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Morphotropic PMN–PT system investigated by comparison between ceramics and crystal

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Abstract

Ferroelectric perovskite ceramics $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ were widely studied over the last 20 years, especially ceramics in the morphotropic phase boundary ($x = 0.3$–0.4). More recently a new interest focuses on single crystals of the same composition grown either by Bridgman or flux technique. Giant electromechanical factor k_{31}, piezoelectric coefficient d_{31}, and field-induced strain S_3 were found ($k_{31} > 0.85$, $d_{31} > 1000$ pC/N, $S > 1\%$) making them very attractive for non-resonant applications. For resonant applications, despite their medium mechanical factor Q_{31} these materials exhibit higher figure of merit $Q_{31}d_{31}$ than the best PZT ($Q_{31}d_{31} > 3 \times 10^5$ for crystal, and $Q_{31}d_{31} > 10^5$ for the best PZT ceramics).

However the origin of these outstanding properties is not well understood. The comparison between ceramics and crystal of the same composition (0.67PMN–0.33PT) towards the macroscopic properties was investigated. First the polarisability of materials was studied. The crystal shows an optimum poling electric field, which gives a maximum electromechanical coupling factor and piezoelectric charge d_{31}. It is believed that this surprising behaviour is due to the domain and phase engineering.

The temperature and electric field stability was investigated for ceramics and crystal for different crystallographic cuts. A discussion is presented on the mechanical losses which are especially unstable.

Keywords: Ferroelectric properties; Piezoelectric properties; Microstructure-final; Perovskites; PMN–PT

1. Introduction

Extraordinary electromechanical properties of new compositions of ferroelectric single crystals were published for over 20 years ago[1] and the feasibility of industrial crystals growth was massively investigated. The electromechanical properties are now available for many new compositions such as $(1-x)Pb(Mg_{1/3}N_{2/3})O_3$–$xPbTiO_3$ ($x = 0.3, 0.33, 0.38$) and for $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ ($x = 0.09, 0.045$).[2]

More recently, nonlinear behaviours and stability started to be studied, especially the differences between these new crystals and common PZT ceramics.[3] Nevertheless the origin of the high piezoelectric response is still unclear. Both ceramics and crystals are available for PMN–PT compositions, and the comparative study is an interesting investigation path to understand both structures behaviours.

First the poling study of ceramics and crystals is presented. The same experimental procedure is commonly used for single crystals as for ferroelectric ceramics. Especially very large electric fields are usually applied to pole single crystals. In the case of morphotropic PMN–PT crystal it was shown that the d_{33} reaches a maximum depending on the poling field.[4] This particular phenomenon is investigated here and correlated with the phase ratio for both structures.

Results on stability under temperature and electric field are then given for the both materials.

2. Ceramics preparation and crystal growth

Colombite $MgNb_2O_6$ precursor was first prepared and then calcined with lead oxide. This pure perovskite PMN–PT powder was then fired at 1250 °C for 10 h in Ø 25 mm × 15 mm pellets. Ceramics were then put in a *Y*-shape crucible and heated at 1280 °C for 4 h in a 30 °C/cm Bridgman

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furnace. One single crystal of Ø 25 mm × 70 mm was grown by pulling down at 1 mm/h. Crystal was cut and Curie points measurements were used to separate the different compositions due to segregation of titanium in the crucible.

Ceramics of the same composition are cut into rectangular bars 10 mm × 2 mm × 1 mm for lateral mode characterization. Crystals were oriented by plotting their pole figure and cut into rectangular bars with same dimensions as ceramics.

Ceramics and crystals composition were chosen to be in the morphotropic phase boundary where both rhombohedral and tetragonal phases coexist, that is to say $x = 0.35$ because this composition exhibits the best electromechanical properties for both ceramics and crystals.

All the samples were electroded with silver paste and heated for 1 h at 450 °C to remove residual stress.

Poling study was conducted by poling both crystals and ceramics with increasing electric fields in an oil bath to avoid electrical arcs. For each poling field, the lateral resonance mode was characterized to determine material constants such as d_{31}, k_{31}, and Q_{31} using IEEE standards on piezoelectricity.[5] The impedance was measured with an HP4194A with a specific sample holder to avoid artificial decrease of mechanical quality factor by limiting the stress value on the sample. The lateral mode coefficients are given in Table 1.

Both crystals and ceramics are assumed to be multiphase with rhombohedral and tetragonal phases.[6,7] A local diffraction pattern is measured around $\langle 0\,0\,2\rangle$ diffraction peak in order to determine the phase ratio.

