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Pressure-Induced Crossover from Long-to-Short-Range Order in $[Pb(Zn_{1/3}Nb_{2/3})O_3]_{0.905}$ $(PbTiO_3)_{0.095}$ Single Crystal

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Abstract

A pressure-induced crossover from normal Ferroelectric-to-Relaxor behavior has been observed in single crystal $[Pb(Zn_{1/3}Nb_{2/3})O_3]_{0.905}$ $(PbTiO_3)_{0.095}$, or PZN - 9.5% PT. Analogy with similar observations for other perovskites indicates that this crossover is a general feature of compositionally-disordered soft mode ferroelectrics. The Pressure-Temperature phase diagram has been also determined.

Complex mixed ABO_3 oxides of the perovskite family find numerous applications in technology because of their exceptional piezoelectric and dielectric properties.[1] Particularly important are compositions near morphotropic phase boundaries (MPBs) where these properties are anomalously high because of the near degeneracy of the two phases which imparts to the lattice greatly enhanced polarizability and ease of poling. In this regard, one of the most widely used materials has been mixed $PbZr_{1-x}Ti_xO_3$ with $x = 0.47$ (or PZT 53/47) which is essentially at the MPB for the PZT system.[1] Compositions on the Zr-rich side of this boundary have rhombohedral symmetry at room temperature whereas compositions on the Ti-rich side have tetragonal symmetry. Despite their wide use, PZTs suffer from the fact that they are available only in ceramic form, and thus attainable properties are significantly lower than is potentially achievable with single crystals. Numerous attempts, extending over several decades, to grow PZT crystals of suitable size have not been successful.

Fortunately, however, it has been found that single crystals of more complex mixed oxides can be relatively easily grown by a flux method over the whole composition range. Specifically, considerable success has been demonstrated in growing mixed crystals between the relaxors $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) or the isomorphous $PbZn_{1/3}Nb_{2/3}O_3$ (PZN) and ferroelectric $PbTiO_3$ (PT)[2,3]. Of the two systems, (1-x) PZN-xPT (or PZN-x PT for short) crystals have been attracting a great deal of recent interest because ultrahigh piezoelectric ($d_{33} > 2000$ pC/N) and electromechanical coupling ($k_{33} \approx 92\%$) coefficients have been achieved for compositions near the MPB ($x \cong 0.09 - 0.095$).[2,3] These coefficients are much larger than those of PZT 53/47 ceramics and have the potential of greatly advancing transducer/actuator technology.

To better capitalize on these developments, there is a large on-going effort aimed at understanding the physical properties of PZN – xPTs. In earlier work,[4,5] we demonstrated the importance of pressure as a variable in elucidating the physics of ferroelectrics and relaxors, and we have now extended the work to PZN – 9.5% PT. In particular, we have studied the dielectric properties of this crystal as functions of pressure, temperature, frequency and electric field and gained much insight into the physics and phase transitions involved. In this letter we report on one aspect of our results, namely, the observation of a pressure-induced Ferroelectric (FE)-to-Relaxor (R) crossover in the absence of an applied field. We have observed a similar crossover in other mixed perovskites[5,6] suggesting that the phenomenon is a general feature of compositionally – disordered oxide ferroelectrics.

PZN is a classic relaxor akin to PMN.[2,7,8] It exhibits a broad, frequency-dependent peak in the temperature (T) – dependent static susceptibility or dielectric constant (ε'). The peak (~ 410 K) defines a dynamic freezing, or glass transition-like temperature (T_m). As in the case of PMN, symmetry breaking compositional and structural disorder brought about by differences in valence (5+ vs. 2+) and ionic radii (0.64 Å vs. 0.74 Å) between the Nb^{5+} and Zn^{2+} ions on the B site of the ABO_3 lattice is believed to be responsible for the relaxor character of PZN. The symmetry breaking (rhombohedral) occurs at the nanometer scale leading to the formation of polar nano-domains which exist well above T_m and increase in size on cooling, but never become large enough to precipitate a long-range-ordered FE state at T_m.[7,8] Rather, critical slowing down of the polarization fluctuations sets in below T_m. Unlike PMN which retains macroscopic cubic symmetry down to cryogenic temperatures, PZN acquires rhombohedral symmetry (R3m) at room temperature.[2]

