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Non Linear Properties of Dense PIN-PT Ceramics.

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ABSTRACT

Nonlinear measurements of dense $63PbIn_{1/2}Nb_{1/2}$-$37PbTiO_3$ (PIN-37PT) piezoceramics, was recorded at 1 kHz and at resonance under driven AC electric fields and axial static pressure. Influence of donor or softener (Mg, Nb) and acceptor or hardener (Mn) was investigated.

Dependence of the real and imaginary parts of the dielectric constant on electric field was compared with PZT hard ceramics and PMN-PT soft ceramics. The mechanical nonlinear behavior of piezoelectric ceramics, characterized by two coefficients (α and β), was measured according to the CENELEC European Standards EN5034-3. The new mechanical nonlinear coefficient β measures the compliance variation. The α and β coefficients of PIN-37PT ceramics, 0.95×10^6 and 3.8×10^6, are larger than that hard PZT8 (0.03×10^6 and 0.3×10^5).

INTRODUCTION

Lead-based relaxor ferroelectric solid solution ceramics with $(1\text{-}x)Pb(B_1B_2)O_3\text{-}xPbTiO_3$ (B_1=Mg, In, Sc, Yb; B_2=Nb, Ta) formula presents a high Curie temperature and exhibit excellent dielectric and electromechanical properties at low and high level, especially at compositions near the morphotropic phase boundary (MPB)[1]. The composition, PIN-37PT, exhibits a length extensional coupling coefficient k_{33} of 65% and a piezoelectric constant d_{33} of 425pC/N for a Curie temperature of 290°C and the ferroelectric-ferroelectric phase transition at 190°C[2]. Such complex perovskites are of greater interest for electronic ceramic devices, piezoelectric actuators, sonar and medical systems.

The dielectric and piezoelectric constants of PIN-37PT, recorded from Standard Procedure[3] at a driven electric field of 1V are presented in table 1. Such a low level coefficient cannot be used for describing the non linear behaviour release in ceramics driven at high mechanical stress or at high ac electric field as in sonar's operating conditions. The purpose of this study is to evaluate the influence donor (Mg, Nb), acceptor (Mn) and synthesized aids as PbO on the dielectric and piezoelectric response on PIN-37PT piezoceramics. The correlation between dielectric constant and dielectric losses is analyzed and interpreted from the point of view of the Rayleigh model. The mechanical nonlinear behavior of piezoelectric ceramics, characterized by two coefficients (α and β) was measured according to the CENELEC European Standards EN5034-3[4].

EXPERIMENT & RESULTS

Electromechanical properties

The perovskite PIN-0.37PT powder ceramics were synthesized from $InNbO_4$, PbO and TiO_2 at 850°C for 2h. Mg, Nb, Mn and Pb were added during re-milling step of perovskite powders. Dense PIN-37PT ceramics were obtained by conventional sintering method at 1150°C.

Electromechanical properties were measured according to the IRE standard method with an Agilent 4294A impedance analyzer (Table 1). Doping with Mn leads to reduction of electric loss.

Properties	PZT-8	PZT-7	PIN-37PT	PIN-3PMN-PT	PIN-37PT +2%PbO	PIN-37PT +0.5%Mn
$\varepsilon_{33}^{T}/\varepsilon_0$@1kHz	1134	1521	2683	2708	2977	1996
$\tan\delta_e$@1kHz (%)	0.2	0.4	2.05	1.9	1.5	0.6
k_{33}	0.68	0.7	0.65	0.65	0.62	0.42
d_{33} (pC/N)	270	339	428	435	429	216
d_{33}Berlincourt (pC/N) (60 Hz)	266	343	429	455	434	230
g_{33} (10^{-3}Vm/N)	27	26	17.8	16.8	15.9	12.1
$M_{33}=(d_{33}/s_{33}^{E})^2$ (C^2/m^4)	315	377	540	553	589	232
Q_{33m}	695	235	66.9	83	71	115
Q_e	500	244	49	53	67	164

Table 1: *Electromechanical properties measured according to the IRE standard method on PIN37PT, PIN-3PMN-PT, PIN-37PT+2%PbO, PIN-37PT+0.5%Mn and $PbZr_xTi_{1-x}O_3$ (PZT-8; Navy Type III,PZT-7 Navy Type I) piezoceramics.*

Whatever the mechanism considered, the doping plays an essential role in the stabilization of domain configuration. In the case of a doping agent acceptor such as manganese in our study, the dielectric constant reduction can be explained by the domain walls mobility reduction. For the PIN-37PT ceramics doped with lead, the ion Pb^{2+} can be considered in the structure as a doping agent isovalent having as consequence to decrease of the Curie temperature and an increase of the dielectric constant at room temperature.

