Fine grains ceramics of PIN–PT, PIN–PMN–PT and PMN–PT systems: Drift of the dielectric constant under high electric field

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Abstract

Lead-based ferroelectric ceramics with \((1-x)\)Pb\((B_1B_2)O_3\)–\(x\)PbTiO\(_3\) formula have emerged as a group of promising materials for various applications like ultrasonic sonars or medical imaging transducers [Y.H. Chen, K. Uchino, J. Appl. Phys. (2001) 3928–3933]. \((1-x)\)PIN–\(x\)PT, \((1-x)\)PIN–\(x\)PT and ternary solutions \(x\)PIN–\(y\)PMN–\(z\)PT ceramics are synthesised using the solid state reaction method [Y. Hosono, Y. Yamashita, H. Sakamoto, N. Ichinose, Jpn. J. Appl. Phys. 42 (2003) 5681–5686]. Our objective is to achieve higher structural transition temperatures than those of PMN–PT ceramics with as good dielectric, piezoelectric and electromechanical properties. Ceramics capacitance and loss tangent are measured when the ac field of measurement increases up to \(E = 0.5\) kV/mm. Behaviours of these materials under ac field are related to their coercive field and Curie temperature.

Keywords: Piezoelectric ceramic; PIN; PMN; PT; Non linear properties

1. Introduction

Complex perovskite so called relaxor Pb\((B_1B_2)O_3\) \((B_1 = \text{Mg, In, Sc...Yb}; B_2 = \text{Nb,...})\) (PMN, PIN, PSN) and PbTiO\(_3\) (PT) show high piezoelectric properties especially for compositions near the morphotropic phase boundary (MPB) [1–3]. Such complex perovskites are of greater interest for electronic ceramic devices, piezoelectric actuators, underwater and medical acoustic transducers. Single crystals [4] and ceramics [5] of PIN–PT, PIN–PMN–PT were investigated. Phase transitions of PIN–PT system were established by temperature dependence of dielectric constant [6] and X ray diffraction [7]. It has been reported that the PIN–PT system has a MPB zone near \(x = 37\), which separates a rhombohedral zone for low PT concentrations from a tetragonal zone for high PT concentrations [7]. The PIN–37PT composition, showing two structural transitions at \(T_{MT} = 140\) °C between two ferroelectric phases and at \(T_C = 300\) °C, exhibits good properties: \(P_r = 0.344\) C/m\(^2\), \(\varepsilon_{33}(\text{@}1\) kHz) = 2670, \(k_p = 57\%\) and \(k_t = 47\%\).

This paper reports a study of PIN–PT and PIN–PMN–PT ceramics and compares their properties with those of PMN–33PT composition [8] which has a lower Curie temperature. Remanent polarisation, coercive field, piezoelectric constants and non linear dielectric properties under high ac electric field were measured and then compared with those of PMN–PT and PZT ceramics [9,10].

2. Ceramics by conventional sintering & hot forging

PIN–PT, PIN–PMN–PT ceramics were synthesised by two steps solid state reaction via Wolframite and Columbite phases. The Wolframite (InNbO\(_4\)) or Columbite (MgNbO\(_4\)) was formed by In\(_2\)O\(_3\) or Mg\(_2\)O\(_3\) with Nb\(_2\)O\(_5\) at 1100 °C for 24 h. The intermediate oxides were then mixed with PbO and TiO\(_2\) and ball-milled with Zirconium micro bead (\(\sigma < 1.6\) mm) using continuous attrition milling setup (Labstar). The mixtures were dried and calcined at...
55 850°C for 2 h to form stoichiometric perovskites. The ultra
56 fine perovskite powder, showing the submicronic grain size
57 (Fig. 1a; σ ~ 0.2 μm), was obtained by re-milling. The green
58 ceramics pellets with density about 50–60% of theoretic density were obtained by axial pressing. The green
59 PIN–PT pellets were hot-forged at 1000°C for 1 h under
60 a pressure of 1 T/cm². The hot-forged ceramics were finally
61 annealed under an O₂ flow at 1200°C for 4 h. Yellow pale
62 translucent ceramics with high relative densities (>98%
63 d_theoretical) were achieved (Fig. 1b). Translucent PIN–PT
64 ceramics show large ceramic grain size over ten microns
65 and fine grain size about 1–2 μm (Fig. 1c). Dense ternary
66 PIN–PMN–PT ceramics (>98% d_theoretical), obtained using conventional sintering, show fine and uniform grain size about
67 2 μm. XRD spectra of both powder and ceramic show only
68 a single-phase perovskite.
69