PT, on the other hand, is the classic soft FE mode ferroelectric which transforms on cooling from the cubic paraelectric (PE) phase to a tetragonal (P4mm) FE phase at ~ 760 K.[4] Its addition to PZN, even at the $0.05 \leq x \leq 0.15$ level, imparts FE character to the mixed crystals.[2] On cooling such crystals transform from the cubic PE phase to a tetragonal FE phase and then to a rhombohedral FE phase.[2]

The single crystal used was a thin plate (0.22 cm^2 x 0.005 cm) oriented with the pseudocubic (100) axis perpendicular to the large faces.[9] Chrome-gold electrodes were deposited on these faces. All the measurements reported here were performed on the sample in the unpoled state. Pressure was generated in conventional apparatus using either pentanes or helium as the pressure transmitting media.[5]

Earlier work[2, 10] suggested that our PZN - 9.5% PT crystal should exhibit normal ferroelectric behavior at 1 bar, and Fig. 1 shows that this is indeed the case. Shown are the temperature dependencies of the real (ε') and loss (tan δ) parts of the dielectric function. The anomalies in both properties across the tetragonal-cubic transformation are characteristic signatures of ferroelectric transitions. The transformation is remarkably sharp for a complex, compositionally-disordered mixed crystal and is thermodynamically first-order as evidenced by the ~ 5 K thermal hysteresis and as reported recently.[10] The transition temperature T_c, taken as corresponding to the peak in $\varepsilon'(T)$ is essentially independent of frequency. The relatively weak frequency dispersion in $\varepsilon'(T)$ at and above the peak is characteristic of many mixed perovskite ferroelectrics. At lower temperatures than shown in Fig. 1 the sample transforms from the tetragonal to a rhombohedral FE phase. The signature of this transformation is a step in $\varepsilon'(T)$, and the transition is first-order with a large thermal hysteresis.

Modest pressure has a remarkably strong influence on the dielectric response of PZT – 9.5% PT. Up to ~ 3 kbar the main influence of pressure is a shift of T_c to lower temperatures with $dT_c/dP = -6.5$ K/kbar, a value comparable to those of many soft mode perovskite ferroelectrics.[4] This effect can be understood in terms of soft mode theory.[4]

Above a few kbar the response changes qualitatively as shown in Fig. 2. The broad $\varepsilon'(T)$ peaks and the strong frequency dispersion on the low-temperature side at the two pressures shown are the hallmarks of a relaxor phase. These characteristics are seen more clearly in Fig. 3 which shows the response at 15 kbar. This response is the classic relaxor response. Note that there is no thermal hysteresis in T_m.

Figure 2 also shows the $\varepsilon'(T)$ anomaly associated with the rhombohedral-tetragonal transition (on cooling at 5 kbar). The anomaly is not observed on cooling at 10 kbar, and it completely vanishes on either cooling or heating at higher-pressures as seen in Fig. 3. Thus, all vestiges of the "tetragonal phase" vanish above ~ 10 kbar. The inset in Fig. 2 shows the Pressure-Temperature phase diagram for PZN – 9.5% PT.

It is thus clear from the above that our PZN – 9.5 PT crystal exhibits a pressure-induced crossover from normal FE-to-R behavior. There has been considerable interest in the properties of relaxors and the FE-R crossover; however, the physics of relaxors and the mechanism for this crossover phenomenon are still unsettled.[11] Relaxor behavior is very prevalent in compositionally-disordered perovskites. The early conventional wisdom (the Smolenskii model) had been that relaxor behavior and the associated diffuse phase transitions in mixed perovskites at 1 bar are induced by compositional fluctuations leading to large fluctuations in transition temperatures.[12, 13] Thus, a common approach of studying these properties has been to vary the composition, and thereby the degree of disorder, in order to induce relaxor behavior.[11] However, this approach introduces complications such as added randomness, lattice defects, lattice strains, and altered interatomic forces. Consequently, there is considerable vagueness in the interpretation and understanding of such experimental results.

