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Influence of donor and acceptor substitutions on the extrinsic behaviour of PZT piezoceramics

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Abstract

A study of the substitution influence of Nb^{5+} and Fe^{3+} impurities on piezoelectric behaviour has been carried out. Different substitution concentrations as well as undoped materials have been performed for ceramics $Pb(Zr_{1-x}Ti_x)O_3$ with $x = 47$ and 40. The different impurity concentrations, and their type, produce variations in the domain wall mobility related to the extrinsic coefficient. This dependence between extrinsic behaviour and impurity concentration is studied for different material structures: the rhombohedral and morphotropic phase boundary (MPB). Two methods are used to characterize the extrinsic and intrinsic behaviours. Elastic and piezoelectric non-linear characterization at resonance has been made in isothermal conditions by impedance and vibration velocity measurements. In order to obtain the intrinsic coefficients, linear characterization at very low temperature has been carried out.

Keywords: Piezoelectric properties; Dielectric properties; PZT; Extrinsic behaviour

1. Introduction

Piezoelectric PZT ceramics have high dielectric and piezoelectric coefficients that are very sensitive to the Zr–Ti composition near the morphotropic phase boundary (MPB), and to the type and quantity of impurities used.

In general, these behaviours are due to the high intrinsic coefficients (produced by the unit cell distortion), and very especially to the important extrinsic effect caused by the domain wall movement.

A good knowledge of the intrinsic and extrinsic coefficients is important to understand the microstructure mechanisms involved, and could help us to optimise material properties, as is the case of new ceramic materials without lead.

The domain wall of these ceramics may be classified as 180° and non-180° types. In the first case, when the wall between two domains with opposite polarization (180°) moves, only the electric displacement D changes, so an extra contribution to the dielectric permittivity is produced. However, the specimen remains the same size, and so no piezoelectric effect is induced. That is to say, these domain wall movements have influence on the extrinsic dielectric coefficient ε_{ext}, but they exercise no influence on the extrinsic piezoelectric d_{ext}. Instead, when the adjacent domains have polarizations at non-180°, both extrinsic effects are produced: the dielectric ε_{ext} as well as the piezoelectric d_{ext} one.

In this work, two different ways of obtaining the extrinsic coefficients are analysed. First, assuming that the intrinsic effect has always a linear behaviour, non-linear measurements are carried out to obtain the extrinsic behaviour. These extrinsic coefficients are compared with the linear coefficients obtained at low signal, which are a superposition of the intrinsic and extrinsic behaviours.

Secondly, it is accepted[1] that when the temperature decreases, the extrinsic effect disappears: the domain wall freeze. Furthermore, the intrinsic phenomenon is near independent on the temperature for these materials. Thus the low temperature measurements allow us to obtain the intrinsic coefficients.

2. Preparation of materials

A conventional oxide mixing process was used to prepare $Pb(Zr_{1-x}Ti_x)O_3$ ceramics, with $x = 0.40$, pure and doped with 1 and 2 wt.% of Nb_2O_5 (softener or donors) or Fe_2O_3 (hardener or acceptors); and $x = 0.47$ doped with 1 wt.% of Nb_2O_5. The

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precursor oxides were mixed in a ball mill, dried, and calcined at 850 °C for 3.5 h. After pressing, 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 of 16–17 mm in diameter and 0.8–0.9 mm in thickness. 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 or morphotropic phase boundary, for $x = 0.40$ or 0.47, respectively.

3. Elastic non-linear measurements

A sinusoidal tension is applied at frequencies in the first radial resonance range of a piezoelectric disc. In the experimental set-up, the measurements of the tension $V(t)$, the current $I(t)$ and the velocity in the disc border $v(R, t)$ (by a laser vibrometer) are taken through a four-channel oscilloscope and a computer data acquisition and processing. The complex impedance $Z = R + \mathrm{j}X$ is calculated.

In order to avoid the overheating of samples, for each frequency and amplitude level, a burst of n cycles is used. The measurements are carried out in the steady-state zone, with a large number of measurement cycles to ensure accuracy.

