Lead-titanate zirconate PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) is a ferroelectric perovskite widely used in applications, especially due to its large piezoelectric response, and its phase diagram is known since several decades [1]. Yet, there is a resurgence of interest for this material, especially focused on the so-called morphotropic phase boundary (MPB) region, $x \approx 0.44 - 0.52$, separating the Ti-rich tetragonal (T with space group $P4mm$) phase from the rhombohedral one (R = $R3m$). The numerous recent neutron, X-ray and electron diffraction studies have been reviewed in Refs. 2, 3, but still new features are appearing [4]. The two ferroelectric phases are connected by an intermediate monoclinic (M = C$m$) phase, where the direction of the polarization vector is intermediate between the T and R structures; in addition, below $\sim 200$ K a doubling of the monoclinic cell has been reported [5], which seems analogous to the transition from high- to low-T rhombohedral structure (from $R3m$ to $R3c$) at lower $x$, with antiphase rotations of the O octahedra about the [111] pseudocubic axis.

On the theoretical side, Hahn [6] proposed a comprehensive description of the PZT phase diagram known at that time, without M phase, based on the Landau expansion of the free energy in powers of the polarization up to the sixth order [7]; after the discovery of the M phase, attempts have been made to obtain such a phase within the same scheme, by introducing an additional order parameter [8], an additional tetragonal invariant [9], or terms beyond the sixth order [10]. Also microscopic descriptions have been provided, based on first principle calculations [11, 12], and recently the inclusion of antiferrodistortive degrees of freedom allowed the known phases of PZT to be reproduced, plus an additional low-T tetragonal variant, again involving rotations of the octahedra [13].

We present anelastic and dielectric spectroscopy measurements of PbZr$_{1-x}$Ti$_x$O$_3$ with $0.455 \leq x \leq 0.53$, providing new information on the nature of the T-M transition and confirming the existence of a further low-temperature transformation in the M phase and even in the T one beyond the MPB region [4].

The ceramic samples have been prepared by the mixed-oxide method; the starting oxide powders were calcined at 800 °C for 4 hours, pressed into bars and sintered at 1200 °C for 2 h, packed with PbZrO$_3$ + 5wt% excess ZrO$_2$ in order to maintain a constant PbO activity at the sintering temperature. The absence of impurity phases was checked by powder X-ray diffraction and densities were about 96% of the theoretical ones. The ingots were cut into bars 4 - 5 cm long and 0.5 - 0.6 mm thick. Electrodes for the anelastic and dielectric spectroscopy measurements were applied with silver paint and the samples were annealed in air at 750 °C for avoiding any effects from the possibly damaged surfaces after cutting. The dielectric susceptibility $\chi = \chi' - i\chi''$ was measured with a HP 4194 A impedance bridge with a four wire probe and a signal level of 0.5 V/mm, between 200 Hz and 200 kHz. The measurements were made on heating/cooling at 1 - 1.5 K/min between 100 to 530 K in a Delta climatic chamber. The dynamic Young’s modulus $E(\omega, T) = E' + iE''$ or its reciprocal, the elastic compliance $s = s' - is'' = E^{-1}$, was measured between 50 and 750 K by electrostatically exciting the flexural modes of the bars suspended in vacuum on thin thermocouple wires in correspondence with the nodal lines. The real part of the Young’s modulus is related to the fundamental resonance frequency by $\omega/2\pi = 1.028 h/\sqrt{E/\rho}$, where $h$ and $l$ are sample thickness and length and $\rho$ its mass density [12]; these quantities depend on temperature much less than $E$, so that in the following we report $s(T)/s_0 \approx \omega^2(T_0)/\omega^2(T)$ with $T_0 = 750$ K. Also the third and fifth modes could be measured, whose frequencies are 5.4 and 13.3 times greater; the fundamental frequencies of the various samples where $\omega/2\pi \approx 1 - 1.6$ kHz, and the Young’s moduli at high temperature, uncorrected for porosity, were $E_0 = s_0^{-1} = 138$, 139, 134 and 125 GPa for $x = 0.455$, 0.465, 0.48 and 53, respectively.