Three phenomena modify the diffraction diagrams:

- Reorientation of domains depending on the electric field: for tetragonal phase $\langle 2\,0\,0\rangle_T$ peak (which has the same $d_{h\,k\,l}$ as $\langle 0\,2\,0\rangle_T$) increases with the quantity of domains that align themselves along the poling field direction. There is no effect on rhombohedral peak.
- Electric field dependence of the phase ratio.
- Electric field dependence of the unit cells parameters.

3. Properties of PMN–PT ceramics and crystals

It has been shown that the very high value of d_{15} in monodomain crystals lead to the high d_{33} in engineered domains crystals[8] (i.e. poling along $\langle 0\,0\,1\rangle$ which is at 54.7° from the spontaneous polarization direction). Starting from the piezoelectric tensor of the monodomain single crystal, it is possible to calculate piezoelectric constants after an arbitrary rotation of the electric field axis. With a summation of the response of the four equivalent domains created by poling along $\langle 0\,0\,1\rangle$ the multidomains properties are thus predicted with a moderate accuracy. The same calculation was conducted here to deduce from the tensor of the single crystal monodomain the properties of the different poling directions and of the ceramics. Following assumptions must be made:

- The tensor of the PMN–PT single crystal monodomain is taken from literature.[7]
- There is no interaction between domains. Domain wall vibration is thus neglected and domains are totally free to move.
- Tetragonal domains are not considered.

For a $\langle 0\,0\,1\rangle$ poling of crystals, four equivalent domains are considered leading to a 4 mm macroscopic symmetry. For a $\langle 1\,1\,0\rangle$ poling of crystals two equivalent domains are considered leading to a 2 mm symmetry. For ceramics 10^4 randomly oriented domains are considered (a large number is necessary in order to recover a 6 mm global symmetry). The effective direction of spontaneous polarization is the $\langle 1\,1\,1\rangle$ direction that is nearest from poling direction. The results of these calculations are given in Table 1 and show for all cases an overestimation of d_{31} value. But the ranking of materials remains the same: crystal cut 3 > crystal cut 2 > ceramics. The origin of the overestimation is believed to be mainly due to the tetragonal domains influence and that internal stresses decrease effective d_{15} of domains.

On the other hand one may believe that mechanical losses should be almost independent on the nature of material, i.e. ceramics or crystal, or at least losses should be greater for ceramics where grain boundaries may introduce additional losses. In fact mechanical quality factor is almost half for crystals, whatever the poling direction of single crystals. This is accompanied with a large increase of electromechanical coupling factor, that is to say that the highly coupled engineered domains exhibit more losses than poorly coupled domains.

4. Poling study

The d_{31} and k_{31} coefficients as a function of electric field to coercive field ratio are shown in Fig. 1. One can see that the properties of PMN–PT ceramics first increase and then saturate for high electric field levels. On the contrary PMN–PT crystals $\langle 1\,1\,0\rangle$pol/$\langle 0\,0\,1\rangle$vib exhibit a maximum for electric field around 400–600 V/mm. The maximum value of the

Table 1
Lateral mode characterization for 0.65PMN–0.35PT as a function of crystallographic cut

Cut pol/vib	k_{31} (%)	ε_{33}^{T} (ε_0)	Q_{31}	s_{11} (10^{-12} Pa^{-1})	d_{31} (pC/N)	d_{31} calc. (pC/N)
$1_{\langle 0\,0\,1\rangle/\langle 0\,0\,1\rangle}$	48	5500	230	48	−650	−1163
$2_{\langle 0\,0\,1\rangle/\langle 1\,1\,0\rangle}$	76	5500	210	22	−850	−1163
$3_{\langle 1\,1\,0\rangle/\langle 0\,0\,1\rangle}$	85	3500	300	55	−1200	−1644
Ceramics	32	1643	764	19	−168	−630

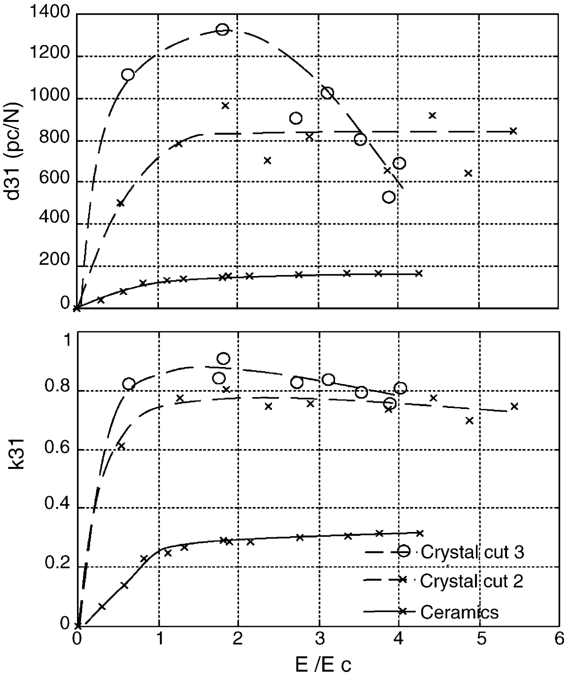

Fig. 1. d_{31} and k_{31} as a function of the poling field to coercive field ratio with E_c(crystals) = 300 V/mm and E_c(ceramics) = 800 V/mm.