For a constant frequency, the burst signal is applied at increasing amplitudes in order to obtain the dependence of the impedance versus the amplitude. The impedance variation, between impedance at high amplitude level $Z(I)$ and the linear or low amplitude one Z_0, $\Delta Z(I) = Z(I) - Z_0$ is shown[2] to be weakly dependent on frequency: this dependence is verified by repeating the measurements at other close frequencies. Near the resonance, it is preferable to insert a serial resistance to prevent the hysteresis phenomenon, because this set-up is similar to a current generator.[3]

An impedancimeter measures the capacitances C^T, at low frequency or free capacitance, and C^p, in the interval between the radial and thickness resonances, corresponding to ε^p_{33}.[4]

The relation $\Delta Z(I)$ can be more linear[2] if I' is used instead of I, and Z'' instead of Z. The corrected current I' is obtained through the electric admittance Y_0 value:

$$Y_0 = \mathrm{j}\omega C^T, \qquad \frac{1}{Z'} = \frac{1}{Z} - Y_0, \qquad I' = \frac{V}{Z'}, \tag{1}$$

and it is proportional to the mean stress $\langle T\rangle$:

$$\left\langle D'\right\rangle = \frac{I'}{\mathrm{j}\omega a} = d_{31}\left\langle T_r + T_\theta\right\rangle . \tag{2}$$

The motional impedance Z'' and reactance X'' are obtained from the capacitance C^p:

$$Y^p = \mathrm{j}\omega C^p = \frac{\mathrm{j}\omega\varepsilon^p_{33}a}{t}, \qquad \frac{1}{Z''} = \frac{1}{Z} - Y^p, \tag{3}$$

where a is the disc area and t is the thickness.

From these magnitudes, the relation $X''(I')$ is obtained, which is approximately a straight line for soft materials (quadratic for hard ones), with a slope that is weakly dependent on frequency in the resonance frequency range. The reactance increase is related to the shift frequency effect (decrease of high level resonance frequency ω_s) and allows us to obtain the stiffness c_{11} and compliance s^E_{11} at high signal:

$$\omega_s = \omega_{s0} - \frac{X'' - X''_0}{\Delta X_0/\Delta\omega}, \qquad c^p_{11} = c^p_{110}\left(\frac{\omega_s}{\omega_{s0}}\right)^2, \qquad s^E_{11} = \frac{1}{c^p_{11}(1-\sigma^{p2})}, \tag{4}$$

where ω_{s0} is the low signal resonance frequency, c^p_{110} the linear stiffness, X'' and X''_0 the reactance at high and low level, $\Delta X_0/\Delta\omega$ the slope of the linear reactance versus frequency, and σ^p is the Poisson modulus.

Finally, from the disc border velocity $v(R, t)$, the mean strain $\langle S\rangle$ is calculated, the relation between the modified electric displacement $\langle D''\rangle$ and $\langle S\rangle$ is obtained, and the piezoelectric coefficients e^p_{31}, d_{31} calculated as:

$$\langle S\rangle = \langle S_r + S_\theta\rangle = \frac{2v(R)}{R\omega}, \qquad \left\langle D''\right\rangle = \frac{I''}{\mathrm{j}\omega a} = \frac{I - VY^p}{\mathrm{j}\omega a}, \tag{5}$$

$$e^p_{31} = \frac{\left\langle D''\right\rangle}{\langle S\rangle} = \frac{d_{31}}{s^E_{11}(1-\sigma^p)}, \qquad d_{31} = \frac{e^p_{31}}{c^p_{11}(1+\sigma^p)}. \tag{6}$$

Fig. 1 (points C–D) shows the linear and non-linear measurements of d_{31} versus s^E_{11}, between the linear behaviour C point, and the highest excitation signal D point. The linear quotient $(d_{31}/s^E_{11})_0$ in this figure is the slope of the straight line between low signal point C and the origin. However, when we join the different non-linear points (between C and D), it is observed that these points are arranged in a straight line with higher slope. By

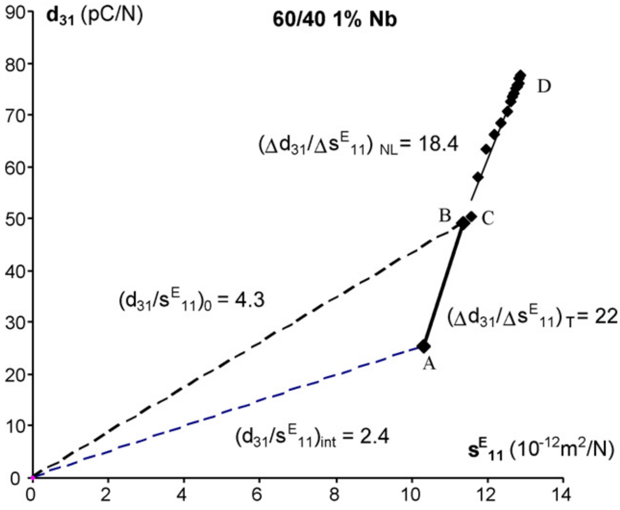

Fig. 1. Piezoelectric coefficient d_{31} vs. compliance s_{11}. A–B, linear measurements, at low-room temperature; C–D, non-linear measurements, at room temperature, low-high signal.

