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Non-linear dielectric and piezoelectric response in undoped and Nb^{5+} or Fe^{3+} doped PZT ceramic system

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Abstract

The dielectric and direct piezoelectric responses in doped and undoped $Pb(Zr_{1-x}Ti_x)O_3$, with $x = 0.40$, 0.47 and 0.60, are experimentally studied. The permittivity and the direct piezoelectric coefficient have been measured by applying subswitching ac electric field and high ac mechanical stress. The influence of the type of defects and their concentrations on the non-linear response have been explored. The experimental data show a considerable mobility increase of ferroelectric–ferroelastic domain walls in donor-doped samples. The correlation between the dielectric constant and dielectric losses is discussed in terms of the Rayleigh law. Our results reveal that the influence of reversible and irreversible domain wall movements on the non-linear dielectric response is determined by defects associated with dopants. The role played by the crystallographic phase in the non-linear response is also analyzed.

Keywords: Dielectric properties; Piezoelectric properties; PZT; Non-linearity

1. Introduction

Dielectric and piezoelectric responses of the lead zirconate titanate solid solution system are mainly determined by its domain structure, but also by the presence of defects that can modify the wall domain mobility. The macroscopic properties of a PZT ceramic will be strongly modified by the addition of small quantities of dopants. Dopants can be classified into two groups: donors (softeners) or acceptors (hardeners). The inclusion of donor impurities leads to the creation of lead vacancies, which minimize the stress of the lattice. Defects produced by donor atoms have no preferential direction and are randomly distributed throughout the material. Hardener impurities will induce the formation of oxygen vacancies, performing complex defects that have electrical dipole moment. These defects can be re-oriented by spontaneous polarization.[1]

The Rayleigh model has been used to describe successfully the dielectric and piezoelectric responses in some PZT ceramics.[2,3] This model assumes that the non-linear response of the material is due exclusively to the irreversible movement of domain walls.[4] Accordingly, a fixed linear correlation between the dielectric constant, ε', and the dielectrical loses, ε'', must be fulfilled, and the relation $m_\varepsilon = \Delta\varepsilon''/\Delta\varepsilon' = 0.42$. However, when $m_\varepsilon < 0.42$ it must be assumed that another mechanism exists that contributes to the permittivity but without contributing to the loses.

The aim of this work is to study the dielectric and piezoelectric responses of PZT as a function of the crystallographic phase and of the type of impurities. Tetragonal, rhombohedral and morphotropic phase boundary samples, doped and undoped, have been manufactured for this purpose. The dielectric response was obtained as a function of the amplitude of the subswitching ac electric field, while the direct piezoelectric one was related to the amplitude of the ac mechanical stress applied.

2. Experimental procedure

The conventional oxide mixing process was used to prepare $Pb(Zr_{1-x}Ti_x)O_3$ ceramics, with $x = 0.40$ and 0.60, pure and doped with 1 and 2 wt.% of Nb_2O_5 (softeners or donors) or Fe_2O_3 (hardeners or acceptors); and $x = 0.47$ doped with 1 wt.% of Nb_2O_5 or Fe_2O_3. The precursor oxides were mixed in a ball mill, dried and calcined at 850 °C for 3.5 h. After being pressed,

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Table 1
Labels used in this work to design the different materials analyzed

Material	Label	ε_{33}^T	$\tan\delta_\varepsilon$ ($\times 10^{-3}$)	d_{33} (pm/V)
$Pb(Zr_{0.60}Ti_{0.40})O_3$	PZT60/40	390	6.5	115
$Pb(Zr_{0.60}Ti_{0.40})O_3$ + 1 wt.% Nb_2O_5	PZT60/40 + 1Nb	470	29	130
$Pb(Zr_{0.60}Ti_{0.40})O_3$ + 2 wt.% Nb_2O_5	PZT60/40 + 2Nb	510	28	150
$Pb(Zr_{0.60}Ti_{0.40})O_3$ + 1 wt.% Fe_2O_3	PZT60/40 + 1Fe	440	4.5	95
$Pb(Zr_{0.60}Ti_{0.40})O_3$ + 2 wt.% Fe_2O_3	PZT60/40 + 2Fe	430	4.4	90
$Pb(Zr_{0.53}Ti_{0.47})O_3$ + 1 wt.% Nb_2O_5	PZT53/47 + 1Nb	1450	23	255
$Pb(Zr_{0.53}Ti_{0.47})O_3$ + 1 wt.% Fe_2O_3	PZT53/47 + 1Fe	630	5.8	180
$Pb(Zr_{0.40}Ti_{0.60})O_3$	PZT40/60	330	14	
$Pb(Zr_{0.40}Ti_{0.60})O_3$ + 1 wt.% Nb_2O_5	PZT40/60 + 1Nb	350	34	70
$Pb(Zr_{0.40}Ti_{0.60})O_3$ + 2 wt.% Nb_2O_5	PZT40/60 + 2Nb	420	18	70
$Pb(Zr_{0.40}Ti_{0.60})O_3$ + 1 wt.% Fe_2O_3	PZT40/60 + 1Fe	320	3.9	
$Pb(Zr_{0.40}Ti_{0.60})O_3$ + 2 wt.% Fe_2O_3	PZT40/60 + 2Fe	330	4.3	