71 3. Electromechanical properties
72
73 Samples were cut in discs (10 mm × 0.5 mm), plates
74 (10 × 2 × 0.5 mm³) and bars (10 × 2 × 1.5 mm³). Silver paste
75 was painted on the polished faces and fired at 700°C during
76 30 min.
77
78 PIN–PT samples were poled in a silicon oil under a
79 4000 V/mm field at room temperature during 10 min whereas ternary PIN–PMN–PT and PMN–PT samples
80 were poled under a 400 V/mm field at 200°C and then
81 cooled down to 50°C under the same field. The tempera-
82 ture dependence of the dielectric constant was measured
83 at 1 kHz using a HP 4192A impedance analyser. Hysteresis
84 loops measurements were made using a Tower-Sawyer set-
85 up using triangle burst waves at 0.1 Hz. Electromechanical
86 properties were measured according to the IRE standard
87 method with an Agilent 4294A impedance analyser.
88
89 Table 1 resumes all the electromechanical constants at
90 low level (0.5 V) for the compositions xPIN–yPMN–zPT,
91 PIN–37PT and PMN–xPT [8]. Fig. 2 presents the tempera-
92 ture dependence of the dielectric constant (ε / ε₀)
93 and the radial coupling coefficient (κ_r) for PIN–37PT, PMN–33PT,
94 PMN–36PT and the two studied ternary compositions.
95
96 The dielectric curves, obtained at 1 kHz, present max-
97 ima at T_max (Fig. 2a) corresponding to the well known
98
tetragonal-cubic phase transition. As expected, $T_{\text{max}}$ increases from 175 to 180 °C, 195 and 290 °C, respectively, for PMN–33PT, ternary and PIN–37PT compositions, i.e., for the ceramics with increasing PIN concentration. The dielectric curves present another anomaly due to the rhombohedral–tetragonal or monoclinic–tetragonal phase transition. This ferroelectric–ferroelectric transition takes place towards 90 °C for the 24PIN–42PMN–34PT and 120 °C for 16PIN–51PMN–33PT. This anomaly is less marked for PIN–37PT and is observed towards 80 °C for the PMN–33PT.

PMN–36PT and PIN–37PT ceramics exhibit nearly the same radial coupling coefficient at RT (Fig. 2b). PMN–36PT ceramics show a decrease of the coupling coefficient from RT ($k_p = 0.55$) to 60 °C, then a continuous decrease up to 160 °C ($k_p = 0.38$) and a drop at 185 °C. This behaviour is consistent with the observed phase transitions of PMN–36PT ceramics: ferroelectric–ferroelectric transition around 80 °C and ferroelectric–paraelectric transition at 180 °C [4]. Ternary compositions exhibit a higher $k_p$ at RT that remains constant up to 85 °C, the temperature of the ferroelectric–ferroelectric transition, then decreases continuously up to 148 and 160 °C before dropping and reaching plateau at 170 and 190 °C, respectively for 16PIN–51PMN–33PT and 24PIN–42PMN–34PT. It is worth noting that PIN–37PT ceramics exhibit only slight decrease of $k_p$ from RT ($k_p = 0.55$) up to 200 °C ($k_p = 0.41$).

The electromechanical properties at low level (0.5 V) of PIN–37PT are comparable with those of PMN–PT set apart piezoelectric $d_{ij}$ constants for which PMN–36PT presents much more important values. Among the two studied ternary compositions, 24PIN–42PMN–34PT presents the best dielectric and electromechanical properties (Table 1).