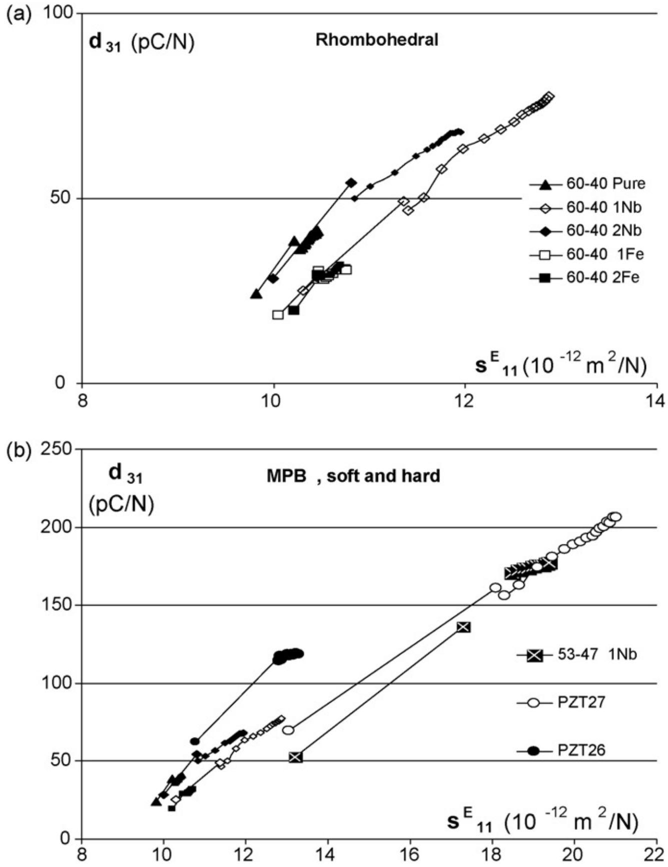

Fig. 2. Non-linear behaviour of piezoelectric d_{31} vs. the compliance s^E_{11}. The slope of this curves $(\Delta d_{31}/\Delta s^E_{11})_{\text{NL}}$ is the extrinsic non-linear behaviour. (a) Different rhombohedral compositions 60-40 (Zr–Ti) doped with Fe or Nb are compared with pure 60-40, and (b) MPB 53-47 with Nb is compared with commercials Pz26, Pz27 (Ferroperm Piezoceramics A/S).

assuming that the intrinsic behaviour is always linear, the slope of the straight line C–D corresponds to the non-linear extrinsic quotient $(\Delta d_{31}/\Delta s^E_{11})_{\text{NL}}$, generally bigger than the corresponding linear one $(d_{31}/s^E_{11})_0$.[5]

It is important to note that this representation agrees with,[1] and that the intrinsic and extrinsic coefficients that could be added are:

$$s = s_{\text{int}} + s_{\text{ext}}, \qquad d = d_{\text{int}} + d_{\text{ext}}, \qquad \varepsilon = \varepsilon_{\text{int}} + \varepsilon_{\text{ext}}. \tag{7}$$

Fig. 2 shows these non-linear behaviours for different materials 60-40 and 53-47 (Zr–Ti) compositions, with different impurity concentrations: Nb and Fe. Pure 60-40 and commercials Pz27, Pz26 (from Ferroperm Piezoceramics A/S) are also plotted as reference.

Table 1 contains the linear and extrinsic piezoelectric coefficients for these compositions. From these figures and tables the following remarks can be derived:

- The behaviour of compositions with Fe impurities are very close to the pure one and with a low piezoelectric d_{31} coefficient and linear $(d_{31}/s^E_{11})_0$ quotient; they show a very low non-linear behaviour, typical for hard ceramics used in power applications.
- Nb compositions show higher $(d_{31})_0$ and $(d_{31}/s^E_{11})_0$ quotient linear values than the Fe compositions for all 60-40 materials. They have a high non-linear behaviour, as do the soft ceramics, with a large difference between the high and low signal measurements.
- Material in the MPB region, with composition 53-47, and Nb impurities is similar to the soft Pz27, with very high piezoelectric $(d_{31})_0$ coefficient, near to 150 pC/N.
- For 1% of Fe and Pz26, extrinsic $(\Delta d_{31}/\Delta s^E_{11})_{\text{NL}}$ quotient have low values, near to 6–7 C/m^2, lower than all others materials where this quotient is near 15–30 C/m^2.