Figure II presents the dynamic compliance curves nor-
FIG. 1: Anelastic spectra of PbZr$\text{$_1$}_x$Ti$\text{$_4$}_x$O$\text{$_3$}$ with varying Ti/Zr ratio. In the real part, both the cooling/ heating (filled/empty symbols) curves are shown; $f = 1 - 1.6$ kHz at high temperature.

Figures and text insert:

- Normalized to $s_0 = s'$ (750 K) for all samples. It is possible to identify without ambiguities the transition temperatures $T_1$ between paraelectric cubic (C) and ferroelectric T phases, and $T_2$ between T and M. Both produce maxima in $s'(T)$, whose temperatures coincide with the corresponding boundary lines in the PZT phase diagram (see Fig. 4 below); the identification of the maximum in $s'$ at $T_2$ with the T-M transformation has already been proposed [13]. The C-T transition is almost second order, as known for Zr-rich compositions, with small hysteresis between cooling and heating, $\Delta T < 3$ K, and is accompanied by a sharp rise of the losses $s''/s'$ on approaching the T phase. The transition at $T_2$ is clearly first order for $x = 0.455$, with $\Delta T = 35$ K, but $\Delta T$ decreases with increasing Ti content and is almost null at $x = 0.48$. The maximum of $s'$ at $T_2$ is not accompanied by any clear anomaly in the losses, which however exhibit an increase in this temperature region in all samples. Such a broad dissipation maximum, labeled $R_2$, is present also at $x = 0.53$, where no T-M transition occurs, and is found also in the dielectric loss $\chi''/\chi'$, so that we suppose that it is mainly due to relaxational dynamics of domain walls (DW). At lower temperature, there is no clear anomaly in $s'$, while those in $s''$ connected with the transition at $T_3$ will be described below.

A comparison between anelastic and dielectric susceptibilities is presented in Fig. 2 for $x = 0.455$. The temperature hysteresis connected with the T-M transformation is found also in the $\chi'(\omega, T)$ curves, but the maximum in $\chi'$ is much less pronounced than in $s'$, also because it is masked by the rise of $\chi'$ on approaching the ferroelectric transition at $T_1$. Rather, a maximum can be identified in the dielectric loss, as evidenced by the dotted vertical lines. The frequency dispersion at high temperature in $\chi'(\omega, T)$ should be due to the thermally activated motion of mobile charged defects, presumably O vacancies accompanying Pb vacancies formed during sintering, and/or charge carriers from the ionization of such defects; the motion of such charges between the DW under the applied ac field causes a relaxation of the polarization (space charge relaxation [14]). Mobile charges may also produce anelastic relaxation by migrating to the 90° DW that become charged during the sample vibration due to piezoelectric effect [15]; the thermally activated (shifting to higher $T$ for higher $\omega$) tail in $s''/s'$ disappearing with the DW above $T_1$, labeled $R_1$, may be due to both this mechanism and to dissipative motion of DW. The same relaxation is also responsible for the frequency dependent rise of $s' (\omega, T)$ on approaching $T_1$ from below, so that the contribution of the C-T phase transformation is actually a step in $s'$ plus a peaked contribution due to fluctuations responsible for the gradual rise of $s$ on approaching $T_1$ from above.

The step-like behavior of $s'$ at $T_1$ corresponds to the fact that $s$ is the strain susceptibility, and strain $\epsilon$ is coupled to the primary order parameter, the polarization $P$, by terms that are linear in $\epsilon$ and quadratic in $P$ (po-
larization reversal does not change strain). According to the widely used Landau expansion of the free energy in powers of the order parameter, such linear-quadratic coupling yields a renormalization of the elastic constants which has a step at the transition temperature, but no additional temperature dependence \[16, 17, 18\].