Dielectric constant, dielectric losses and piezoelectric coefficient have been measured at low level amplitude.

the samples were sintered between 1200 and 1250 °C, according to the material composition, in a saturated PbO atmosphere. The samples were cut into discs with a diameter of 16–17 mm and a thickness of 0.8–0.9 mm. Silver electrodes were painted on both sides of the discs. After polishing, they were heat treated at 600 °C for 30 min to release stress induced during the polishing and to remove organic materials.

Scanning electron micrographs showed an average grain size between 3.0 and 3.5 μm. X-ray diffraction analysis revealed the crystallographic phase expected: rhombohedral, tetragonal or morphotropic phase boundary, for $x = 0.40$, 0.60 or 0.47, respectively. Abbreviated names are assigned in this work to each composition as described in Table 1.

Dielectric measurements were taken in a capacitance comparator bridge, by applying subswitching ac voltage at frequency of 1 kHz.[5] Piezoelectric measurements were obtained by the Berlincourt method. A sinusoidal force (3 Hz) of variable amplitude was applied to the sample, superposed to a constant compression force. The piezoelectric coefficient was obtained from the relation between the fundamental frequency components of the electrical charge and the applied force.

The need for a pre-stress in the piezoelectric measurements introduces an additional variable that must be taken into account, because the piezoelectric response depends on its value.[4] For this reason, and also because the frequencies of the electrical and piezoelectric measurements are not the same, both measurements cannot be quantitatively compared. Elsewhere, the object of this work consists in comparing the non-linear response as a function of the type of material.

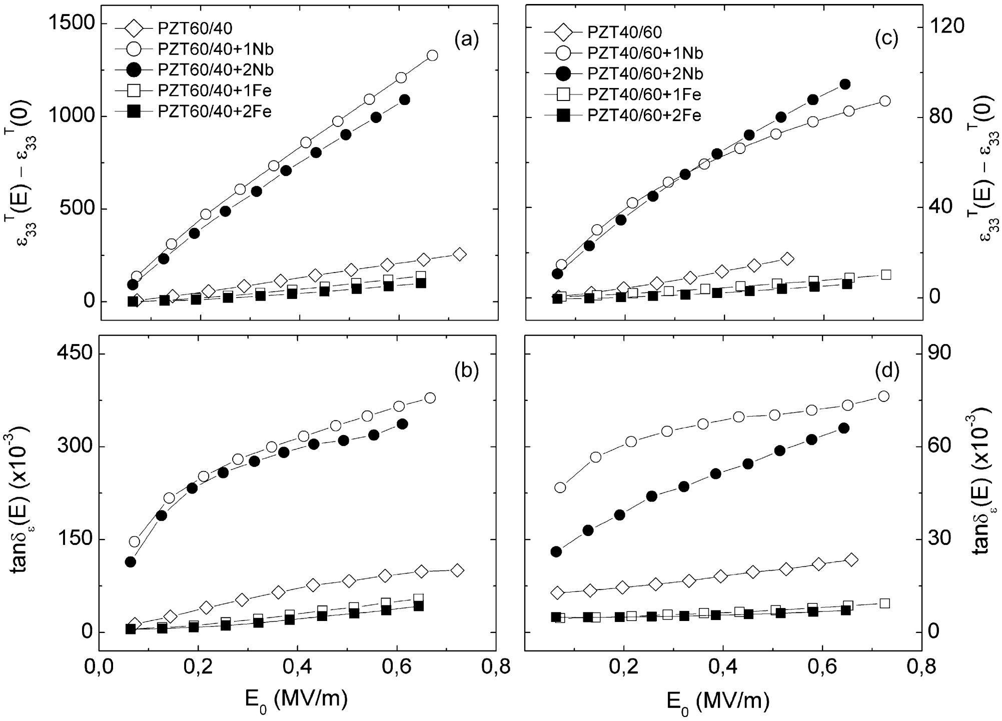

Fig. 1. Field dependence of dielectric behaviour, for different types and concentrations of dopants. For rhombohedral phase: (a) non-linear dielectric constant and (b) dielectric losses. For tetragonal phase: (c) non-linear dielectric constant and (d) dielectric losses.

