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A Raman and dielectric susceptibility study of superparaelectric PLZT ceramics

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Abstract. Raman and dielectric susceptibility experiments have been performed on 9/65/35 PLZT ceramics. Pseudo-first-order Raman scattering is interpreted as resulting from the coupling of hard modes with the quasi-static polarization and/or distortion. An increase of the spatial correlation function of the polarization as the temperature decreases is thus inferred from the behaviour of the intensity of polar modes. Built-in stresses are also suspected to contribute to the intensity of all modes, even at high temperatures. The relaxation of the polarization has been studied between 360 and 480 K using dielectric susceptibility measurements. The corresponding relaxation times are large and most likely related to the motion of ferroelectric nanodomains. When the PLZT ceramics are cooled from high temperature to room temperature, the correlation length of the polarization extends but the simultaneous drastic increase of the relaxation times of the polarization prevents any onset of a ferroelectric long-range order.

1. Introduction

PZT ($\text{PbZrO}_3\text{-PbTiO}_3$) ceramics have been used as actuators for a long time, due to their interesting piezoelectric properties, particularly in the vicinity of the 65/35 (Zr/Ti) composition. At room temperature, these ceramics are ferroelectric with a tetragonal or rhombohedral distortion depending on the Zr/Ti ratio, except for high Zr concentrations, for which an orthorhombic antiferroelectric structure is obtained [1]. Despite the difference in the nature of interactions (antiferroelectric for PbZrO_3 , ferroelectric for PbTiO_3) no competition occurs and all room-temperature phases of this system are rather well defined. Above a Curie temperature which lies between 766 K (PbTiO_3) and 503 K (PbZrO_3), PZT ceramics become paraelectric with a perovskite-type cubic structure. Doping with lanthanum lowers the transition temperature and makes these ceramics transparent to visible light. For lanthanum compositions between about 7% and 12%, the expected Curie temperature should lie near 300 K [2]. Nevertheless no ferroelectric phase can be obtained by cooling the sample down to 200 K [3] and these ceramics are said to exhibit a 'diffuse phase transition', the nature of which is not clearly understood at the moment. It should be noted that, due to their method of preparation and to grain boundaries at which segregation may take place, some heterogeneities in the chemical composition of these ceramics are expected, resulting in local variations of the Curie temperature.

Dielectric susceptibility measurements have been performed by Keve and Annis [3] on 8/65/35 and 9/65/35 compositions, where this notation refers to $x/y/1-y$ in the chemical formula $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ of PLZT. These authors report a rounded maximum

of the real part of the 1.6 kHz permittivity at a temperature T_c lying around 380 K (but depending on x). Furthermore, a ferroelectric phase (named β) can be stabilized by application (and subsequent removal) of an electric or a stress field, provided the temperature is maintained below $T_f \simeq T_c - 100$ K. The structure of the different phases has been proposed by the preceding authors to be cubic above T_c , not well elucidated but macroscopically cubic between T_f and T_c (' α phase') and ferroelectrically distorted below T_f . Depending on the La/Zr/Ti content, the corresponding field-induced long-range distortion can be orthorhombic, rhombohedral or tetragonal at room temperature [4]. No evidence for a long-range ferroelectric order has been directly detected in thermally depoled samples, even when cooled down to 200 K [3]. Nevertheless, microregions have been observed by TEM [5] at room temperature in 8/70/30 thermally depoled samples, and the corresponding local distortion has been found to be orthorhombic [6].

The behaviour of ferroelectric relaxors is understood as resulting from the slowing down of interacting ferroelectric nanodomains [7] and these systems can be considered as superparaelectric [8]. In this context, it is interesting to have a better knowledge of the dynamic properties of these nanodomains and of the correlation length of the polarization. In this paper we report dielectric susceptibility and Raman scattering experiments from which information about the relaxational behaviour and the spatial correlation function of the polarization are derived.

2. Raman scattering

The high-symmetry phase of PLZT is cubic with each atom located on an inversion centre. No Raman spectrum is thus expected in the paraelectric phase when considering only first-order scattering processes, unless induced by a breaking of symmetry [9, 10]. In this case, Raman scattering can be understood as arising from a second-order process involving the coupling of phonons with some static or quasi-static distortion [11] and/or polarization [12]. Such an interpretation was formerly given by Geisel and Keller [13] for the normally forbidden but observed Raman spectra of ammonium halides in their disordered phase.