We consider now the T-M transition at \(T_2\), mainly signaled by a peak in \(s')\) and temperature hysteresis in all the susceptibilities. The T-M phase transformation is predicted to be second order \[9\] or near-to-second order \[8\] and the crossover to first-order character with decreasing \(x\) may be understood by considering that \(x = 0.455\) is at the boundary between R and M phases (Fig. 4), and the T-R transition must be of the first order, lacking a group-subgroup relationship between the T and R space groups.

A most remarkable feature is the amplitude of the peak in \(s'(T)\), which is even larger than the step at \(T_1\) for \(x = 0.465\) and 0.48; in fact, as noted above for the C-T transition at \(T_1\), coupling terms between polarization \(P\) and strain \(e\) of the type predicted for PZT are linear in \(e\) and quadratic in \(P\), and should therefore yield a step and a not a maximum in the elastic constants. The peak exhibited by \(s (\omega, T)\) at \(T_2\) is frequency independent (see Fig. 2) and therefore cannot be attributed to the motion of domain walls, as for the rising part of \(s(\omega, T)\) below \(T_1\); in addition, it can hardly be attributed to fluctuations, which are not expected to play a significant role for a first-order transition like that at \(x \approx 0.46\) and should also appear in the imaginary part. The most obvious explanation for such a large effect on \(s'\) is a linear coupling between strain and order parameter; in that case, strain follows the order parameter and a Curie-Weiss-like divergence is expected in the corresponding elastic compliance, as in a proper ferroelastics \[16, 17\]. We show that this explanation is possible at a T-M transition characterized by a deviation of the polarization from the tetragonal \(c\) axis with little change of the magnitude, namely \(P_1 = P_2\) gradually increase at \(T_2\) with \(P_3\) remaining almost constant, as supposed by Hudak \[8\] and verified in Monte Carlo simulations \[4\]. The term that couples \(T_{2g}\)-type shears, \(e_i\) with \(i = 4 - 6\) (Voigt notation: \(e_4 = e_{23}\), etc.) with polarization is \[6, 8, 18\]  

\[ F_{P_{2x}} = Q_{44}(e_4 P_2 P_3 + e_5 P_3 P_1 + e_6 P_1 P_2) \]

if at the M-T transition the order parameter is \(P_1 = P_2 \ll P_3 \simeq \text{const}\), then the first two terms become bilinear in \(e_4, P_2\) and \(e_5, P_1\), and the change of the corresponding elastic compliances \(s_{44}\) and \(s_{55}\) is expected \[16, 17\] to be \(\Delta s_{44} = \Delta s_{55} \propto (T_0 - T_1)^{-1}\), where \(T_0 \simeq T_1\) is the temperature at which the Landau coefficient of the term quadratic in \(P\) vanishes. The shape of the peaks in \(s\) even suggests that the divergence occurs at \(T_0 \simeq T_2\), as if there was a new order parameter associated with the transverse polarization \(P_1\) or, almost equivalently for \(P_1 \ll P_3\), to the tilt angle of the polarization away from the \(c\) axis \[7, 8\]. Yet, we are prevented from making a strong statement on this point from the complications involved in the determination of the contributions of these shear elastic constants to the Young’s modulus of the ferroelectric polycrystal, from the temperature dependence of other elastic constants \[8\] and from the possible broadening due to even small inhomogeneities in the Ti/Zr ratio, whose effect is amplified by the steep slope of the \(T_2(x)\) line (25 times steeper than \(T_1(x)\), see Fig. 4).

