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Extrinsic coefficient charcterisation of PZT ceramics near the morphotropic phase boundary

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PZT ceramics with high piezoelectric coefficients have high extrinsic contributions. This extrinsic behaviour, which is related to the domain wall movement, produces high non-linear effects that are sometimes inconvenient, for example when it increases the losses in power devices. The relation between extrinsic behaviour and non-linearities could be used to provide a good extrinsic characterization of materials in order to optimise the piezoelectric devices. In all cases the physical explanation of the behaviour is sought. The aim of this work is to study the dependence of the linear and non-linear dielectric, piezoelectric and mechanical coefficients on the Ti fraction in PZT ceramic compositions near the morphotropic phase boundary (MPB). The dependence of these coefficients on the defect concentration is also analysed. Hard ceramics belonging to Ferroperm Piezoceramics, with two different acceptor dopant levels, high and low, have been measured.

Keywords: Piezoelectricity, Ferroelectric domains, Extrinsic.

Caracterización del coeficiente extrínseco en cerámicas PZT cerca de la transición de fase morfotrópica.

Las cerámicas PZT con coeficientes piezoeléctricos elevados poseen contribuciones extrínsecas grandes. Este comportamiento extrínseco, relacionado con el movimiento de las paredes de los dominios, comporta efectos no lineales grandes que no siempre son deseables, por ejemplo, al incrementar las pérdidas de los dispositivos piezoeléctricos. Esta correspondencia entre efectos extrínsecos y no linealidades puede ser utilizada para caracterizar las cerámicas con el fin de optimizar sus propiedades piezoeléctricas. En todos los casos se busca una interpretación física de los resultados obtenidos. El objetivo de este trabajo es el estudio de la dependencia de los coeficientes lineales y no lineales dieléctricos, piezoeléctricos y elásticos con la fracción de Ti en cerámicas PZT con composiciones de Zr-Ti cerca de la transición de fase morfotrópica (MPB). También se analiza la dependencia de estos coeficientes con la concentración de impurezas, utilizando para ello cerámicas de Ferroperm Piezoceramics del tipo duras y con dos niveles de dopaje aceptor, alto y bajo.

Palabras clave: Piezoelectricidad, Dominios ferroeléctricos, Extrínseco.

1. INTRODUCTION

The crystal structure near the PZT morphotropic phase boundary (MPB) changes with the composition of Ti-Zr from rhombohedral (low Ti quantity) to tetragonal (high Ti) through a narrow monoclinic phase. All these PZT materials present domain structure with domain wall of 180º and non-180º between the directions of the domain polarisation of adjacent domains. The variations in the crystal structure impose variations on the possible adjacent polarisation domain, since not all the combinations are possible.

The different type of polarisation between adjacent domains produces different effects. The 180º domain wall contributes only to dielectric behaviour, while non-180º walls also contribute to the elastic compliance and piezoelectric coefficients.

The domain wall movement is also very dependent on the dopants. The type and the quantity of these impurities help to stop the domain growth. A high extrinsic behaviour implies higher coefficients.

All these effects imply not only high coefficients, but also dielectric, elastic and piezoelectric non-linear behaviours (1-4). Sometimes these effects are undesired, for example when the losses in high power devices increase.

The aim of this paper is to study the influence of the composition and doping quantities on the properties of ceramics. Special attention is given to the non-linear properties that can provide information about the extrinsic behaviour produced by the domain wall movements.

The series material studied in this paper have compositions in the interval: $0.479 < x < 0.495$, x=Ti fraction of $PbZr_{(1-x)}Ti_xO_3$ (PZT). Two series of materials (made by Ferroperm Piezoceramics A/S) have been used with high (H) or low (L) acceptor dopants.

2. LINEAR CHARACTERIZATION

The dielectric permittivity, both real and imaginary, depends very much on the structure, and therefore on the x fraction of Ti in the PZT composition. When the composition is near the MPB there are more domain wall orientations, and thus a large surface domain wall with a low energy may remain. Fig. 1 shows that ε_{33} increases with the x Ti fraction when it approaches the MPB. This plot also shows that high doped ceramics (H) have higher dielectric constant than ceramics with low impurities (L).