Illuminating insights into the physics of the FE-to-R crossover have come from recent high-pressure studies. It has now been demonstrated that this crossover can be induced by the application of hydrostatic pressure in many compositionally – disordered ABO_3 perovskites of fixed chemical composition,[5,6] in addition to PZN – 9.5% PT, and it is believed to be a general phenomenon in soft FE phonon mode (or highly polarizable) systems. Since pressure clearly does not induce increased compositional fluctuations and disorder, the pressure results brought into question the early mechanism for relaxor behavior in the perovskites. In contrast to changing the composition at 1 bar, pressure changes only the interatomic interactions and balance between long – and short - range forces making it easier to get to the essential physics.

It has been fairly well established that the compositionally-induced disorder in the perovskites, including PMN and almost certainly also in PZN, produces local polar clusters, or nano-domains, which nucleate with decreasing temperature at temperatures much higher than the peak in $\varepsilon'(T)$.[7] These domains are dispersed as islands in the host lattice and result from short-range correlated ionic displacements. We have proposed that both the pressure– and the composition– induced crossover can be explained in terms of a large decrease in the correlation length, r_c, among the polar nano-domains with pressure – a unique property of soft FE mode systems where the soft mode frequency, ω_s, controls the polarizability of the host lattice and, thereby, r_c.[5] Specifically, $\omega_s(r_c)$ increases (decreases) with increasing pressure, and the effects are quite large, the correlation volume decreasing by over an order of magnitude in a few kilobars.[5]

Physically, we envision each disorder-related local dipole inducing polarization (or dipoles) in adjoining unit cells of the highly polarizable host and forming a dynamic "polarization cloud" whose extent is determined by r_c. At high temperatures, r_c is small, and the polarization clouds are effectively polar nano-domains. With decreasing T at low pressures, the rapidly increasing r_c couples these nano-domains into rapidly growing polar clusters and increases their Coulombic interactions. Ultimately, these clusters percolate (or permeate) the whole sample and precipitate a static, cooperative long-range ordered FE state at $T<T_c$. At sufficiently high pressure, on the other hand, the clusters increase in size on decreasing T in the PE phase, but do not become large enough to permeate the whole sample (or grains) to precipitate a FE transition. Rather, the clusters exhibit dynamic "slowing down" of their fluctuations at $T<T_m$ leading to the observed relaxor behavior. Because r_c decreases continuously with increasing pressure, the polar clusters become smaller with increasing pressure

– a fact that accounts for the observed increase in frequency dispersion and the suppression of the dielectric anomally with pressure (Figs. 2 and 3).

We believe that the above picture is applicable to PZN – 9.5% PT. In this crystal we expect two types of local polar nano-domains. The first is associated with the Zn^{2+}/Nb^{5+} -induced disorder, which in pure PZN leads to a low temperature R phase. The second is associated with local, highly polarizable PT nano-domains. It is also quite conceivable to have correlations among the two types of domains, thereby strengthening the driving force for the onset of a FE order. At 1 bar, the relatively large concentration of polar PT nano-domains drive the system into long-range FE order as their polarization clouds become larger on lowering T and ultimately engulf the whole sample below T_c. Modest pressure reduces r_c, sufficiently, reducing the correlations among the nano-domains and resulting in the FE-to-R crossover.