These measurements address the issues raised by Vanderbilt and Cohen \[9\] on the existence of a softening of a shear elastic constant, as implied by treatments of the M phase in terms of free energy expansions up to the sixth order only, and on temperature hysteresis versus compositional inhomogeneity for explaining the coexistence of T and M phases observed in diffraction experiments \[10\]. The softening of the shear elastic constants \(c_{44}\) and \(c_{55}\) indeed exists and is large at the T-M transition, though we cannot tell with certainty whether the tilt angle of polarization from the \(c\) axis is a real order parameter requiring a new instability \[7, 8\]; the existence of such a softening should anyway serve as a guide in constructing the ever improving microscopic models of PZT and similar ferroelectric perovskites \[4, 10, 11\]. Regarding the nature of the T-M transformation, we confirm that it is second-order well within the M phase, but becomes first-order with temperature hysteresis for \(x < 0.48\), so that the region of coexistence between T and M observed by Noheda (hatched in Fig. 4) does not imply compositional inhomogeneity of their samples.

We discuss now the anomalies at \(T_3\), connected with
the possible onset of octahedral rotations. An experimental $T_3$ line exists only for the R phase, which passes from $R3m$ to $R3c$ with tilting of the O octahedra about [111] directions, while its extension into the M phase is controversial [3, 24, 21], and that in the T phase is only theoretical [4]. In fact, it is still controversial whether superlattice reflections observed in diffraction spectra at liquid He temperatures are due to rotations of the octahedra, with the M phase passing from $Cm$ to $Cc$ [3], or instead to coexistence of the $Cm$ and $R3c$ structures [3, 24, 21]. Figure [3] shows that an anomaly within the M phase indeed occurs in the imaginary parts of the susceptibilities, while nothing noticeable is found in the real parts. The arrows in Fig. [3] point to a transition temperature $T_3$, under the assumption that the elastic losses behave as in most cases at phase transitions, namely with a rise on cooling down to the transition temperature, where a more or less sharp edge is found, depending on frequency (see Fig. [2] at $T_3$); a clear rise is not observed for $x = 0.455$ and 0.465, but it might be absorbed by a decrease of the relaxation $R_2$ (Fig. [1]) and a sharp edge is identifiable. The dielectric loss presents a broader step or peak, whose temperature correlates with that in the $s''$ step; at the higher Ti content, $\chi''/\chi'$ starts changing slope around 120 K, but the step could not be measured because of limitations in the temperature range. The curves in Fig. [3] are measured on cooling exciting the first flexural mode for $s$ and at 1 kHz for $\chi$, but they are perfectly reproduced on heating and an increase of frequency slightly increases the overall dissipation level leaving unchanged the shape and temperature of the anomalies; in addition, they are unaffected by annealing in air at 750 °C in order to eliminate possible surface damage after cutting the samples. These features indicate that a structural transformation indeed occurs at $T_3$ and is a bulk rather than a surface effect, so confirming the extension of the $T_3$ line in the M phase.

The appearance of a clear step in $s''$ even at 53% Ti, well within the T phase, further confirms the prediction of the antiferrodistortive instability also in this phase [3]. Figure [4] presents the established experimental phase diagram [1, 3] together with the recently calculated one [1, 4] (gray lines), and with the transition temperatures deduced from the anelastic spectra: $T_1$ and $T_3$ from the maxima in $s''$ (the error bars indicate the hysteresis between cooling and heating) and $T_3$ from the kink in $s''$.

FIG. 4: Experimental [1, 3] and calculated [4] (gray lines) phase diagram of PZT. The line $T_3$ is the onset of transitions involving rotations of the O octahedra. The full symbols are the transition temperatures deduced from the anelastic spectra: $T_1$ and $T_3$ from the maxima in $s''$ (the error bars indicate the hysteresis between cooling and heating) and $T_3$ from the kink in $s''$.

In terms of Curie-Weiss-like behavior of the $s_{44}$ and $s_{55}$ compliances in the M phase, since the deviation angle of the polarization from the tetragonal c axis is linearly coupled with the $e_{44}$ and $e_{55}$ strains. The low temperature transformation involving antiferrodistortive tilting of the octahedra is confirmed to exist in the M and even in the T phase, at least up to a Ti fraction of 53%.

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