

Morphotropic PMN-PT system investigated through comparison between ceramic and crystal

Gaël Sebald, Laurent Lebrun, Benoît Guiffard, Daniel Guyomar

LGEF, INSA de Lyon, Villeurbanne, France

Abstract

Ferroelectric perovskite ceramics $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ were widely studied over the last twenty 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 ($k_{31}>0.85$, $-d_{31}>1000\text{pC/N}$, $S>1\%$) 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 ($Q_{31}d_{31}>3.10^5$ for crystal, and $Q_{31}d_{31}>10^5$ for the best PZT ceramic).

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

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

Introduction

Extraordinary electromechanical properties of new compositions of ferroelectric single crystals were published for over 20 years ago¹ and the feasibility of industrial crystals growth was massively investigated. The electromechanical properties are now available for many new compositions such as $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ ($x=0.3$, $x=0.33$, $x=0.38$) and for $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ ($x=0.09$, $x=0.045$)².

More recently, nonlinear behaviours and stability started to be studied, especially the differences between these new crystals and common PZT ceramics³. 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 field⁴. 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.

1. 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 hours in $\text{Ø}25\text{mm} \times 15\text{mm}$

pellets. Ceramics were then put in a Y-shape crucible and heated at 1280°C for 4 hours in a 30°C/cm Bridgman furnace. One single crystal of Ø25mmx70mm was grown by pulling down at 1mm/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 10x2x1mm³ 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 1hour 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 lateral resonance mode was characterized to determine material constants such as d_{31} , k_{31} , and Q_{31} using IEEE standards on piezoelectricity⁵. 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 phases⁶⁻⁷. A local diffraction pattern is measured around <002> 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 <200>_T peak (which has the same d_{hkl} as <020>_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

2. 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 crystals⁸ (i.e. poling along $\langle 001 \rangle$ 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 $\langle 001 \rangle$ 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 ceramic.

Following assumptions must be made:

- The tensor of the PMN-PT single crystal monodomain is taken from literature⁷
- 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 $\langle 001 \rangle$ poling of crystals, four equivalent domains are considered leading to a 4mm macroscopic symmetry. For a $\langle 110 \rangle$ poling of crystals two equivalent domains are considered leading to a 2mm symmetry. For ceramics 10^4 randomly oriented domains are considered (a large number is necessary in order to recover a 6mm global symmetry. The effective direction of spontaneous polarization is the $\langle 111 \rangle$ 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 > ceramic. 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. ceramic 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.

3. Poling study

On figure 1 are shown d_{31} and k_{31} coefficients as a function of electric field to coercive field ratio. 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 $\langle 110 \rangle_{\text{pol}} / \langle 001 \rangle_{\text{vib}}$ exhibit a maximum for electric field around 400-600V/mm. The maximum value of the piezoelectric coefficient is associated with a maximum of stiffness s_{11} because dielectric permittivity and electromechanical factor are almost constant (around 4000-5000 ϵ_0 , and $k_{31}=0.8-0.9$ for fields over 200V/mm).

Poling 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 $\langle 001 \rangle$ as shown on figure 1). As a consequence we investigated the phase ratio of the PMN-PT single crystals ($\langle 110 \rangle_{\text{pol}} / \langle 001 \rangle_{\text{vib}}$) and ceramics in order to understand this phenomenon.

On figure 2 are shown diffraction diagrams for both crystals and ceramics. One can see that for the ceramic 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 $\langle 001 \rangle$ poling direction induces larger piezoelectric response than $\langle 111 \rangle$ poling direction⁹. 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.

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 $\langle 001 \rangle$ favours the rhombohedral phase⁷, and the results presented here suggests that poling along $\langle 110 \rangle$ 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.

4. Stability

Lateral mode for different temperature cycles shows (figure 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 $\langle 110 \rangle$ poling because $T_{R/T} < 90^\circ\text{C}$), but completely reversible when temperature goes under 30°C . For $\langle 001 \rangle$ 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 distinguishable on permittivity versus temperature⁷ although crystals are multiphase at room temperature and explains the variations of the coupling factor for temperature cycles.

Increasing electric fields leads to nonlinear resonance mode for both ceramics and single crystals above 1V/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 on figure 3b. Electromechanical coupling factor remains to its initial value (85% for crystals and 32% for ceramics). Losses exhibit a large increase for fields over 0.1V/mm for ceramics and 0.06V/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 behaviour¹⁰, 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 as¹¹:

$$S_{x=0} = \frac{4}{\pi} d_{31} E_3 Q_{31} \quad (1)$$

Comparison between ceramic and <110> crystal gives for 1V/mm: $S_{\text{ceramic}}=9.5 \cdot 10^{-5}$ m/m and $S_{\text{crystal}}=12 \cdot 10^{-5}$ m/m. When Q_{31} begin to decrease (the “cut-off” electric field) strain levels are $S_{\text{ceramic}}=1.7 \cdot 10^{-5}$ m/m (with $E=0.1\text{V/mm}$) and $S_{\text{crystal}}=2.75 \cdot 10^{-5}$ m/m (with $E=0.06\text{V/mm}$). As a conclusion we can say that crystals are more stable than ceramics. It is interesting to note that strain for 1V/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.

Conclusion

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

- Domain and phase engineering in crystals reveals surprising behaviours that don't 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 1200pC/N to 600pC/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.