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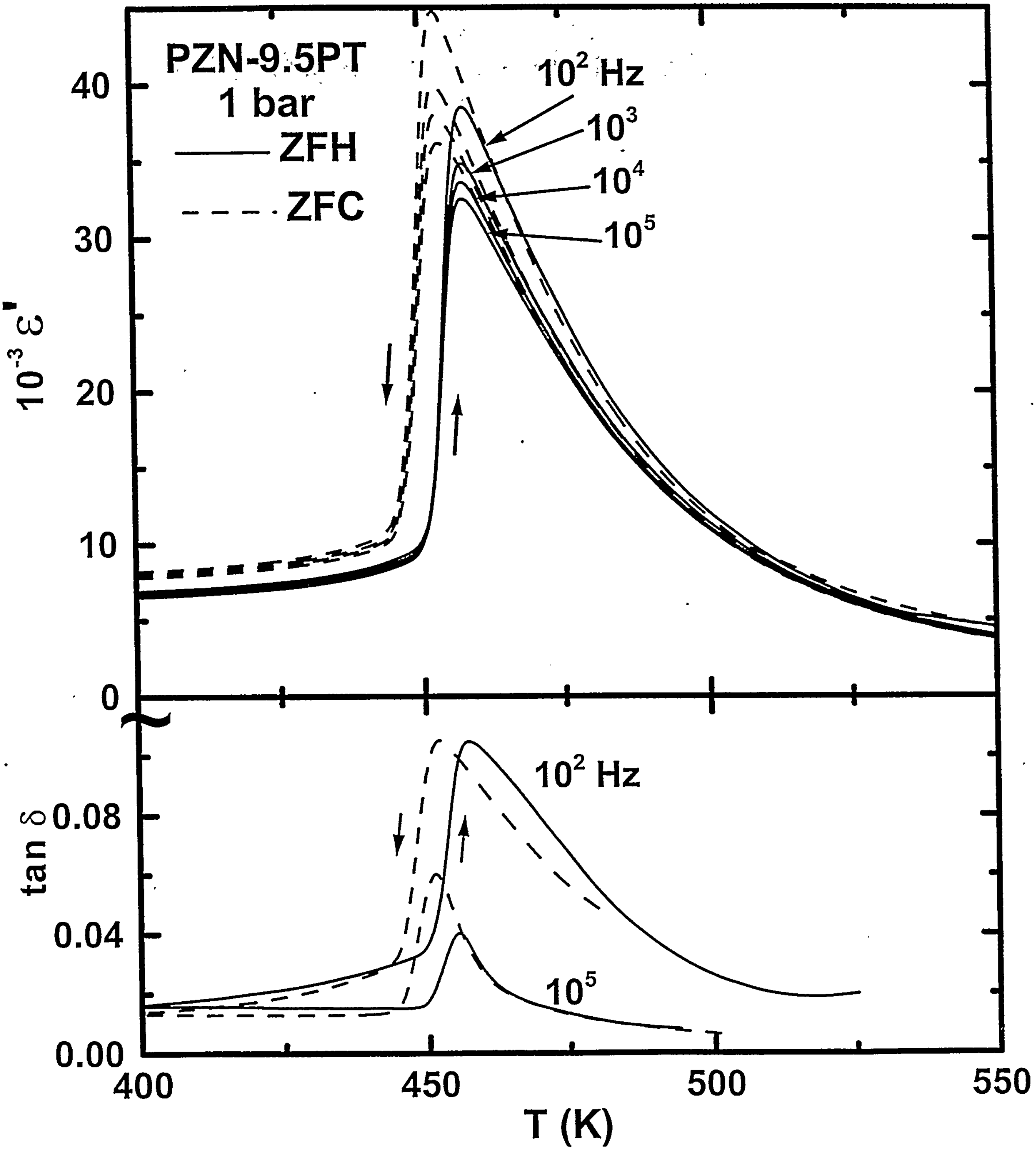
Figure Captions

Fig. 1. Temperature dependences of the dielectric constant (ε′) and dielectric loss (tan δ) of PZN – 9.5% PT at 1 bar. Results for both zero (applied) field heating (ZFH) and zero field cooling (ZFC) are shown.

Fig. 2. Temperature dependence of the dielectric constant (ε′) of PZN – 9.5% PT on ZFC at 5 and 10 kbar. The inset shows a tentative Pressure-Temperature phase diagram.