In Fig. 2, the plot of dielectric losses shows a minimum

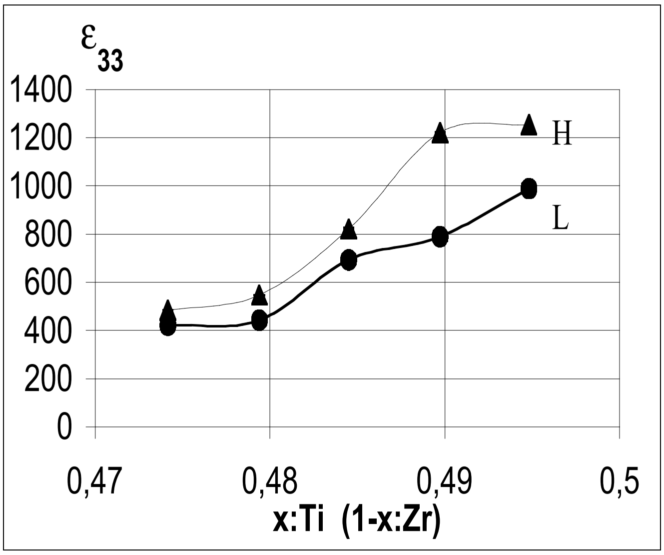

Fig. 1- Dielectric constant versus x: Ti fraction in PZT composition. (H) High and (L) low doping quantities.

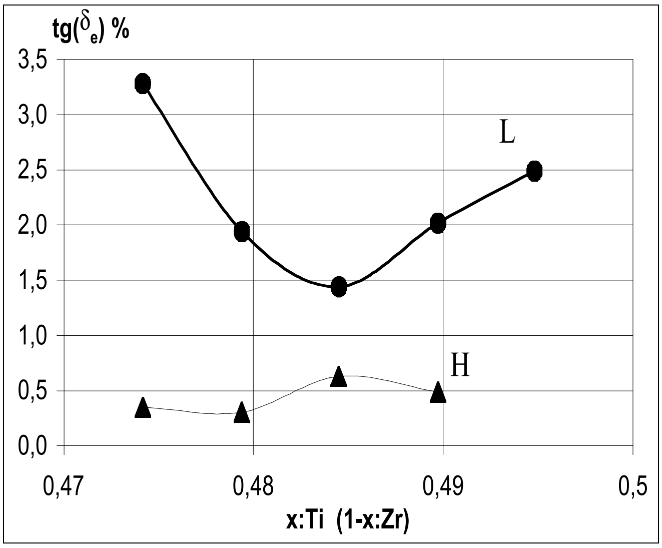

Fig. 2- Dielectric losses versus x. (H) High and (L) low doping quantities.

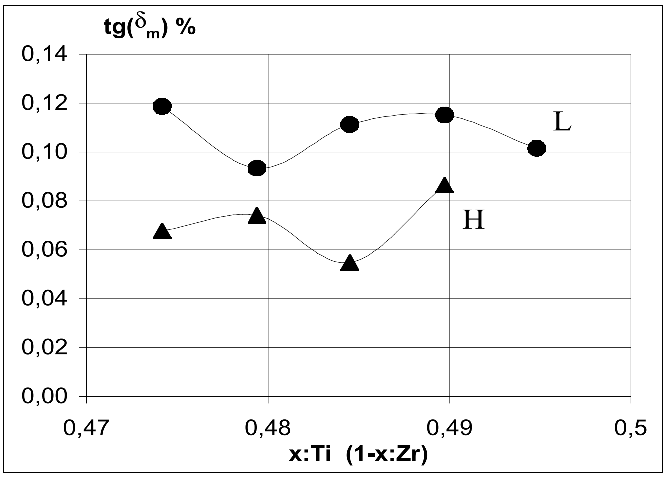

Fig. 3- Mechanical tangent of losses versus x.

of losses for a composition near x=0.485. However, the most significant aspect is the decrease of losses with the high defect concentration (H). This effect could be explained if we consider that the movement of the domain wall is a bending, so it appears as reversible and without any increase in the losses. This bending model allows a reversible commutation of dipoles near the wall domain when an electric field is applied, which returns to the original orientation when the electric field disappears.

The above behaviours are also observed in the mechanical losses, measured at resonance, Fig. 3: the losses are lower for high doped ceramics (H).

