannot exclude that the technique of sample preparation has an influence on the position of the $T_T(x)$ line in the high $x$ region, considering that it may affect the fraction of R and M phases [6].

In figure 7 we drew the $T_T(x)$ line straight until the MPB and then again straight with a higher slope in order to interpolate the only available point in the T phase (dashed line). Such a kink at the MPB is not actually observed; it might be either smoother or a more discontinuous step and future work is necessary in order to clarify this point.

3.5. $T_T(x)$ border and the tolerance factor

The occurrence of tilting transitions of the BO$_x$ octahedra is an extremely common phenomenon in ABO$_3$ perovskites, and it has been rationalized in terms of the tolerance factor [51, 52]

$$t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}},$$

which is 1 if the mean ionic radii, usually taken from Shannon’s tables [53], exactly match the A–O and B–O lengths in a cubic cell. When $t < 1$, the B–O bond is too long with respect to the A–O one; hence the A–O–A network exerts a compression over the network of octahedra, which rotate in order to accommodate the mismatch while keeping the B–O bonds long. The A–O bonds are $\sqrt{2}$ longer and therefore weaker and have larger thermal expansion than the B–O bonds; therefore $t$ always decreases on cooling, and when it drops below a critical value, within the interval $0.97 < t < 1$ for most perovskites [54], a tilting transition occurs. The tolerance factor can also be decreased in a solid solution by increasing the mean ionic radius in the B sublattice or decreasing that in the A sublattice. Moreover, a sequence of tilting transitions may occur on cooling and/or changing of the ionic radii, usually through more symmetrical tilt patterns first, like rhombohedral $a^\prime a^- a^\prime$, and then to the more distorted orthorhombic patterns [51, 52]. This framework is widely adopted to explain the phase diagrams of all types of perovskites with chemical substitutions, including the ferroelectric ones [10, 55] and even in the presence of O vacancies [56], and PZT is no exception. The Shannon radii of Ti and Zr in octahedral coordination are 0.605 and 0.72 Å, respectively, yielding $t = 1.027$ for PbTiO$_3$, which indeed undergoes below $T_C$ off-centering of Ti in too large and untitled octahedra, to $t = 0.97$ of PbZrO$_3$, which undergoes an $a^0 b^- b^-$ tilt transition with AFE shifts of the cations [57], having passed through the more symmetrical rhombohedral $a^- a^- a^+$ structure at intermediate compositions. Conforming to the above discussion, the $T_T(x)$ line encloses the region of low tolerance factor, namely low $T$ and low $x$, possibly with some discontinuity when passing from the T to the R + M region, from $x > 0.5$ down to $x = 0.18$. At this point it does not proceed to the maximum value at $x = 0$, but decreases sharply. The departure from the expected monotonic rise has been already noted and explained in terms of competition between the O AFE phase with $a^- a^- c^0$ tilt and the R FE phase; this would cause a frustration of the Pb displacements and consequently inhibit octahedral tilting, which is coupled with such displacements [10].

The presence of a phase transition at a $T_{IT}(x)$ merging with $T_T(x)$ around $x \sim 0.17$ alternatively suggests that the phase (R + M)$_1$, in addition to the cation shifts away from (111), has an initial stage of octahedral tilting. In other words, if a structural transition occurs in that temperature range, it seems more likely that its driving force acts on the octahedral tilting rather than on antiferroelectric cation shifts. In this manner the depression of the boundary of the R3c phase is a consequence of the fact that the mismatch between (Ti/Zr)-O bonds and Pb–O bonds has been relaxed by the first tilting transition at $T_{IT}$ and further cooling below $T_T$ is necessary in order to trigger the final $a^-a^-a^-$ pattern. In this view, the frustration between the FE and AFE phases would mainly broaden and split into two stages the tilting transition, and the depression of the combined $T_{IT} - T_T$ line near $x = 0.17$ is much less important than that of the $T_T$ curve alone. The existence of coupling between tilts and polar modes is recognizable by the effect of the transition at $T_T$ on the polarization [58, 59], and dielectric susceptibility [8] (see also the present data), by the reduction of the extrinsic contribution to the piezoelectric effect in the tilted R3c phase [60] and is also indicated by first-principle calculations [61].