Fig. 3 Temperature dependences of the dielectric constant (ε′) and dielectric loss (tan δ) of PZN – 9.5% PT at 15 kbar for both ZFH and ZFC.



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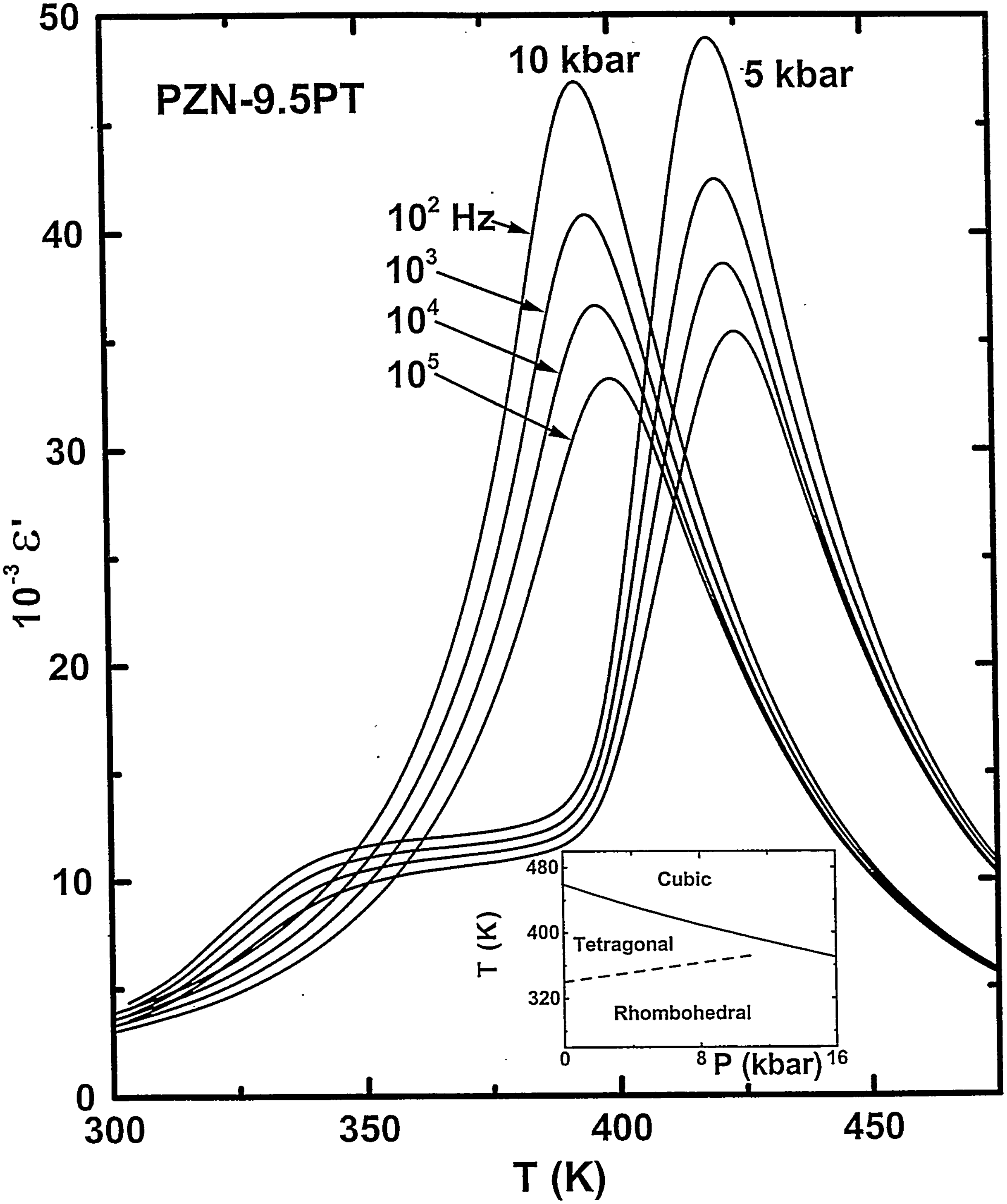