Drift measurements or ac electric field dependences of the dielectric constant were measured up to 1 kV/mm. Sinusoidal signal at 1 kHz, generated from a HP 3314 A function generator, was amplified by a Kepco Bipolar Amplifier. A EG&G 5210 Lock-in Amplifier and an integration capacitance ($C_i$) allow to measure the capacitance ($C$) at the sample connections.
The ac electric field dependence of the dielectric constant $\varepsilon_{33}/\varepsilon_0$ at 1kHz for poled ceramics are reported in Fig. 4. All ceramics present linear drift: the dielectric permittivity $\varepsilon_{33}/\varepsilon_0$ increases linearly with the ac applied electric field ($E_{ac}$). It is related to some motions of the ferroelectric domain walls under the electric field. This is generally known as the “extrinsic contribution”. This linear drift is observed up to 300 V/mm for PIN–37PT and typical hard PZT–4D material while 24PIN–42PMN–34PT, 16PIN–51PMN–33PT and PMN–33PT exhibit linear drift up to 250, 150 and 120 V/mm. Above those fields, the latter ceramics show an accelerated drift behaviour: the permittivity increases very abruptly with the applied electric field. This thermal runaway phenomenon due to the increase of dielectric losses is in agreement with the observed low $T_C$.

The higher the Curie temperature is, the higher is the required electric field to switch the polarization between adjacent ferroelectric domains. Therefore, the linear-drift

Table 2
Curie temperature, coercive field and remanent polarisation of PMN–PT, PIN–PT and PIN–PMN–PT ceramics

<table>
<thead>
<tr>
<th></th>
<th>PMN–33PT</th>
<th>PMN–36PT</th>
<th>16PIN–51PMN–33PT</th>
<th>24PIN–42PMN–34PT</th>
<th>PIN–37PT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C$ (°C)</td>
<td>160</td>
<td>180</td>
<td>180</td>
<td>195</td>
<td>300</td>
</tr>
<tr>
<td>$E_C$ (V/mm)</td>
<td>580</td>
<td>710</td>
<td>890</td>
<td>1020</td>
<td>1660</td>
</tr>
<tr>
<td>$P_r$ (C/m²)</td>
<td>0.29</td>
<td>0.450</td>
<td>0.316</td>
<td>0.314</td>
<td>0.344</td>
</tr>
</tbody>
</table>
region for PIN–37PT and PZT–4D is larger than that for
ceramics containing PMN, and the accelerated drift region
is not observed.

The linear drift can be characterized by the Rayleigh
coefficient: \( \xi = \frac{1}{\varepsilon_{ij}} \times \frac{\varepsilon_{ij} \varepsilon_{ij} \varepsilon_{ij} \varepsilon_{ij}}{C_{16} C_{17}} \). As expected, the Rayleigh coef-
ficients of PIN–37PT and PZT–4D have the same value,
\( \alpha = 3.4 \), and increases to 17.2, 27.4 and 33.4 for ternary
and PMN–33PT ceramics.

5. Conclusions

Among PIN–xPT compositions, PIN–37PT presents the
best dielectric and electromechanical properties at low level
[5]. Such a behaviour is characteristic of morphotropic
compositions. The important values of \( d_{ij}, s_{ij}, d_{ij} \) and the
low \( Q_{m} \) values of PIN–37PT are characteristic of a soft
material.

The electromechanical properties of PIN–37PT are com-
parable to those of PMN–PT except lower dielectric and
piezoelectric \( d_{ij} \) constants. The dielectric constant at room
temperature is directly related to the Curie temperature:
generally, the more the Curie temperature is raised, the
lower is the dielectric constant at room temperature.
PIN–37PT presents a Curie temperature \( T_{C} = 300 \text{C} \)
higher than that of PMN–36PT, \( T_{C} = 180 \text{C} \). Its dielectric
constant and thus its piezoelectric constants at room tem-
perature are lower than those of PMN–36PT. The incorpo-
ration of PIN in PMN–PT ceramics results in an increase
of structural transition temperatures and thus a decrease
of the dielectric constant at room temperature.

The electromechanical properties of ternary ceramics
are similar to those of PMN–PT ceramics, the difference
between dielectric constants being compensated by the
higher electromechanical coupling coefficients.

The temperature dependence of the planar electrome-
chanical coupling coefficient shows that the higher the
Curie temperature is, the better is the stability of \( k \). There-
fore, the higher the ferroelectric–ferroelectric temperature
transition is, the more the decrease of \( k \) is delayed. These
same tendency should be observed for the other electrome-
chancial constants.

Our purpose is thus to synthesise materials having struc-
tural transition temperatures high enough to delay the drop
of the electromechanical properties when temperature is
increased. However, power applications require high
dielectric and piezoelectric constants. From this point of
view, PIN–PMN–PT ceramics seem to be a good
candidate.

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