3. Results and discussion

Fig. 1(a–d) show the variation of the dielectric constant and dielectric losses as a function of the amplitude of the electric field applied to rhombohedral and tetragonal samples, doped and undoped. The quantity $\varepsilon_{33}^{T}(0)$ corresponds to the linear values of the dielectric constant, as reported in Table 1.

It can be seen that in both rhombohedral samples and tetragonal ones, the softener impurities produce a significative rise in the dielectric constant and losses in relation to the pure material, while the hardener impurities produce a diminution of them. This can be attributed to the fact that the lead vacancies produced by the softener will increase the mobility of the domain walls as a consequence of the drop in the stress of the lattice. Otherwise, the complex defects produced by the hardener must be oriented in the direction of the applied field, and they make the movement of the domain walls difficult.[6] It must be noted that, for the same defect concentration, the effect of the softener is notably greater than that of the hardener. For the same type of impurities, no clear correlation between the concentration and the non-linear properties is observed.

For similar defect densities, the differences observed in each phase due to the defect type are only due to the interaction between defects and domain walls. Otherwise, the amount of dopants added do not change the original characteristics of the PZT.[1] So, the differences found in the dielectric response of a single phase of PZT can only be attributed to the different influences of the defects on the domain wall dynamics.

In Fig. 2, the increment of the dielectric constant is shown as a function of the crystallographic phase for the same type of dopants. It can be seen that the rhombohedral samples, donor or acceptor doped, will undergo a greater increment of the dielectric constant than the tetragonal samples. This fact suggest that the arrangement of the defects in the domain structure favours the mobility of domain walls more in the rhombohedral than in the tetragonal phase.

In the morphotropic phase boundary, the increment of the dielectric constant for both dopants is an intermediate value between the rhombohedral and tetragonal behaviour. The behaviour of PZT53/47 + 1Nb is similar to PZT60/40 + 1Nb (rhombohedral phase), while PZT53/47 + 1Fe behaves similarly to PZT40/60 + 1Fe (tetragonal phase). This behaviour may be due to the displacement of the phase boundary by the addition of dopants.[1]

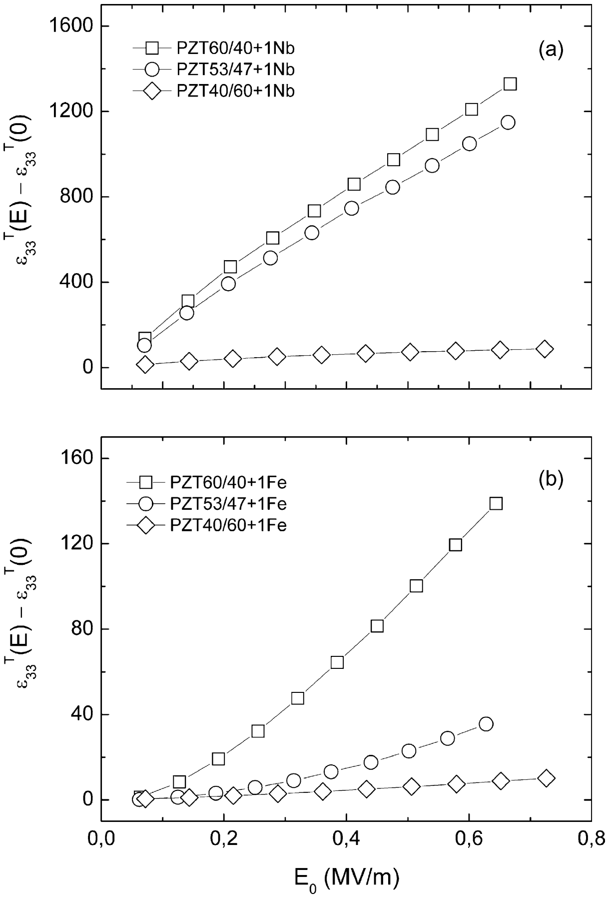

Fig. 2. Field dependence of non-linear dielectric constant, for different phases: (a) doped with Nb^{5+} and (b) doped with Fe^{3+}.

In Fig. 3, the relation between losses and dielectric constant is shown. For all materials that have been studied, a linear correlation was observed to exist between them. The slope $m_\varepsilon = \Delta\varepsilon''/\Delta\varepsilon'$ is defined for each material, and their values are