Dielectric Drift

The Non-linear dielectric response was measured by monitoring the voltage across a 9.96 F capacitor in a Sawyer–Tower arrangement. The voltage across the capacitor was measured using the EG&G 5210 Lock-in Amplifier. The Rayleigh law has been used to describe the dielectric drift response in a piezoelectric ceramic[7,8]. According to the Rayleigh model, the mean values of the dielectrics constants ε' and ε'' have this form:

$$\boldsymbol{\varepsilon}' = \boldsymbol{\varepsilon}_L + \boldsymbol{\alpha} \mathbf{E}_0 \quad \text{and} \quad \boldsymbol{\varepsilon}'' = \frac{\mathbf{4}}{\mathbf{3\pi}} \boldsymbol{\alpha} \mathbf{E}_0 \quad \text{then} \quad m\varepsilon_{\varepsilon} = \frac{\varepsilon''}{\delta\varepsilon'} = \frac{4}{3\pi} \cong 0.42$$

where E_0 is the amplitude of the applied electric field, E is the instantaneous value of the electric field, α is the Rayleigh coefficient and ε_L is the dielectric constant at zero-field amplitude. The ratio between the value of the dielectric losses and the dielectric constant is a constant.

Figure 1 presents the variation of ε'versus driven electric field and the ratio m_ε values of PIN-37PT ceramics. Table 2 summarizes results recorded on the ceramic up to 500V/mm. The m_ε values, which correspond to the curve slope ε''= f(δε') in Fig1., are about 0.45, very close to the value predicted by the Rayleigh model. The Rayleigh coefficients (α_{AC}^{T}) of $2.1\cdot10^{-3}$, $1.92\cdot10^{-3}$, $1.4\cdot10^{-3}$, $1.03\cdot10^{-3}$m.V^{-1} were measured for PIN-37PT undoped and doped with 2%PbO, 3%PMN and 0.5%Mn, respectively. It is worth noting that the Rayleigh coefficient of ceramics doped with Mn is close to those of hard $PbZr_xTi_{1-x}O_3$ ceramics(PZT-7 and PZT-4D; Navy Type 1) .