piezoelectric coefficient is associated with a maximum of stiffness s_{11} because dielectric permittivity and electromechanical factor are almost constant (around 4000–5000ε_0, and k_{31} = 0.8–0.9 for an electric field over 200 V/mm).

The poling of a ferroelectric material consists in orientation of domains along the electric field direction. In the case of single crystals the existence of a maximum of stiffness/piezoelectric coefficient may only be explained with domain engineering and/or phase engineering, because it is not true for all poling directions (for example poling along ⟨0 0 1⟩ as shown in Fig. 1). As a consequence we investigated the phase ratio of the PMN–PT single crystals (⟨1 1 0⟩pol/⟨0 0 1⟩vib) and ceramics in order to understand this phenomenon.

The diffraction diagrams for both crystals and ceramics are shown in Fig. 2. One can see that for the ceramics the rhombohedral to tetragonal phase ratio is almost constant. For single crystals a minimum of phase ratio is observed around the same field as the maximum of d_{31}. A deconvolution of diffractograms led to an initial phase ratio of 50%, a minimum around 40% and then an increase up to 45%. A clear correlation is thus established between phase ratio and piezoelectric coefficient.

The domain engineering concept introduced by Yin et al. for 0.955PZN–0.045PT rhombohedral single crystals explains why ⟨0 0 1⟩ poling direction induces larger piezoelectric response that ⟨1 1 1⟩ poling direction.[9] The results presented here suggest that in case of morphotropic compositions the piezoelectric properties are maximized not only by domain engineering but also by phase engineering.

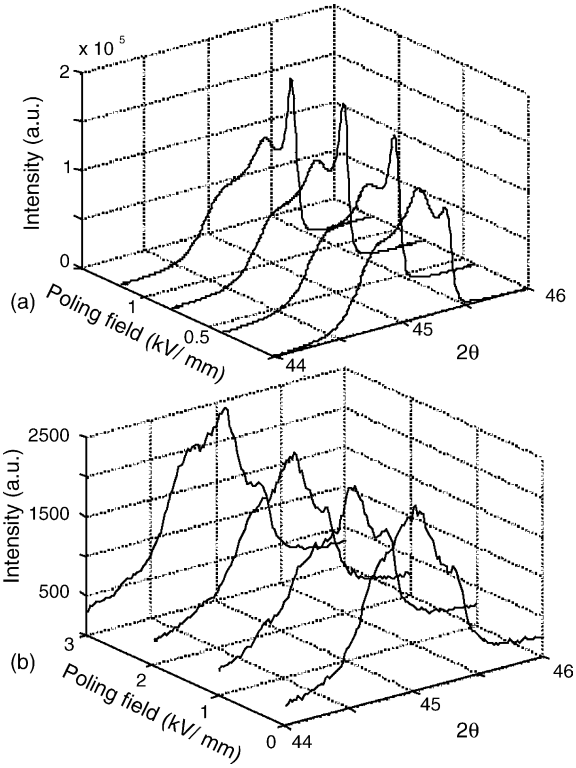

Fig. 2. Local diffractogram around ⟨0 0 2⟩ peak for (a) single crystals and (b) ceramics.

For ceramics phase engineering is not observed which is consistent to the fact that no maximum of piezoelectric coefficient is observed. Poling a morphotropic PMN–PT single crystal along ⟨0 0 1⟩ favours the rhombohedral phase,[7] and the results presented here suggests that poling along ⟨1 1 0⟩ may favours tetragonal domains at limited fields. Consequently poling a ceramic favours either rhombohedral or tetragonal depending on the orientation of the crystallite, and thus inducing limited dependence of the phase ratio on the electric field.

