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Piezoelectric Resonance Investigation of Zr-rich PZT at Room Temperature

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Abstract

We study the piezoelectric resonances in poled PZT ceramics by means of a microscopic model. It connects the microscopic vibrations of the ionic units, cooperatively producing the piezoelectric effect, with the macroscopic piezoelectric parameters. The behaviour at the resonance is well described in a wide range of frequencies, allowing the calculation of piezoelectric constants and the electromechanical coupling factors in terms of microscopic quantities. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

The use of piezoelectric ceramics is quite extended, because of their reliability in producing detectors, actuators and different useful devices.[1] However, this cooperative effect is still not completely understood. Early attempts made by Schrödinger, Larmor and Born to use modern lattice dynamics in the description of piezoelectricity were unequal to the task of predicting anything better than a rough approach to the order of magnitude of the piezoelectric effect in the simplest structures.[2] Piezoelectricity is a property appearing in all 20 non-centrosymetric crystal classes,[3,4] and then includes a lot of types of materials, among ferroelectrics.

The use of modern calculation techniques allowed some authors to obtain valuable first-principle results for the piezoelectric parameters in some simple compounds.[5,6] In perovskites the calculations based on LAPW-LDA provide some explanations about the origin of ferroelectricity and piezoelectricity in these materials.[7] Recently some authors[8,9] presented calculations of piezoelectric properties in pure and mixed perovskites.

All these calculations are not entirely based on first principles, because they always use some input from experiments, such as the lattice constant, which is critical to get stable structures.

Escaping from first-principles and *ab initio* calculations, we propose a microscopic approach to the piezoelectric resonances. The model described in this work is based on a classical forced and dumped oscillator and allows the expression of the piezoelectric coefficients and the electromechanical coupling factors in terms of microscopic quantities.

The material investigated in this work is the well-known PZT: a lead zirconate-lead titanate solid solution ($PbZr_{1-x}Ti_xO_3$). In the Zr-rich region of compositions it presents a ferroelectric phase with rhombohedral geometry below the ferroelectric transition temperature. This phase is divided into two other ferroelectric regions (F_{RL} and F_{RH} for low and high temperature phases, respectively), in which the positions of cations and oxygen octahedra play a fundamental role.[10,11] The transition temperature (T_{LH}) between them varies from room temperature up to 150°C, depending on composition.[4]

2 Experimental

We have characterised the piezoelectric resonances in PZT 96·3/3·5 + 1% wt. Nb_2O_5 ceramic samples. They were sintered at the Shanghai Institute of Ceramics, Shanghai (China) by ordinary methods. The samples were silver-electroded and poled by applying 2 $kV\,cm^{-1}$ during 10 min at 125°C, in silicon oil medium.

The dielectric response was determined by means of a Hewlett Packard HP4194A-LF impedance

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*To whom correspondence should be addressed. Fax: + 34-91-397-85-79; e-mail: noe.cereceda@uam.es analyser, and characterised using a specially designed software.[12,13] By this way we collected data for the elastic constants, piezoelectric coefficients and electromechanical coupling factors in complex form.

3 Theoretical Model

The model simplifies the material assuming an arrangement of ions placed into alternating layers of positive and negative charges along the ferroelectric axis. In this approach it is assumed that positive charges (+2) correspond to the Pb^{2+} ions, and the negative charges (−2) correspond to the $[(Zr/Ti)O_3]^{2-}$ packed ions.

We assume the motion of these layers to be described by a forced-dumped oscillator, where $k(d)x_\pm$ is the restoring force, $M_\pm\gamma(d)\mathrm{d}x_\pm/\mathrm{d}t$ is the viscous force, and $qE_{\mathrm{eff}}(d)\exp\{-i\omega t\}$ is the effective electric force, driven by the external applied field, $E_o\exp\{-i\omega t\}$. The net displacement, $x = x_+ - x_-$, connects with the extension of the material, caused by, lets say, an accordion effect.