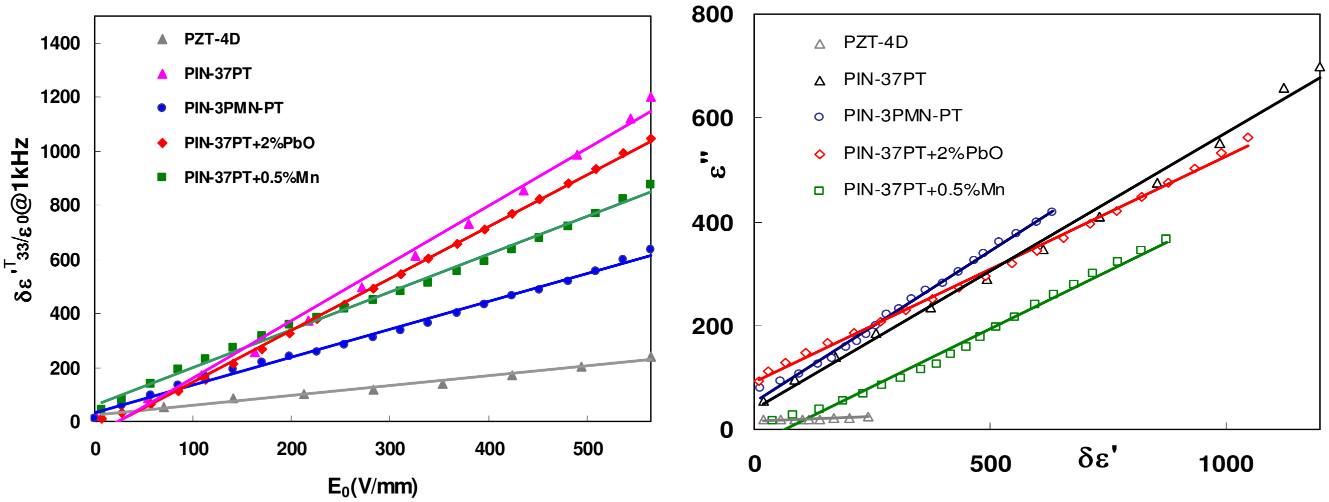

Figure 1: *δε' of PIN-37PT undoped and doped with 2%PbO,3% PMN , 0.5% Mn and* $PbZr_xTi_{1-x}O_3$ *(PZT-4D, Navy Type 1) poled ceramics versus driven electric field (left) and* m_ε *(right).*

Material	d (% $d_{theoretical}$)	ε_{33}	$\tan\delta_{lin}$ (%)	m_ε	α^T_{AC} [m/V] (relative value)
PIN-37PT	98	2683	2.05	0.45±0.01	$2.1\cdot10^{-3}$
PIN-3PMN-PT	97.5	2708	1.9	0.47±0.01	$1.03\cdot10^{-3}$
PIN-37PT+2%PbO	99	2977	1.5	0.43±0.01	$1.92\cdot10^{-3}$
PIN-37PT+0.5%Mn	97	1996	0.6	0.44±0.01	$1.40\cdot10^{-3}$
PZT-4D	99	1300	0.4	0.19±0.01	$3.65\cdot10^{-4}$

Table 2: *Linear relative dielectric constant value* ε_L *, dielectric loss* $\tan\delta_{lin}$*, ratio* m_ε *and Rayleigh coefficient* a^T_{AC} *for PIN-37PT, PIN-3PMN-PT, PIN-37PT+2%PbO, PIN-37PT+0.5%Mn and* $PbZr_xTi_{1-x}O_3$ *(PZT-4D, Navy Type 1) poled ceramics.*

Mechanical Nonlinear Behavior

The non linear loss coefficient α was measured according to the method developed by Gonard et al.[5] and Albareda et al[6]. The coefficient α quantifies the variation of the mechanical loss tangent $\tan\delta_m$ versus the square mean strain <S>: $\alpha=\Delta\tan\delta_m/\Delta<S>^2$, α is measured in longitudinal mode on free rods driven at the series resonance frequency f_s at increasing voltages.

The variation of $\tan\delta_m$ can be expressed as: $\tan\delta_m = \tan\delta_{m0} + \alpha <S^2>$ where $\tan\delta_{m0} = 1/Q_{m0}$ is the small signal mechanical loss tangent. This method consists in measuring the resistance R_1, resonance frequency f_s, and current I, when a sweep frequency is used for each excitation level. The HP 4194A network analyzer is used in gain-phase mode. The applied voltage V and the current I through the ceramic can be obtained as functions of frequency. To avoid the hysteresis phenomena, the electrical measurements V and I are performed by downward sweeping frequency.

The slope of the curve presenting the mechanical loss ($\tan\delta_m$) and the relative change of compliance ($\Delta S_{33}/S_{33}$) versus square mean strain $<S>^2$, allows to deduce **α** & **β** coefficients. The mechanical nonlinear behavior of piezoelectric ceramics is characterized by two coefficients.

The samples are cylindrical rods driven in longitudinal mode. The samples were suspended in air by two thin wires soldered on each end face.

Figure 2 and table 3 present the mechanical loss, and the relative change of compliance versus square mean strain of PIN-37PT undoped and doped with 2%PbO, 3%PMN and 0.5%Mn, respectively. Comparison with hard PZT-7 and PZT-8 ($PbZr_xTi_{1-x}O_3$) ceramics are given.
These data indicate that the **α** coefficient of PIN-37PT doped with Mn is the lowest value obtained for the PIN-37PT ceramic systems ($0.96.10^{-6}$). Addition of PbO does not influence the behaviour of the ceramic while doping with Mn and Mg (by addition of PMN) leads to a decrease of the **α** coefficient. The coefficient of Mn doped ceramics is still larger than that of hard PZT-7 ($0.63.10^{-6}$).