Raman experiments have been performed on transparent 9/65/35 PLZT ceramics between 300 and 720 K. Samples of about $3 \times 3 \times 5$ mm³ have been cut from hot-pressed PLZT disks and optically polished. Their temperature was varied through a regulated furnace provided with strain-free windows. The 514.5 nm line of an argon laser monitored at a power of 200 mW was used as source and the scattered light was analysed through a triple monochromator Dilor Z 24 spectrometer.

The room temperature Raman spectrum is presented in figure 1(a). Four broad and strong lines are observed, two of which (at about 545 and 750 cm⁻¹) are well defined. The two other lines overlap, but frequencies can be estimated to be 220 and 315 cm⁻¹. In their IR study of 9/65/35 ceramics, Lurio and Burns [14] reported for the TO modes the frequencies of 210, 290 and 525 cm⁻¹. Similar results (210, 300 and 530 cm⁻¹) were obtained for PZT (0/75/25) ceramics by Zelezny *et al* [15]. These IR frequencies agree fairly well with those determined from our spectra. In their Raman study of KTN, Manlief and Fan [10] suggested that the lines they detected at 202, 279 and 555 cm⁻¹ (labelled as TO₂, TO₃ and TO₄ respectively) appeared as 'first-order' Raman because of the relaxation of symmetry. A higher-frequency line located at 748 cm⁻¹ was assigned by these authors to a second-order TO₂ + TO₄ process. Nevertheless, it is seen in figure 1(a) that 'first-order-like' lines have widths (about 100 cm⁻¹) which are quite similar to that of the TO₂ + TO₄ line and usually observed in second-order processes involving phonons with wavevectors extending over a

large part, if not the totality, of the Brillouin zone. It should be noticed that TO2 and TO4 are odd parity polar modes with reference to the cubic structure, whereas TO3 is a silent (non-polar) mode which does not couple to the polarization. Unfortunately, because of the overlapping of TO2 and TO3 lines, only qualitative information can be obtained about the difference in the behaviour of these two modes. This point will be discussed later.

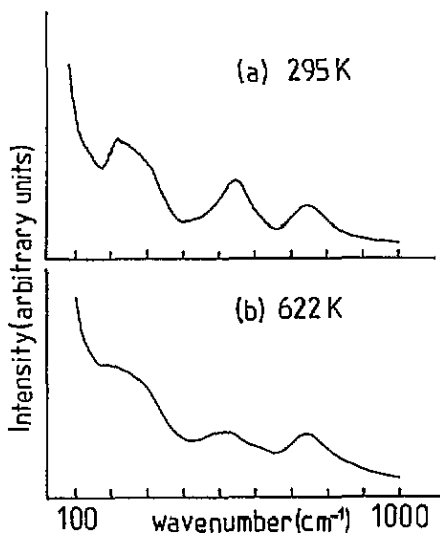


Figure 1. Depolarized Raman spectra obtained at (a) room temperature and (b) 622 K in PLZT ceramics.

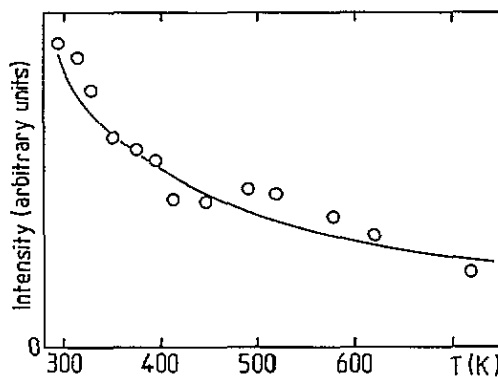


Figure 2. The temperature variation of the integrated and temperature-normalized intensity of the TO4 mode.