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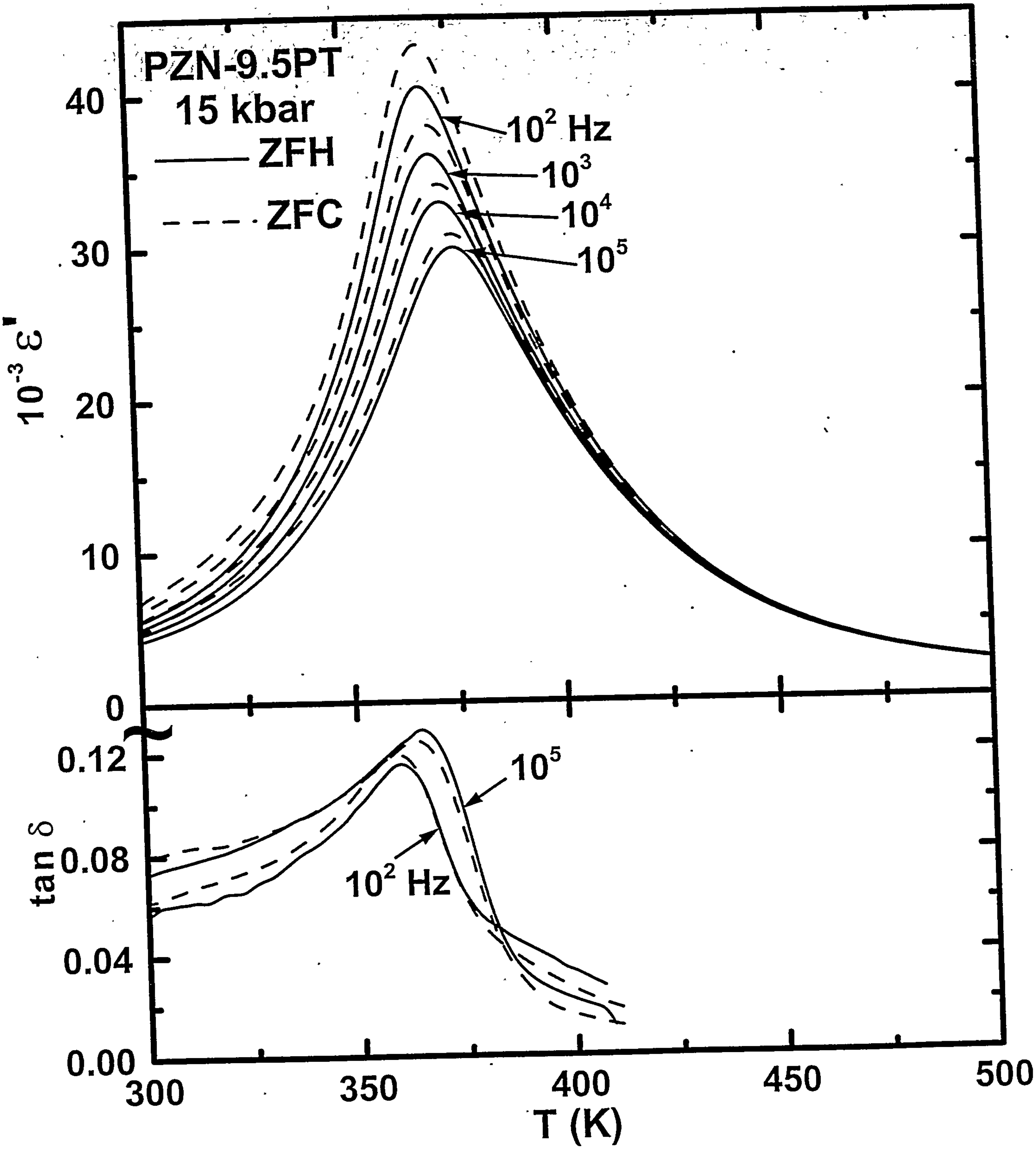

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