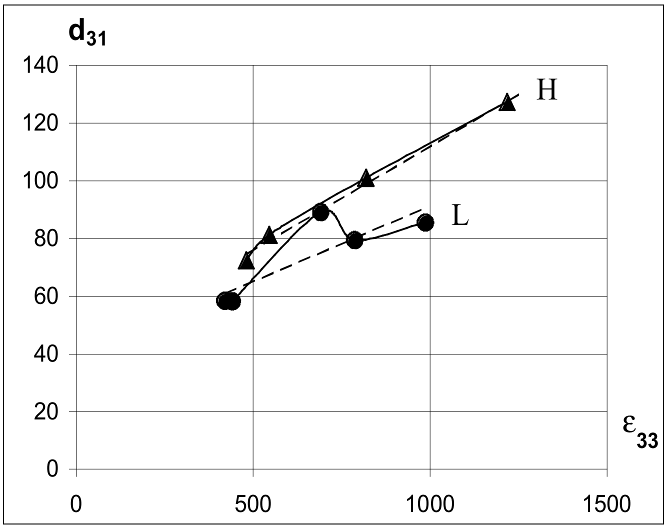

Fig. 4- Piezoelectric d_{31} coefficient versus dielectric constant.

As with the dielectric constant, the piezoelectric coefficient d_{31} increases with the x Ti fraction. Since this dependence is similar to the dielectric constant ε_{33}, Fig. 4 relates both coefficients. It is shown that there is a linear relation between these coefficients, with a bigger piezoelectric coefficient for the ceramics with high (H) doping acceptors. This result implies that the impurities favour the non-180º domain wall more than the 180º, since the non-180º wall increases not only the dielectric coefficient but also the piezoelectric one.

3. NON-LINEARITIES

3.1 Dielectric non-linearity

The non-linear measurements are made at 1kHz, by a modified comparison capacitance bridge that is compensated at low signal in order to obtain the non-linear contribution to the electric displacement D(E), and the non-linear dielectric constant increment $\Delta\varepsilon_{NL}(E,E_0)$, at every instantaneous electric field, E. To prevent overheating of the ceramics due to the high signal excitation, burst signal excitations with only 5 cycles are used.

After the subtraction of the antisymmetric contribution ε_A (a low contribution that depends on the polarisation) the symmetric contribution ε_S is analysed: a discrimination is made between the irreversible contribution ε_α, which corresponds to the dependence on the electric field amplitude $\varepsilon_\alpha(E_0)$ only, and the reversible contribution $\varepsilon_\beta(E,E_0)$, which depends on the instantaneous electric field:

$$\Delta\varepsilon_{NL}(E,E_0)= \varepsilon_A(E,E_0) + \varepsilon_S(E,E_0) = \varepsilon_A(E,E_0) + \varepsilon_\alpha(E_0) + \varepsilon_\beta(E,E_0). \quad [1]$$

The measurements show a non-linear behaviour typical for hard piezoceramics: firstly, the irreversible contribution ε_α is proportional to the square of the electric field amplitude E_0^2; secondly, the contribution of the reversible ε_β is greater than the irreversible ε_α non-linearity, as can be observed in Fig. 5. Thus these materials have lower losses. This behaviour is greater for highly doped ceramics, and is very interesting for high power applications, because low losses and low non-linear losses are required for such devices. The bending wall domain effect could explain this low contribution to the losses.

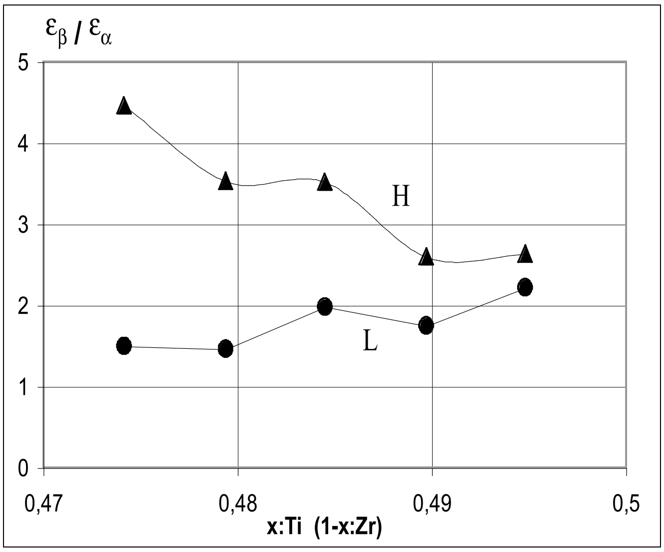

Fig. 5- Quotient between the reversible ε_β and irreversible ε_α non-linear dielectric constant, versus x.