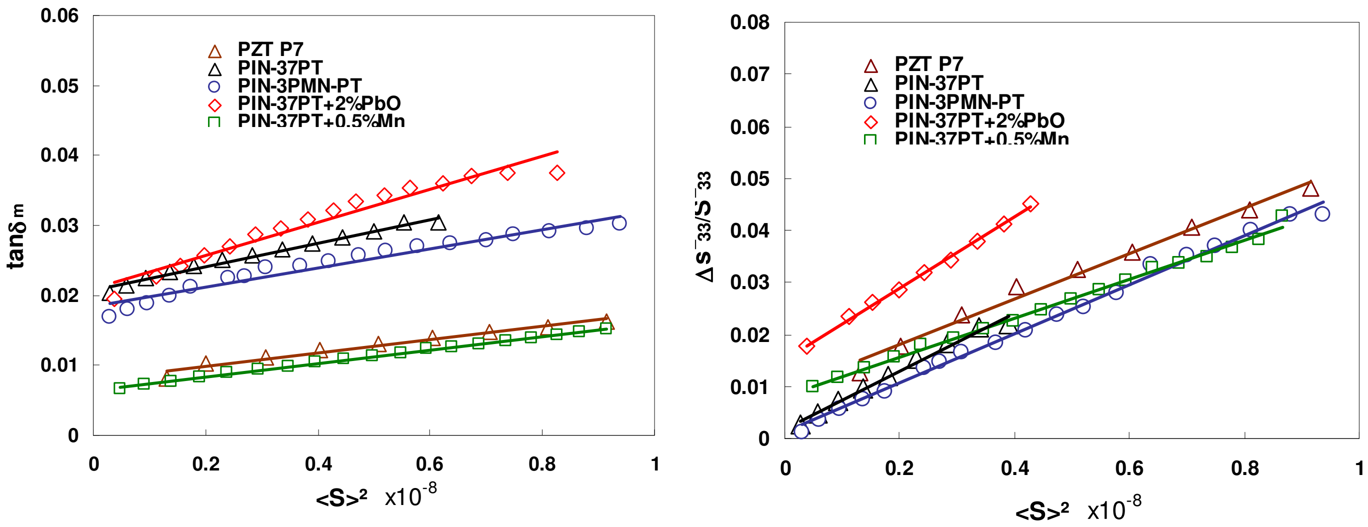

Figure 2: *Compliance increase (left) and mechanical loss tan δm (bottom) versus square mean strain, for longitudinal resonators of PIN-37PT undoped and doped with 3%Pb+3% PMN+ 0.5% Mn, and* $PbZr_xTi_{1-x}O_3$ *(PZT-7 Navy Type I) ceramics.*

Properties	PZT-8	PZT-7	PIN-37PT	PIN-3PMN-PT	PIN-37PT +2%PbO	PIN-37PT +0.5%Mn
$\tan\delta_{0m}$	$0.27\cdot10^{-2}$	$0.96\cdot10^{-2}$	$2.0\cdot10^{-2}$	$1.8\cdot10^{-2}$	$1.97\cdot10^{-2}$	$0.65\cdot10^{-2}$
α	$0.03\cdot10^{6}$	$0.63\cdot10^{6}$	$1.5\cdot10^{6}$	$1.4\cdot10^{6}$	$2.3\cdot10^{6}$	$0.96\cdot10^{6}$
β	$0.30\cdot10^{6}$	$3.5\cdot10^{6}$	$7.0\cdot10^{6}$	$4.9\cdot10^{6}$	$5.7\cdot10^{6}$	$3.8\cdot10^{6}$

Table 3: *Mechanical loss* $\tan\delta_{m0}$ *and* α *&* β *coefficients for longitudinal resonators of PIN-37PT undoped and doped with 2%PbO, 3% PMN and 0.5% Mn; and* $PbZr_xTi_{1-x}O_3$ *(PZT-8; Navy Type III,PZT-7 Navy Type I) ceramics.*

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