The thickness dependence is included in the description, according with the principle that piezoelectricity is a macroscopic cooperative phenomenon, with the boundary conditions playing a fundamental role. The complex dielectric response is

$$\varepsilon^* = \varepsilon_{cd} + \frac{A}{(\omega_0^2 - \omega^2) - i\omega\gamma} \tag{1}$$

where $\omega_0^2 \equiv k(d)/M$ is the characteristic frequency of the system, $A(d)$ is the amplitude of the resonance, $\gamma(d)$ is the corresponding dumping factor and M is the effective mass, defined as $1/M = 1/M_+ + 1/M_-$. Only these thickness-dependent parameters are needed to characterise the resonance, as shown below. The 'clamped' dielectric constant, ε_{cd}, does not depend on sample thickness.

4 Results and Conclusions

As it is known, disk geometry possesses thickness-extensional, and radial mode vibrations. Figure 1 represents the found dielectric response for PZT 96·5/3·5 + 1% wt. Nb_2O_5 ceramic during the thickness mode resonance in a sample with $d = 0{\cdot}4$ mm thickness and $2r = 1$ cm diameter. Points and crosses represent the experimental points for real (ε') and imaginary (ε'') parts, respectively. Lines represent the corresponding theoretical fits, according to eqn (1). As can be seen, each fit reproduces adequately the experimental behaviour in a wide range of frequencies.

We studied both thickness and radial mode resonances for samples with different sizes. Figure 2 reproduces the dependence of the parameters ω_o, A, and γ versus thickness for the longitudinal mode resonance. A similar study has been made for radial mode resonance. Table 1 summarises the results.

The behaviour found for the characteristic frequency, $\omega_o(d)$, agrees with the expected one, because it is determined by the boundary conditions. As can be observed from Fig. 1, there exists a 'jump' in the dielectric constant, $\Delta\varepsilon$, which is not size-dependent and can be defined as $\Delta\varepsilon' \equiv \varepsilon'(\omega \to 0) - \varepsilon'(\omega \to \infty) = A(d)/\omega_o(d)$. This jump is related to the electromechanical coupling factor as follows: at the thickness mode resonance we expect $\varepsilon'(0) = \varepsilon_{33}^p$ and $\varepsilon'_{cd}(\infty) = \varepsilon_{33}^s$, so we may write, according to Meitzler:[14]

$$k_t^2 = \frac{\Delta\varepsilon}{\varepsilon(0)} = \frac{\Delta\varepsilon}{\Delta\varepsilon + \varepsilon_{cd}} \tag{2}$$

which is the thickness electromechanical coupling factor.

We may interpret this as follows. Extrapolating to the case in which the atomic chains consist of only two unit cells ($d = 2a$), there exists a *microscopic* elastic constant, K_d, and an associated characteristic frequency, $\omega_o(2a)$. Then, for $\omega_o(d)$ we may write

$$\omega_o^2(d) = (K_d/M)(2a/d)^2, \tag{3}$$

where a is the lattice parameter. In our samples we found that $\omega_o(2a)/2\pi \cong 2{\cdot}8\times10^{12}$ Hz, which is a reasonable value for a low-laying purely ionic mode resonance.

For the total viscous force we consider that the cooperative effect during the resonance leads to a sharing of the atomic viscous force and to a total viscous force parameter expressed by

$$\gamma(d) = \Gamma_d(2a/d)^2 \tag{4}$$

where $\Gamma_d = \gamma(2a)$ is constant.