5. Stability

The lateral mode for different temperature cycles shows (Fig. 3a):

- For ceramics the lateral coupling factor is almost constant (variations <5%) with very low hysteresis. This is due to a diffuse rhombohedral to tetragonal (R/T) phase transition.
- For crystals the proximity of a sharp (R/T) transition leads to large variations when temperature remains under the transition temperature for both poling directions. Crossing the transition induces large hysteresis (only for ⟨1 1 0⟩ poling because $T_{R/T} < 90\,^{\circ}C$), but completely reversible when temperature goes under 30 °C. For ⟨0 0 1⟩ poling, the transition appears for higher temperatures. But the non-hysteretic variation is very similar for the two crystals and larger than for ceramics. The sharp R/T transition is clearly

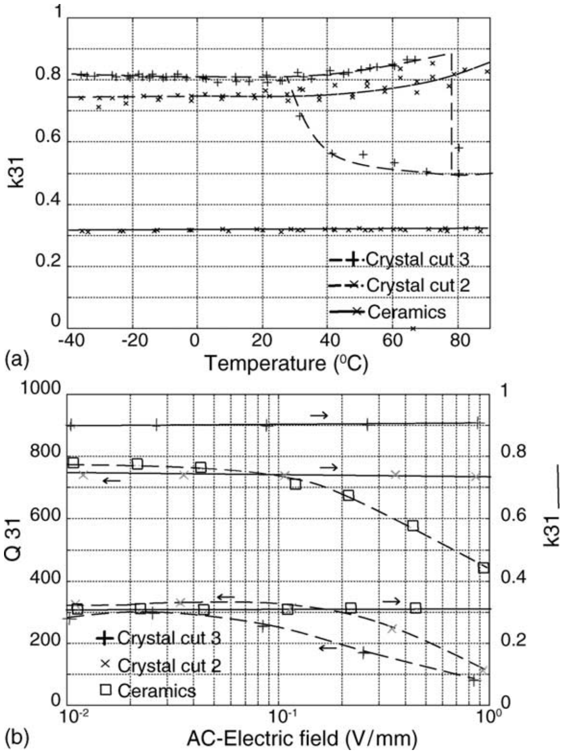

Fig. 3. Stability of ceramics and single crystals as a function of (a) temperature, and (b) AC electric field.

distinguishable on permittivity versus temperature[7] although crystals are multiphase at room temperature and explains the variations of the coupling factor for temperature cycles.

Increasing electric fields lead to nonlinear resonance mode for both ceramics and single crystals above 1 V/mm where resonance peak becomes asymmetric and where jumps phenomena occur. For electric fields under this limit, all parameters are almost constant except mechanical losses as represented in Fig. 3b. Electromechanical coupling factor remains to its initial value (85% for crystals and 32% for ceramics). Losses exhibit a large increase for fields over 0.1 V/mm for ceramics and 0.06 V/mm for crystals (and do not depend on the poling direction).

High strain levels usually induce: (i) increase the value of s_{11} leading to Duffing's oscillator behaviour,[10] and (ii) increase mechanical losses leading to high heating and limitation of strain. For PMN–PT materials the increase of losses occurs for about the same fields for crystals and ceramics, although strain levels are very different. For linear regimes, strain at the centre of the bar can be written as:[11]

$$S_{x=0} = \frac{4}{\pi} d_{31} E_3 Q_{31}. \tag{1}$$

Comparison between ceramics and $\langle 1\,1\,0 \rangle$ crystal gives for 1 V/mm: $S_{\text{ceramics}} = 9.5 \times 10^{-5}$ m/m and $S_{\text{crystal}} = 12 \times 10^{-5}$ m/m. When Q_{31} begin to decrease (the "cut-off" electric field) strain levels are $S_{\text{ceramic}} = 1.7 \times 10^{-5}$ m/m (with $E = 0.1$ V/mm) and $S_{\text{crystal}} = 2.75 \times 10^{-5}$ m/m (with $E = 0.06$ V/mm). As a conclusion we can say that crystals are more stable than ceramics. It is interesting to note that strain for 1 V/mm is almost the same for crystals and ceramics which implies that $Q_{31}d_{31}$ figure of merit tends to the same value for both materials.

6. Conclusion

The comparison between ceramics and crystals of same composition leads us to following conclusions:

- Domain and phase engineering in crystals reveals surprising behaviours that do not exist in ceramics. Here is presented the poling study which shows an optimisation of piezoelectric coefficient as a function of poling field.
- Electric field amplitude effect is almost the same for crystals and ceramics.
- Temperature stability confirms a sharp R/T transition for crystals and a diffuse one for ceramics.

The correlation between piezoelectric coefficient optimisation and phase ratio has been presented. But this is not the only origin to this optimum considering that the phase ratio varies from 50% to 40% whereas d_{31} varies from 1200 pC/N to 600 pC/N. Many other phenomena may influence piezoelectric performances such as for example extrinsic effect that can be modified by the size of engineered domains. Further experimentations are necessary to understand this phenomenon.

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