Any studied ceramics verify the Rayleigh law, as always occurs for hard ceramics, even though the quotient $\varepsilon''/\varepsilon_\alpha$, between the dielectric losses and the irreversible contribution to the increase of the dielectric constant, has a value very close to 0.43, as predicted by the Rayleigh law.

3.2 Mechanical non-linearities

Measurements have been taken of the 1st radial mode at resonant frequency with burst excitation. A laser vibrometer enables the velocity vibration measurement to be taken. The method used, described in (5-6), consists in taking impedance measurements at constant frequency near the resonance. The increase of the real and imaginary part of impedance are related to the increases of mechanical losses $\Delta tg\,(\delta_m)$ and shift frequency, respectively, and thus to the compliance increase Δs^E_{11}. The increase of the compliance has a quadratic dependence on the mean stress, $\Delta s^E_{11} = c\langle T\rangle^2$, Fig. 6, as in the case of hard ceramics. This dependence is similar for the mechanical losses increase.

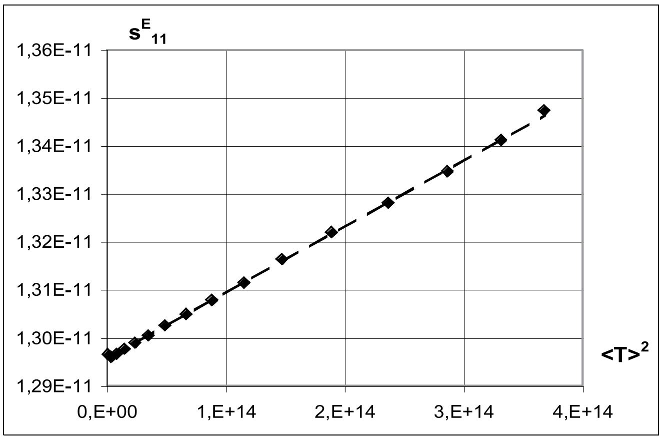

Fig. 6- Non-linear compliance increase versus quadratic mean stress.

4. EXTRINSIC BEHAVIOUR

From the previous non-linear measurements, it is possible to obtain the extrinsic piezoelectric behaviour of the e_{31} coefficient. From the mechanical non-linear measurements it is possible to obtain the values of:

a) The mechanical contribution to the electric displacement is calculated from the mechanical current: $D_m = I_m / A\omega$.

b) From the linear and the non-linear variation of the compliance, the compliance at high level is obtained (4-6)

$$s^E_{11}(T) = s^E_{11}(T=0)\cdot(1+\frac{\Delta s^E_{11}}{s^E_{11}}) = s^E_{11}(T=0)\,(1+\frac{\Delta X_m}{\overline{Z}}). \quad [2]$$

c) From the velocity vibration v(R), measured by the laser, the mean strain <S> and the main stress $\langle T_r+T_\theta\rangle$ are calculated (4):

$$\langle S\rangle = \langle S_r + S_\theta\rangle = \frac{2\,v(R)}{R\omega}, \quad [3]$$

$$T = \langle T_r + T_\theta\rangle = \frac{\langle S\rangle}{s^E_{11}(1-\sigma)}. \quad [4]$$

Assuming that in the resonance the electric field verifies E=0.