On the other hand, $A(d) \propto 1/d^2$ is connected with the fact that $\Delta\varepsilon$ is constant:

Table 1. Dependence of the fitting parameters with thickness (d) and radius (r)

	Thickness mode	*Radial mode*
ω_o^2	$\propto 1/d^2$	$\propto 1/r^2$
γ	$\propto 1/d^2$	$\propto 1/r^4$
A	$\propto 1/d^2$	$\propto 1/r^2$

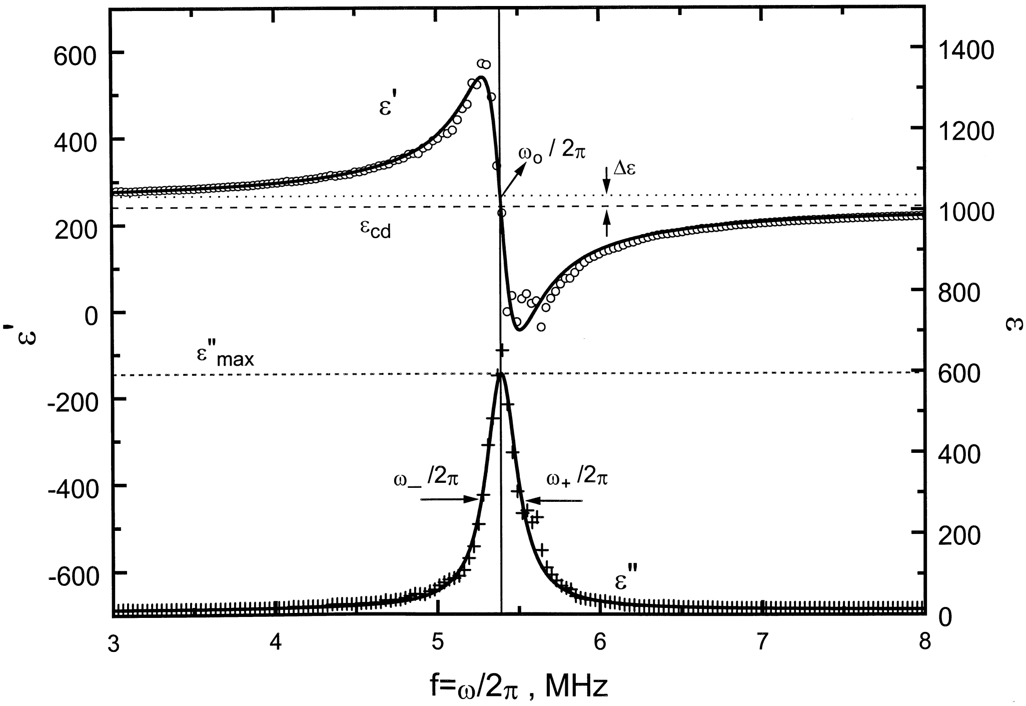

Fig. 1. Thickness mode resonance in the PZT 96·5/3·5 + 1% wt. Nb_2O_5 sample. ε' and ε'' represents real and imaginary parts of eqn (1). The fitting parameters are indicated in the plot.