4. Linear low temperature behaviour

To complete these extrinsic piezoelectric measurements, low temperature measurements have been carried out. It is assumed[1] that at low temperature the domains are “frozen”, so there is no domain wall movement and only the intrinsic effect contributes to the dielectric and piezoelectric effects. It is also assumed[1] that the intrinsic behaviour is independent of temperature. So, from these measurements it is also possible to obtain the intrinsic coefficient (from low temperatures measurements) as well as

Table 1
Linear coefficients of compliance $(s^E_{11})_0$, relative dielectric permittivity $(\varepsilon^T_{33})_0$ and piezoelectric coefficient $(d_{31})_0$; linear $(d_{31}/s^E_{11})_0$, extrinsic $(\Delta d_{31}/\Delta s^E_{11})$ and intrinsic $(d_{31}/s^E_{11})_{\text{int}}$ piezoelectric quotients

PZT (Zr/Ti)	$(s^E_{11})_0$ ($\times 10^{-12}$ m^2/N)	$(\varepsilon^T_{33})_0$	$(d_{31})_0$ (pC/N)	$(d/s)_0$ (C/m^2)	$(\Delta d/\Delta s)_{\text{NL}}$ (C/m^2)	$(\Delta d/\Delta s)_{\text{T}}$ (C/m^2)	$(d/s)_{\text{int}}$ (C/m^2)	α_{s11} (ext/int)	α_{s12} (ext/int)	α_ε (ext/int)	α_d (ext/int)	$\alpha_d/\alpha_\varepsilon$ (ext/int) (%)
60/40 1% Fe	10.45	407	29	2.8	6 ± 3	27	1.8	0.04	0.12	0.97	0.6	62
60/40 2% Fe	10.48	401	29	2.8	25 ± 7	36	1.9	0.03	0.1	0.84	0.5	60
60/40 1% Nb	11.36	417	49	4.3	19 ± 5	23	2.5	0.07	0.1	1.22	0.95	78
60/40 2% Nb	10.82	440	54	5.0	13 ± 3	32	2.8	0.08	0.14	1.15	0.91	79
60/40 Pure	10.22	351	38	3.8	30 ± 3	35	2.5	0.04	0.1	0.79	0.58	73
53/47 1% Nb	17.30	1244	136	7.9	11 ± 4	20	4.0	0.31	0.44	1.97	1.56	79
Pz 27	18.10	1645	163	8.9	14 ± 3	18	5.3	0.39	0.69	1.9	1.34	71
Pz 26	12.80	1323	117	9.1	7 ± 5	27	5.8	0.19	0.39	1.42	0.88	62

Extrinsic measurements in the non-linear experiments $(\Delta d_{31}/\Delta s^E_{11})_{\text{NL}}$, and different temperature ones $(\Delta d_{31}/\Delta s^E_{11})_{\text{T}}$. From low and room temperature measurements, quotients between extrinsic and intrinsic coefficients: compliances $\alpha_{\text{s11}} = s_{\text{ext11T}}/s_{\text{int11}}$, $\alpha_{\text{s12}} = s_{\text{ext12T}}/s_{\text{int12}}$, dielectric $\alpha_\varepsilon = \varepsilon^T_{\text{ext}}/\varepsilon^T_{\text{int}}$ and piezoelectric $\alpha_d = d_{\text{extT}}/d_{\text{int}}$. Quotient between piezoelectric and dielectric $\alpha_d/\alpha_\varepsilon$ ones. Different PZT doped compositions and commercial material Pz27, Pz26 (Ferroperm Piezoceramics A/S).

the extrinsic one (from the difference between low and room temperature measurements).

Measurements at fundamental radial resonance and first overtone have been carried out at room and low temperature (15 K), to obtain the material piezoelectric constants. In Fig. 1, the linear values $d_{31\mathrm{LT}}$ and $s^E_{11\,\mathrm{LT}}$ have also been plotted at low temperature (point A). So it should correspond to the intrinsic coefficient, thus obtaining $(d_{31}/s^E_{11})_{\mathrm{int}}$.

The extrapolation of the straight line joining the non-linear measurement points (C–D), with the afore-mentioned slope $(\Delta d_{31}/\Delta s^E_{11})_{\mathrm{NL}}$ is close to the low temperature point A. This fact could be interpreted as a confirmation of all the mentioned hypotheses: non-linear as well as temperature coefficient increase are produced only by the extrinsic behaviour.