Finally, the piezoelectric coefficient d_{31} is obtained:

$$d_{31} = \frac{D_m}{T}. \quad [5]$$

The plot of d_{31} versus s^E_{11}, Fig. 7, enables us to see the linear as well as the non-linear behaviour (4): The linear piezoelectric coefficient $e_{31lin} = d_{31} / s^E_{11}$ is measured from the linear, or low level values. This representation of the non-linear behaviour shows that there is a linear dependence between Δd_{31} and Δs^E_{11}. If we assume that the non-linearities are caused by the domain wall movement, then this dependence corresponds to

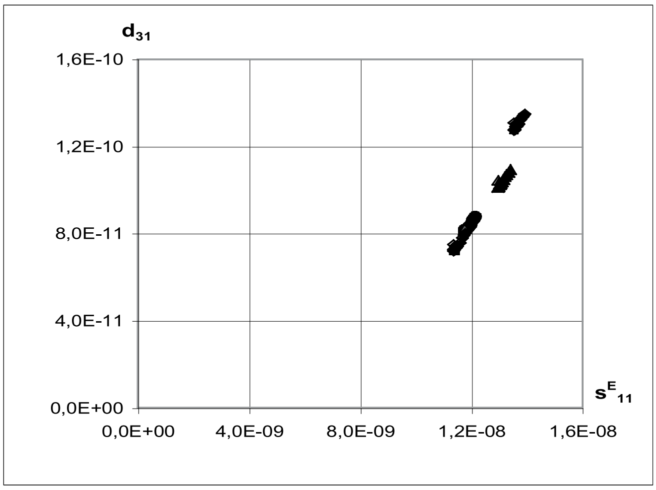

Fig. 7- Piezoelectric d_{31} versus compliance s^E_{11}.

the extrinsic contribution. The slope $e_{31ext}=\Delta d_{31}/\Delta s^E_{11}$, related to the non-linear measurements allow us to measure of the extrinsic coefficient. These coefficients are generally different to the linear coefficient, which has both contributions: intrinsic and extrinsic.

In all these ceramics, the extrinsic coefficient is higher than the linear one. Fig. 8 shows the linear and extrinsic values of e_{31} piezoelectric coefficients for high and low doped ceramics. These measurements imply that for low doped ceramics (L) the extrinsic e_{31} coefficient depends strongly on the x Ti fraction. For ceramics with high quantity of defects (H), this dependence is very low, while for this series the linear value is higher than for the low doped ceramics (L).

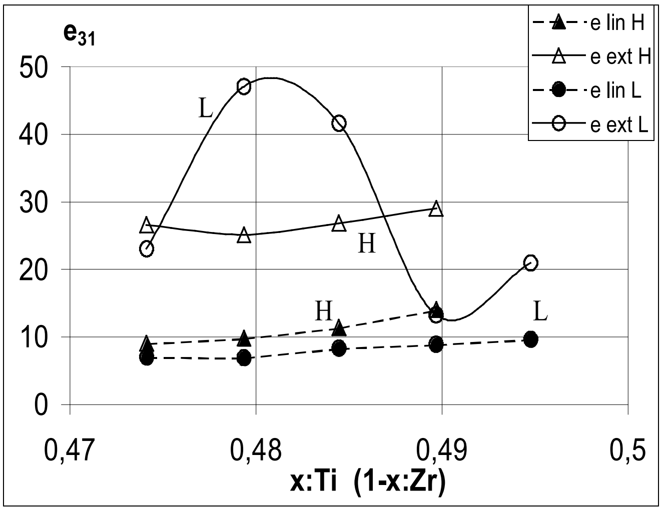

Fig. 8- Extrinsic and linear piezoelectric e_{31}.

The non-linear or extrinsic coefficients are higher than the intrinsic ones, so this extrinsic phenomenon improves the ceramic piezoelectric characteristics, but also causes the non-linear behaviour at high signal.

5. CONCLUSIONS

The behaviour of PZT ceramics is strongly dependent on the crystal structure as well as on the defect concentration. All dielectric, piezoelectric and elastic coefficients increase near the morphotropic phase boundary, MPB. The analysis of different contributions to the dielectric increases, reversible and irreversible, allow us to minimize the losses for power ceramic applications. The reversible contribution that may be due to the bending of the domain wall is greater in ceramics with high doping concentration, so these ceramics present lower dielectric and mechanical loses.

Due to the domain wall movement, the extrinsic contribution produces high dielectric and piezoelectric coefficients, and can be well characterized through the non-linear measurements. In this paper, the extrinsic piezoelectric coefficient e_{ext} has been measured and is higher than the linear one e_{lin}. This domain wall movement is very sensitive to the doping concentration, so the study of the non-linear behaviour could optimize the composition and doping concentration of ceramics.

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