3.6. Nature of the intermediate phase below $T_{IT}$

Although the transition at $T_{IT}$ had never been reported before, the existence of an additional phase of still controversial nature in the PZT phase diagram near the boundary to the
O phase is indicated by electron diffraction experiments. In such experiments, \( \frac{1}{2} [kll] \) reflections have been observed near room temperature, which are incompatible with both the O and R phases, and were at first attributed to in-phase tilting of the octahedra [7]. Later, it was argued that rotations or distortions of the O octahedra would not be sufficient to produce spots with the observed intensities [9]; moreover, in-phase rotations would not produce reflections with \( h = k \), which are instead observed, and are generally unlikely to occur in perovskites with \( t \) only slightly smaller than 1 [10]. The superlattice reflections have therefore been attributed to antiferroelectric shifts of Pb away from (111) in the (110) directions, as in the neighboring AFE O phase. A difficulty in characterizing the new structure is that the superlattice reflections are observed only in electron diffraction, but not in x-ray and neutron diffraction [9]; possible reasons are the small scattering intensities due to the different cross sections in the different techniques, and the occurrence of these atomic displacements as surface effects in the very thin samples used for TEM [9]. Nonetheless, a narrow region of intermediate phase between the AFE O and FE R phases has been proposed [10], untilted \( Pm \) at higher temperature and tilted \( Pc \) below the usual \( T_\text{r} \) border. According to this phase diagram, \( T_\text{IT} \) would correspond to the transition from \( R3m \) to \( Pm \).

While the present measurements on ceramic samples prove that the presence of an intermediate phase below \( T_\text{IT} \) is a bulk phenomenon, we feel that the question whether the transition involves only cation shifts or also octahedral rotations is yet open, in view of the expected small intensity of reflections connected with O shifts [9]. The issue should be clarified by careful neutron diffraction experiments, which are more sensitive to O displacements and do not involve the uncertainties connected with very thin samples where surface effects are important and the actual temperature under the electron beam may be considerably higher than expected.

We can make conjectures on the nature of the transition at \( T_\text{IT} \) based on our susceptibility experiments and on the arguments given above on the driving force for octahedral tilting. If it is indeed an initial stage of the rotations of the octahedra, it may be a tilt pattern intermediate between those of the O and R\(_3\) phases, like \( a^-a^-b^- \) [10], or it may involve the \( M_3 \) in-phase rotation modes [8, 62]. Indeed, although no experimental phonon-dispersion data are available for PbZrO\(_3\) [63], first-principles calculations indicate that the whole \( R_{25} \rightarrow M_3 \) branch is unstable, and not only the \( R_{25} \) mode of anti-phase rotations [64]. It is therefore possible that a combination of the two types of instabilities produces a relatively disordered tilt pattern, which becomes the ordered \( a^-a^-a^- \) (\( R3c \)) or \( a^-a^-b^- \) (\( Pc \)) structure below \( T_\text{r} \). The concept of disordered tilts has been proposed for explaining why the techniques providing snapshots of the local structure, the x-ray absorption spectroscopies EXAFS and XANES and the pair distribution function from neutron diffraction, do not see any change when crossing the tilt transitions of perovskites like NaTaO\(_3\) [65] and PZT [66]. The situation is similar for most of the apparently displacive transformations in perovskites involving off-centering of cations, like the FE transitions in BaTiO\(_3\) and PbTiO\(_3\). The issue has been solved by assuming that those transitions have an important order–disorder component, so that the Ti atoms are off-center also in the cubic phase, but without correlation between different cells [67, 68]. The application of the same concept to the transitions involving concomitant rotations of the octahedra about more than one direction is less obvious, since completely disordered tilts would require excessive distortions of the octahedra. Yet, the idea that the \( R3m \) phase of PZT is untilted on the average but locally tilted has been adopted by other authors [7, 8], also to justify the fact that first-principle calculations indicate the tilted \( R3c \) structure and not the \( R3m \) one as the ground state of PZT [61].

In our case, the initial disorder in octahedral tilting below \( T_\text{IT} \) would be favored by the disorder in the Pb–O–Pb network, and the fact that long-range order settles below \( T_\text{r} \) provides a rationale for the different aspects of the two anomalies: the one at \( T_\text{IT} \) is diffuse due to the frustration of the tilts, while that at \( T_\text{r} \) is sharp. We therefore suggest the following picture near the border with the AFE O phase. The positions of the Pb atoms are slightly shifted away from the (111) FE displacements in a disordered manner, due to the frustration between the FE and AFE phases [10]. This type of disordered Pb displacement has also been proposed to exist at compositions near the MPB, based on neutron diffraction experiments, and has been put in relationship with the monoclinic distortions [9, 23]. The disorder in Pb positions does not need to set in below \( T_\text{IT} \) and may exist already just below \( T_\text{c} \), but it does not change the average Pb–O bond lengths; hence the average pressure exerted by the Pb–O network on the octahedra and the temperature of the onset of the tilt instability should be little affected. The disorder in the Pb–O network, rather than depressing the tendency to tilting, would make the tilts disordered. On further cooling, the long-range elastic interactions would trigger the ordering into the final \( a^-a^-a^- \) pattern below \( T_\text{r} \).