To evaluate these results, the extrinsic effect has been measured in two ways: on the one hand, from the slope of the straight line joining the non-linear measurement points (C–D), and obtaining the quotient $(\Delta d_{31}/\Delta s^E_{11})_{\mathrm{NL}}$. Secondly, the slope of the straight line joining the two linear measurement points at low and room temperature (A and B) has been calculated. If we accept that the extrinsic effect disappears at low temperature, the afore-mentioned intrinsic quotient $(d_{31}/s^E_{11})_{\mathrm{int}}$ (near to point A) could be obtained. The extrinsic quotient $(\Delta d_{31}/\Delta s^E_{11})_{\mathrm{T}}$ is obtained, assuming that at room temperature the linear coefficients d_{31}, s_{11} are the addition of intrinsic and extrinsic coefficients (Eq. (7)).

Table 1 shows these coefficients, for different ceramics, verifying that both extrinsic coefficients $(\Delta d_{31}/\Delta s^E_{11})_{\mathrm{NL}}$ and $(\Delta d_{31}/\Delta s^E_{11})_{\mathrm{T}}$ are similar for all materials except for the hard Pz26 and 60-40 1% Fe doped.

Table 1 also shows the quotient $\alpha_d = d_{\mathrm{extT}}/d_{\mathrm{int}}$, which inform us about the extrinsic contribution in these materials: a high extrinsic coefficient value represents a high mobility of the domain wall.

It may be observed that:

- Extrinsic compliance $\alpha_{s12} = s_{\mathrm{ext12T}}/s_{\mathrm{int12}}$ is higher than the $\alpha_{s11} = s_{\mathrm{ext11T}}/s_{\mathrm{int11}}$ one.
- Both piezoelectric $\alpha_d = d_{\mathrm{extT}}/d_{\mathrm{int}}$ and dielectric $\alpha_\varepsilon = \varepsilon_{\mathrm{extT}}/\varepsilon_{\mathrm{int}}$ quotients have very low values in Pure and Fe compositions. They are optimised for MPB and commercial compositions.

The comparison between the quotient of piezoelectric coefficients $\alpha_d = d_{\mathrm{extT}}/d_{\mathrm{int}}$ and the dielectric ones $\alpha_\varepsilon = \varepsilon_{\mathrm{extT}}/\varepsilon_{\mathrm{int}}$ is also shown in Table 1. It is shown that these quotients are related, but are different from one material to another. Only the extrinsic effect due to non-180° domain wall contributes to the piezoelectric coefficient (and thus, to the quotient $\alpha_d = d_{\mathrm{extT}}/d_{\mathrm{int}}$), because only this microstructure produces a variation of the specimen dimensions when the domain wall moves. However, the extrinsic effect due to all the domain wall (180° and non-180°) exercises an influence on the quotient of dielectric coefficients $\alpha_\varepsilon = \varepsilon_{\mathrm{ext}}/\varepsilon_{\mathrm{int}}$.

The dielectric quotient $\alpha_\varepsilon = \varepsilon_{\mathrm{extT}}/\varepsilon_{\mathrm{int}}$ is greater than the piezoelectric one $\alpha_d = d_{\mathrm{extT}}/d_{\mathrm{int}}$, so the quotient $\alpha_d/\alpha_\varepsilon$, is always less than 1. It is very similar from one composition to another, 75% approximately, but this proportion decreases to 60–62% in the Fe doped and hard commercial Pz26 materials. There are two possible explanations for this effect: either this quotient could inform us about the proportion of non-180° domain wall in the ceramic above-mentioned; or it is due to a partial polarization of samples producing a lower extrinsic piezoelectric effect.

5. Conclusions

The comparison between extrinsic non-linear measurements $(\Delta d_{31}/\Delta s^E_{11})_{\mathrm{NL}}$ and linear ones $(\Delta d_{31}/\Delta s^E_{11})_{\mathrm{T}}$ at different temperatures, shows an interesting concordance. These results are consistent with the hypothesis that both the non-linear and the temperature behaviours are due only to extrinsic effects.

The non-linear measurements allow us to obtain information about extrinsic phenomena that complete other measurements, and enable the Ti–Zr compositions and impurity concentrations to be optimised.

Acceptor impurities such as Fe produce low extrinsic behaviour. There is a low mobility domain wall, and also low losses and non-linearities, which benefit the power applications.

Nb or donor impurities increase the domain wall mobility, so both the piezoelectric and the dielectric extrinsic coefficients are higher. This phenomenon is also greater for compositions near the morphotropic phase boundary (MPB).

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