A typical high-temperature Raman spectrum is represented in figure 1(b). The comparison of spectra at 295 K (a) and 622 K (b) shows that two bands, namely TO2 and TO4, exhibit a significant decrease in their intensity at high temperature. In contrast, the integrated intensity of the 750 cm^{-1} line does not vary so much with temperature, taking into account the Bose-Einstein factor. Because of the overlapping between TO2 and TO3 lines, a quantitative measurement of the intensity of the TO2 line would not be reliable. We have reported in figure 2 the integrated and temperature normalized intensity of the TO4 line between room temperature and 720 K.

As previously mentioned, in perovskite structures where first-order Raman lines are normally forbidden, the non-zero intensity of the so-called 'first-order' lines related to polar modes can be understood as the result of a second-order scattering involving the hard modes and the quasi-static polarization [12]. The time Fourier transform of the polarization $P(\mathbf{r}, t)$ contains terms centred at nearly zero frequency corresponding to the relaxational process and components at the frequencies of the hard phonon modes. The second-order contribution to the electronic polarizability can thus be written as

$$\delta\alpha^{(2)} = \sum_q \mathcal{R}^{PP}(q) P(q) P(-q) + \sum_q \sum_j \mathcal{R}^{PQ}(q, -q, j) P(q) Q(-q, j) + \sum_q \sum_{j, j'} \mathcal{R}^{QQ}(q, -q, j, j') Q(q, j) Q(-q, j') \quad (1)$$

in which $P(q)$ is the relaxational polarization and $Q(q, j)$ is the polar normal mode with frequency $\omega(q, j)$. The second-order Raman intensity is proportional to the averaged square of the polarizability [16] and the first two terms of equation (1) will thus result in contributions to the intensity involving the correlation function of the relaxational polarization. The first term is expected to be responsible for quasi-elastic scattering. However, the frequencies characterizing the relaxational lattice polarization do not exceed several hundreds of MHz in perovskite structures [25, 30], and the corresponding processes cannot be observed using Raman spectroscopy. Normally forbidden single-phonon Raman lines will appear at frequencies close to $\omega(q, j)$ as a consequence of the second term in equation (1). The integrated intensity of lines resulting from such a process is expected to increase with the spatial correlation function of the polarization when decreasing the temperature, as experimentally observed for the TO4 mode in figure 2. The third term in equation (1) is at the origin of the usual second-order combination lines, and most particularly of the TO2 + TO4 line which appears at about 750 cm^{-1} in PLZT ceramics.

It can be guessed from figure 1 that the intensity of the non-polar mode does not decrease significantly when the temperature increases, contrary to what observed for the TO2 and TO4 modes. Moreover, the polar 545 cm^{-1} line does not disappear completely at temperatures as high as 720 K (i.e. above the Curie temperature of the lanthanum-free 65/35 PZT compound). These two observations suggest that static distortions exist in the ceramics even at high temperatures. They could be responsible for the activation of the non-polar TO3 mode, and contribute partly to the second-order Raman intensities of TO2 and TO4 modes, in addition to the second-order process resulting from dipolar interactions (equation (1)). Such quadrupolar interactions were already suggested in KTN [17, 18] and are highly favoured in the case of PLZT ceramics because of the mismatches appearing at grain boundaries. The resulting short-range strain field has been detected through strong shoulders close to main Bragg peaks in x-ray experiments, but seems to be lacking in annealed powders of the same composition [19], as expected.

It is thus concluded that quadrupolar interactions resulting mainly from the polycrystalline state already exist at high temperature in PLZT ceramics. They give rise to an asymmetric widening of the x-ray diffraction peaks and most likely contribute to the Raman scattered intensity. In addition, when the temperature decreases, dipolar interactions take place. Their increasing correlation length is revealed through the variation of the intensity of the polar modes, as stated above. This behaviour has been also evidenced by the results obtained by Burns and Dacol [20]: their refractive index curve as a function of the temperature shows a deviation from 'regular behaviour' below about 639 K, which has been shown [21] to give a measurement of the space and time-averaged square of the polarization.

Finally, a low-frequency mode which hardens from $50 \pm 2 \text{ cm}^{-1}$ at 720 K to about 65 cm^{-1} at room temperature has been detected. An accurate determination of its frequency is precluded at temperatures lower than 500 K because of its weaker intensity and of the increase of the quasi-elastic scattering.