3.7. Signatures of the transition at \( T_\text{IT} \) in the previous literature

There is abundant literature on PZT near the \( x = 0.1 \) composition, so that it seems appropriate to examine possible signatures of the transition at \( T_\text{IT} \) in previous studies, which had been overlooked because they are smaller and less definite than the anomalies at \( T_\text{r} \).

A first indication of a transition at \( T_\text{IT} \) comes from a minor step in the steeply falling \( P(T) \) curve of PZT 90/10 in figure 6 of [26], although it had not been recognized as such, being less clear than the transition at \( T_\text{r} \). The temperature dependence of the rhombohedral angle \( \alpha(T) \) in PZT 90/10 may also be re-examined. Such an angle is related to the octahedral tilt angle in the R structure [69], and the lack of clear change of slope of \( \alpha(T) \) at \( T_\text{IT} \) was explained [25] as due to dynamic fluctuations of the tilt angle above \( T_\text{r} \), an explanation very similar to the assumption of an R\(_1\) phase of disordered tilts. The difference is that the tilt disorder in the R\(_1\) phase would not be dynamic but almost static with onset around \( T_\text{IT} \).
The fact that the local symmetry of PZT 90/10 is lower than rhombohedral is confirmed by recent infrared and Raman spectroscopy experiments [62], where several additional modes are observed, besides those of a uniform R phase. Such modes are compatible with the additional disordered Pb shifts in the orthorhombic directions [9, 10] but also with the $M_2$ in-phase tilt mode of the O octahedra [62], which, together with the anti-phase $R_{25}$ mode, would produce a disordered tilt pattern. In the same study, dielectric susceptibility curves of PZT 90/10 are shown, which are very similar to those of figure 2, except for the lack of a clear anomaly at $T_{IT}$; the hump in the imaginary part, however, appears with 2% La doping [62].

4. Conclusions

New anelastic and dielectric spectroscopy experiments are presented on PbZr$_{1-x}$Ti$_x$O$_3$ with $0.1 < x < 0.17$ and $0.42 < x < 0.452$, providing new information on the phase diagram of PZT at the critical compositions near the antiferroelectric and morphotropic borders. The peak in the elastic compliance, whose amplitude and sharpness are maximum in the narrow composition range $x = 0.465 \pm 0.005$, in the middle of the MPB, is associated with the transverse instability of the polarization and therefore with the minimum of the anisotropy of the free energy. It is discussed why its frequency dependence and linearity can hardly be explained by finely twinned R phase alone, and rather indicate the presence of a monoclinic phase, possibly stabilized by the internal random strains and coexisting with the rhombohedral one. The $T_F(x)$ line is also shown to be perfectly continuous up to the MPB, which, together with the smooth evolution of the anelastic spectra with varying composition, provides evidence against a clear border between rhombohedral and monoclinic phases, and rather confirms the recent structural studies where the two structures are found to coexist over a broad composition range.

At $x = 0.1$, a new diffuse phase transformation is found at $T_{IT} \approx 480$ K, which is interpreted as the onset of disordered tilting of the O octahedra, before the long-range ordered tilt pattern develops at the well established sharp transition at $T_T = 368$ K. Indications of such a phase transformation from earlier literature are also reported. On increasing Ti content, $T_{IT}$ decreases and merges with $T_T$ around $x \sim 0.17$. In this interpretation, the onset temperature for octahedral tilting monotonically increases from $T_T = 0$ within the Ti-rich tetragonal phase up to the antiferroelectric transition of PbZrO$_3$. The well known depression of $T_F(x)$ below $x = 0.18$ would be due to the fact that the mismatch between the cation radii is partially relieved at the initial transition at $T_{IT}$. The combined $T_{IT} - T_T$ border presents a much shallower depression near $x = 0.17$, but further anelastic and dielectric experiments at additional compositions with $x < 0.25$ are necessary to clarify the exact shapes of the borders of the phase diagram, for example if the $T_{IT}$ line merges with $T_T$, as depicted in figure 7, or crosses it and proceeds, as proposed by Woodward et al [10]. Yet, the exact nature of the intermediate phase or phases close to the border with the AFE O phase should be clarified by additional diffraction experiments, analyzed with the consciousness of the existence of a transition at $T_{IT}$.

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