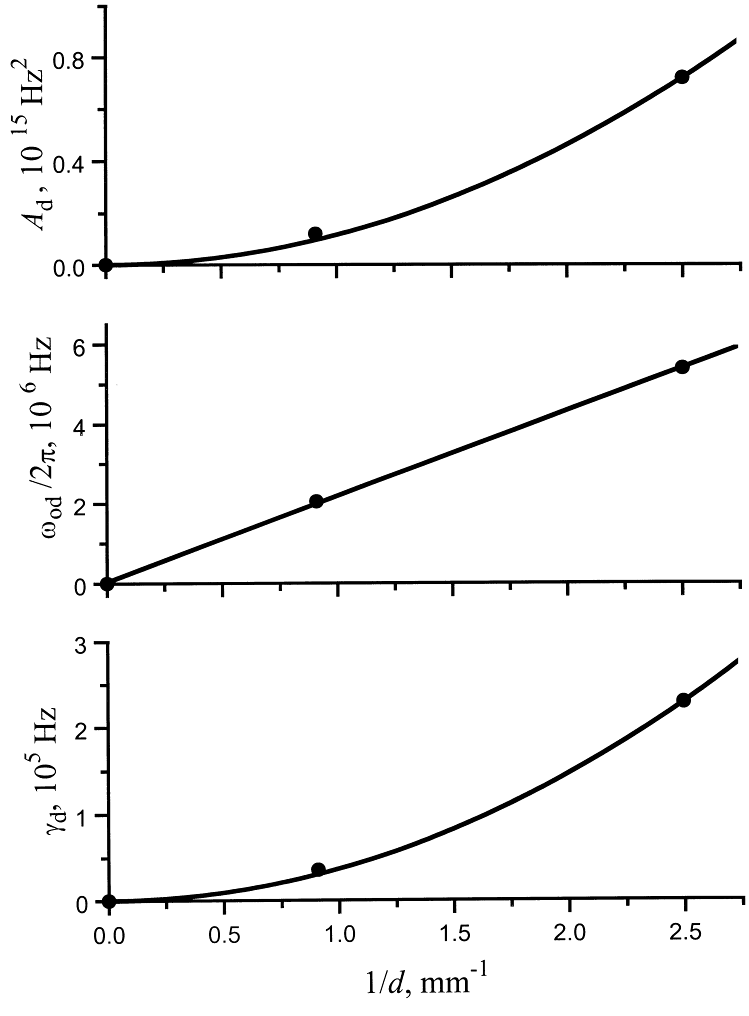

Fig. 2. Thickness dependence of the fitting parameters A, ω_{od} and γ.

$$\Delta\varepsilon(d) = \frac{A(d)}{\omega_o^2(d)} = \frac{4\pi N q^2}{M}\frac{E_{\mathrm{eff}}(d)/E}{\omega_o^2(d)} \tag{5}$$

In a centrosymmetric (non-piezoelectric) ionic crystal, the ratio (E_{eff}/E) is given by $\Delta\varepsilon/3$, combining Lorentz's and Claussious-Mossotti's relations.[15]. In a piezoelectric crystal the strength of $E_{\mathrm{eff}}(d)$, driven by the external field E, is shared by $(n_+ n_-) = [(d/2)/a]^2$ charged pairs. The effective electric field E_{eff} results in

$$E_{\mathrm{eff}}(d)/E = \frac{\Delta\varepsilon}{3}[2a/d]^2 \tag{6}$$

From the above discussion, we may get the piezoelectric coefficient d_{33} as follows:

$$d_{33} \equiv \frac{\delta d/d}{E} = \frac{x/2a}{E} = \frac{1}{2}\frac{(q/M)(E_{\mathrm{eff}}(d)/E)}{a\omega_o^2(d)} \tag{7}$$

and using eqns (5) and (6) we get

$$d_{33} = \frac{1}{2}\left(\frac{q}{aK_d}\right)\frac{\Delta\varepsilon_d}{3} \tag{8}$$

By using the values $q = 2e, a = 4$ Å, $K_d = 4\times10^4$ (dyn cm^{-1}) and $\Delta\varepsilon_d = 30$, we get $d_{33} \cong 101\times10^{-12}$ CN^{-1}. This value is somewhat smaller than $1/h_{33} \cong 320\times10^{-12}$ CN^{-1}, used to estimate it, but it lies in an expected value according with the bibliography.

The results and the above theoretical development are also applicable to radial mode piezoelectric resonances. Figure 3 represents the results found for the dielectric response through the radial mode resonance. As can be observed, this resonance is narrower than the thickness one.

In order to calculate now the piezoelectric coefficient d_{31} we use now the values $K_r = 4\times10^4$ dyn cm^{-1} and $\Delta\varepsilon_r = 5$, where the sub-index 'r' indicates 'radial'. Then, by using eqn (8) applied to this resonance, we get $d_{31} = 11{\cdot}6\times10^{-12}$ CN^{-1}, which is in good agreement with the observed one during the standard characterisation. The planar electromechanical coupling factor, k_t, can be easily calculated by again using Meitzler criterion,[14] using now $\varepsilon'_{cd} = \varepsilon'_r(\infty) = \varepsilon^p_{33}$, $\varepsilon'_r(0) = \varepsilon^T_{33}$, and the relation $\varepsilon^p_{33} = \varepsilon^T_{33}(1 - k_t^2)$. Table 2 shows the final results obtained in comparison with the previously done macroscopic characterisation.