3. Dielectric susceptibility

Samples of about $5 \times 5 \times 0.5 \text{ mm}^3$ have been cut from the same 9/65/35 PLZT batch as used for Raman experiments. They have been polished and provided with silver painted or gold sputtered electrodes. Their dielectric susceptibility has been measured between 360 K and 480 K in the frequency range 10^{-2} Hz to 1 MHz, using an impedancemeter Schlumberger

1260. Results are usually represented as Cole-Cole or ϵ versus $\ln \omega$ plots. We have reported in figure 3 such Cole-Cole diagrams obtained on 9/65/35 PLZT samples. The results are not so far from being located on a semi-circle centred near the ϵ' axis at 483 K (a) but significantly below when the temperature is decreased (b).

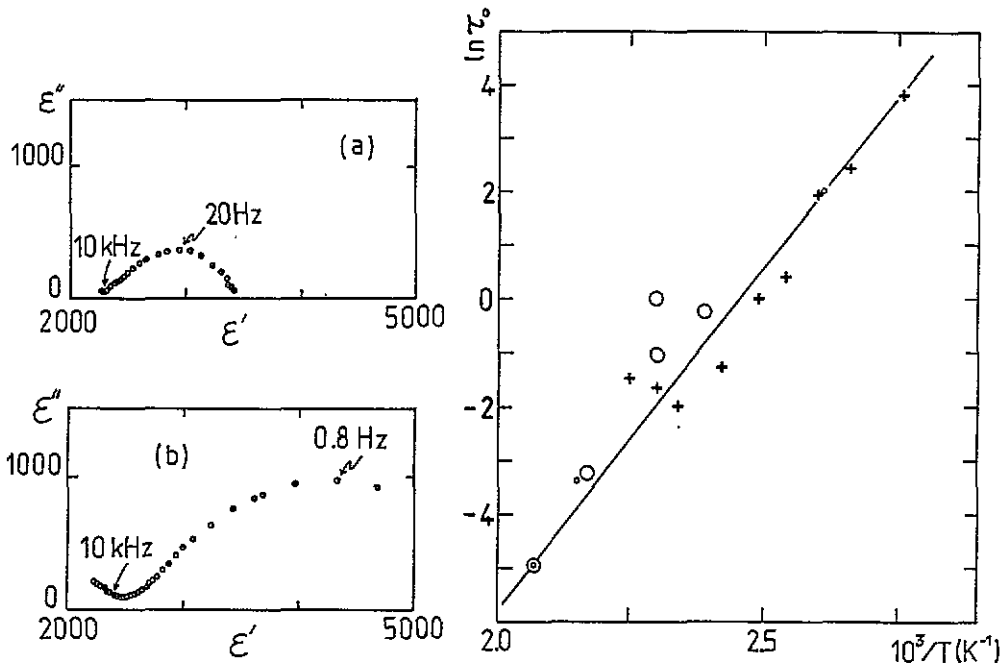


Figure 3. Cole-Cole plots obtained on PLZT samples at (a) 483 K and (b) 435 K. ϵ' and ϵ'' are the real and imaginary parts of the dielectric permittivity respectively.

Figure 4. Variation of the centre of the distribution of the relaxation times as a function of the temperature. Different symbols refer to different samples and electrodes.

One of the most commonly used and the most physically understandable models for relaxors is a many-well potential in which jumps are characterized by a thermally activated time τ . A distribution $f(E)$ in the potential barriers implies a distribution $g(\tau)$ in the relaxation times, and the dielectric permittivity should be written as

$$\epsilon(\omega) = \int \Delta \epsilon g(\tau) d\tau / (1 + i\omega\tau). \quad (2)$$

For a monodisperse process, $g(\tau) = \delta(\tau - \tau_0)$ where δ is the Dirac function, and $\epsilon(\omega)$ is given by the classical Debye relaxator function, with the consequence that the Cole-Cole plots are half circles centred on the ϵ' axis. If the activation energies obey a Gaussian distribution centred at E_0 , relaxation times will follow the (log-normal) Wagner distribution

$$g(\tau) = (\tau \sqrt{\pi \Delta \ln \tau})^{-1} \exp\{-[\ln(\tau/\tau_0)]^2 / [\Delta \ln \tau]^2\} \quad (3)$$

with

$$\tau_0 = \tau^* \exp(E_0/kT) \quad (4)$$

and the distribution widths of energies and relaxation times will be related through [22]

$$\Delta E = kT \Delta \ln \tau / \sqrt{2}. \quad (5)$$

Actually, the determination of the parameters characterizing the relaxation time distribution does not depend drastically on the model used [23, 24], so that τ_0 and $\Delta \ln \tau$ can be obtained from a Cole–Cole distribution as well.