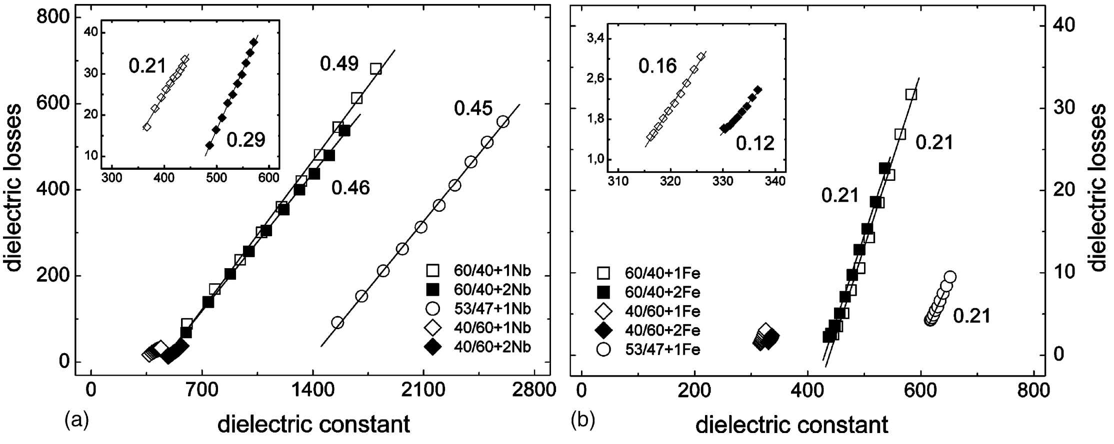

Fig. 3. Relation between dielectric losses and dielectric constant for different phases and concentrations of dopants: (a) doped with Nb^{5+} and (b) doped with Fe^{3+}.

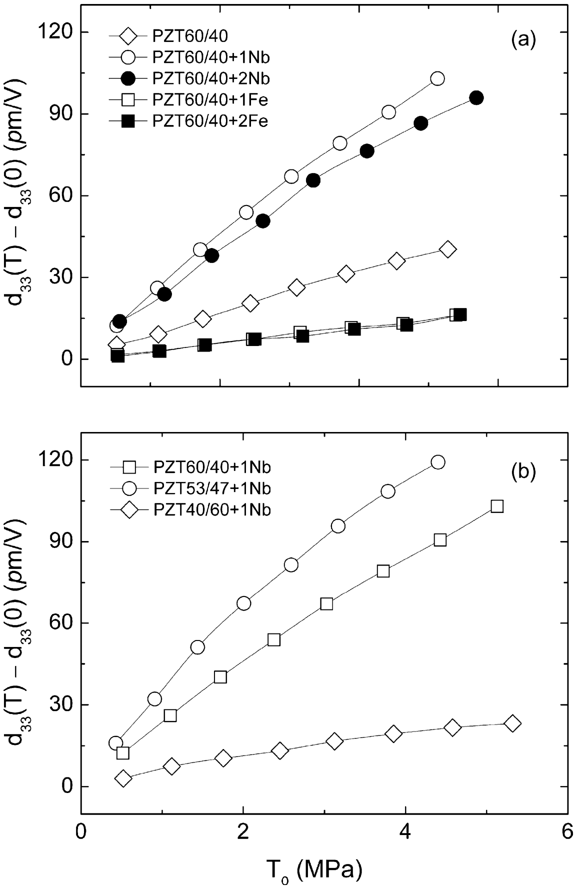

Fig. 4. Non-linear direct piezoelectric coefficient as a function of the amplitude, T_0, of the applied stress: (a) for the rhombohedral phase, doped with different impurities and (b) for different phases, all doped with Nb^{5+}.

shown in the same figure. Materials in the morphotropic phase boundary show the expected values[5]: PZT53/47 + 1Nb behaves as predicted by the Rayleigh model, but in PZT53/47 + 1Fe a low value is obtained. All materials doped with hardener impurities show a non-Rayleigh behaviour. The existence of reversible movement of domain walls is suggested, which can be explained by the effect of the pinning between the complex defects and the domain walls.[7] Otherwise, tetragonal samples show low values of m_ε for all types of dopants, indicating that they do not fit the Rayleigh model. This suggests that in the tetragonal structure the domain distribution will make wall movement difficult, and the action of an electric field will always produce a reversible movement of the domain walls.

In Fig. 4, direct piezoelectric coefficient is shown as a function of the type of dopants and as a function of the crystallographic phase. The value of $d_{33}(0)$ corresponds to the linear value of the piezoelectric constant, reported in Table 1. The results show relations similar to those encountered in the dielectric response, and confirm the hypothesis that the non-linear response is associated to the movement of domain walls and their interaction with defects. Otherwise, the fact that the same dependence is observed in the piezoelectric response as in the dielectric one suggest that, in PZT systems, only non-180° walls contribute to the non-linear dielectric and piezoelectric response.

4. Conclusions

Bearing in mind the relation between the increments of the dielectric losses and the dielectric constant, only materials in rhombohedral phase or in morphotropic phase boundary doped with donor impurities fit adequately with the Rayleigh model. Donor impurities considerably increase the mobility of domain walls and also the dielectric and piezoelectric non-linear response. The non-linear response is greater in the rhombohedral than in the tetragonal phase or in morphotropic phase boundary.

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