According to all these results, there is a simple description of the piezoelectric resonance in terms of microscopic quantities, establishing a connection between the usual interpretation (macroscopic) and the fundamentals of the material. In principle, this microscopic approach could be used directly in other piezoelectric perovskites, and possibly in other piezoelectric materials. Our description works quite well not only at frequencies close to the resonances, but also far from them.

Table 2. Comparison of the results obtained after analysis with the 'standard' method and with the 'microscopic' approach

	d_{33}	d_{31}	k_t	k_p
Macrosc	[< 320]*	11·5	0·35	0·14
Microsc	101	11·6	0·33	0·12

* Not directly determined. Estimated using $d_{33} < 1/h_{33}$. Parameters d_{33} and d_{31} are given in units of $\times10^{-12}$ C/N.

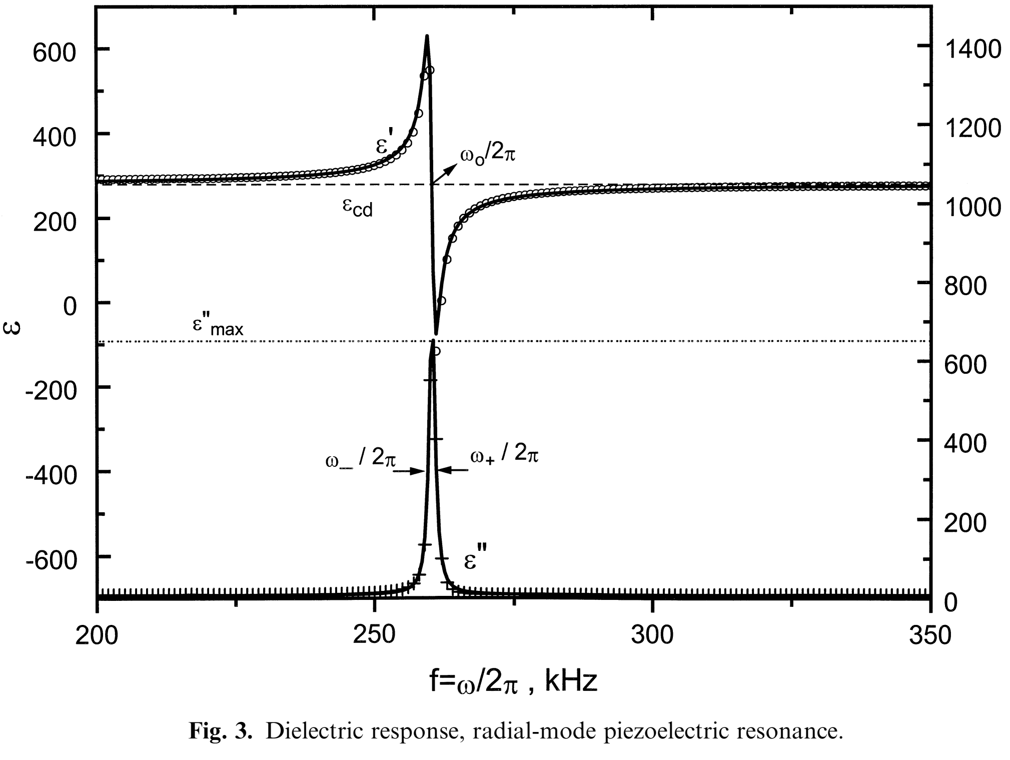

Fig. 3. Dielectric response, radial-mode piezoelectric resonance.

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