We have presented in figure 4 the variations of $\ln \tau_0$ versus the reciprocal temperature. These results have been obtained from different samples provided with different electrodes, as stated above. The leading relaxation times are large (about 1 s at 420 K and several hours at room temperature) compared with those usually involved in other ferroelectric relaxors such as doped potassium tantalates [25]. It is therefore suggested that the relaxational processes occurring in this frequency range involve rather large ferroelectric nanodomains. The size of the microregions observed by TEM in 8/70/30 samples [5] ranges between 10 and 30 nm and could thus correspond to these nanodomains. The centre E_0 of the distribution of the activation energies is estimated from figure 4 and equation (4) to be about 11 600 K. This value could seem at first glance unreasonably high. Following the model proposed by Néel [26] for superparamagnetic systems, the activation energy for the reorientation of a whole polar domain should be proportional to the total dipolar moment of the domain (and consequently to its volume) and to the anisotropy factor. According to the size of the domains involved in this case, such a high value of the energy barrier is not surprising: the anisotropy factor of about 6×10^{-4} eV nm⁻³ given by Viehland *et al* [27] results in a mean size of the clusters of 12 nm, which is in the range of those observed experimentally [5]. It should be kept in mind that, due to the local structural distortion [4, 6], this anisotropy factor most likely involves an elastic contribution in addition to the electrostatic term.

Figure 5 gives the variation of the width $\Delta \ln \tau$ of the relaxation time distribution versus T^{-1} . This distribution broadens as the temperature decreases, as usually expected, and the width obeys rather well a linear dependence on the reciprocal temperature. Assuming equation (5) derived from the Wagner's model is valid, we have estimated and reported in figure 6 the width ΔE of the Gaussian energy distribution in the temperature range investigated. The broadening of the energy distribution at low temperature is most likely to be related to the size dispersion of the ferroelectric nanodomains [27]. Recent TEM observations [28] performed on 12 and 15/40/60 PLZT ceramics have shown that a coarsening of nanodomains occurs on cooling. Most particularly, for 15/40/60 samples in which a diffuse phase transition is expected, nanodomains coexist with tweed-like macrodomains below room temperature. This coarsening of nanodomains is in qualitative agreement with the increasing of the polarization length inferred from Raman experiments.

Figures 4 to 6 do not show any anomaly in the relaxation times within the temperature range studied. The dielectric susceptibility maximum reported at about 380 K by Keve and Annis [3] was also observed in our study but should not be considered as the signature of a phase transition. As already emphasized [29], a peak in the real part of the susceptibility is obtained in superparamagnetic systems in which the reorientation of clusters is characterized by a thermally activated relaxation time. Furthermore, the temperature T_{\max} at which $\epsilon'(T)$ exhibits a maximum is expected to depend on the frequency, as observed in our experiments. It is thus strongly suspected that the dielectric susceptibility maximum detected by Keve and Annis [3] is merely related to the superparaelectric behaviour of PLZT ceramics.

Dielectric permittivity measurements were previously done by Schmitt and Dörr [30] in a higher frequency range. Their results are consistent with monodisperse processes centred at relaxational frequencies lying between approximately 2 and 30 MHz, suggesting that other excitations than those presently discussed are involved.

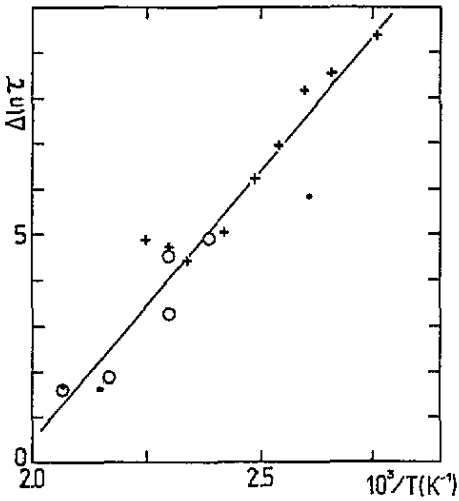


Figure 5. Variation of the width of the relaxation time distribution as a function of the temperature. Different symbols refer to different samples and electrodes.

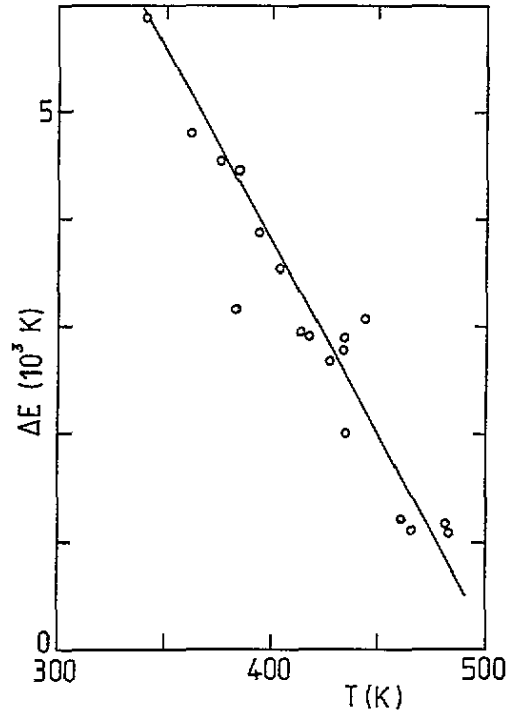


Figure 6. Variation of the width of the energy distribution of the potential barriers as a function of the temperature, according to equation (5) in the text. The line is a guide for the eyes.

Larger relaxation times than those reported in the present paper can be attained through the measure as a function of time of a macroscopic quantity related to the polarization, such as high frequency (e.g. 10 kHz) dielectric susceptibility [18] or Raman intensity. These experiments are in progress and the results obtained for temperatures lower than 360 K seem to be, at first sight, consistent with those presented in figure 4.

4. Conclusion

The static and dynamic behaviour of PLZT ceramics seems to be governed by the polycrystalline and heterogeneous character of these materials. Built-in stresses appearing preferentially at grain boundaries are at the origin of quadrupole interactions even at high temperatures, which induce Raman scattering normally forbidden in perovskite-type structures. Moreover, chemical heterogeneities, among which those resulting from grain boundary segregation, are responsible for the smearing of the transition to a ferroelectric state. As already suggested [20], ferroelectric nanodomains nucleate most likely in regions where a depletion in lanthanum occurs. From a statistical point of view, built-in stresses as well as chemical heterogeneities should be considered as playing the role of random fields.

According to a model proposed by Vugmeister and Glinchuk [31], ferroelectric ordering can occur in highly polarizable lattices containing paraelectric defects. The determining parameter of the model is nr_c^3 , where n is the concentration of impurities nucleating the

ferroelectric microregions and r_c is the polarization correlation radius. When $nr_c^3 \gg 1$, the onset of long-range order induces a ferroelectric phase transition, but short-range order only is expected in the opposite case, resulting in what these authors call a 'polar glass'.

Actually, PLZT ceramics should rather be considered as superparaelectric glasses, since their dynamic properties are described through relaxation phenomena characterized by large times, suggesting that this relaxation is related to the motion of the ferroelectric nanodomains. When the temperature is decreased, the correlation length of the polarization extends, as illustrated by the behaviour of the TO4 Raman line intensity, but the relaxation times increase drastically according to equation (4) and the freezing of the system prevents any onset of the long-range order.

The behaviour of such materials is usually very sensitive to applied fields. More particularly, different $\epsilon(T)$ curves should be obtained in field cooled (FC) and zero-field cooled (ZFC) experiments. Such measurements are in progress and will be reported in a next paper.

Acknowledgments

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