Table caption

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

Figure Caption

Figure 1 : d_{31} and k_{31} as a function of the poling field to coercive field ratio with $E_c(\text{crystals})=300\text{V/mm}$ and $E_c(\text{ceramic})=800\text{V/mm}$

Figure 2 : Local diffractogram around $\langle 002 \rangle$ peak for single crystals (a) and ceramics (b).

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

Cut pol/vib	ζ_{31} (%)	ϵ_{33}^T (ϵ_0)	Q_{31}	s_{11} (10^{-12}Pa^{-1})	d_{31} (pC/N)	d_{31} calc. (pC/N)
1- $\langle 001 \rangle / \langle 001 \rangle$	48	5500	230	48	-650	-1163
2- $\langle 001 \rangle / \langle 110 \rangle$	76	5500	210	22	-850	-1163
3- $\langle 110 \rangle / \langle 001 \rangle$	85	3500	300	55	-1200	-1644
Ceramic	32	1643	764	19	-168	-630

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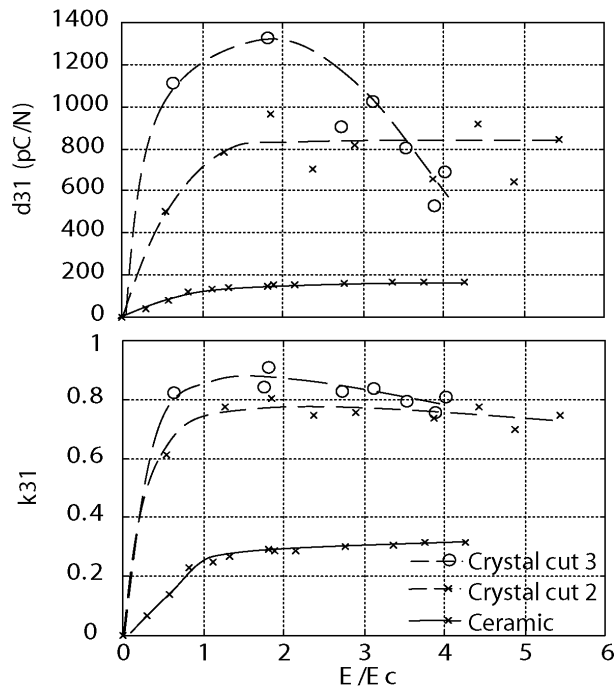


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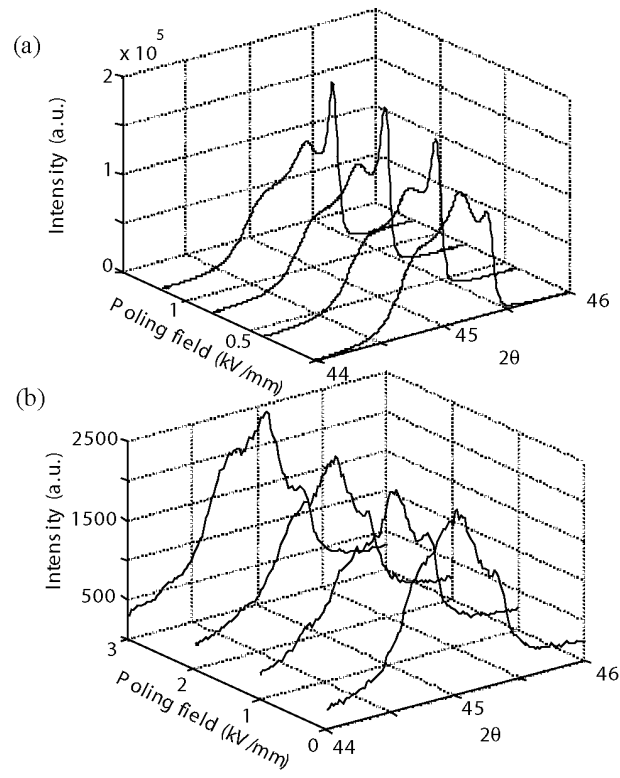


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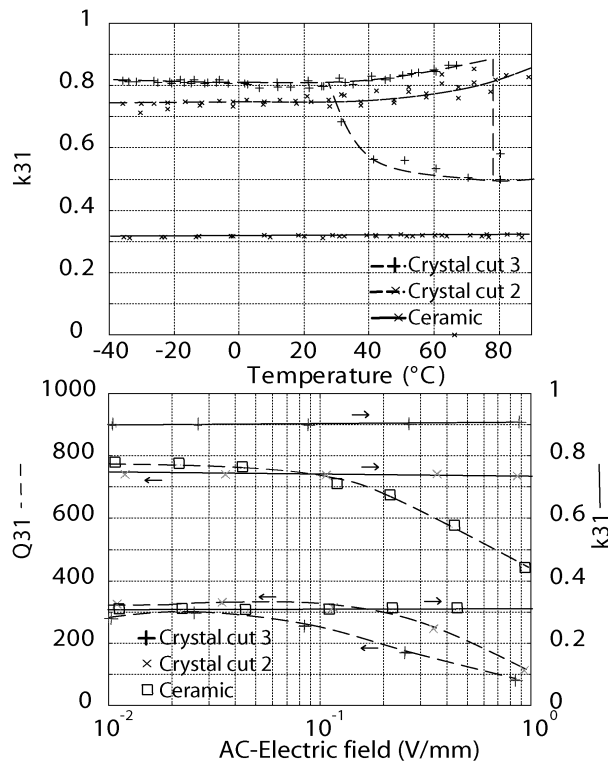


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References

- 1 Kuwata, J., Uchino, K., Nomura, J., Dielectric and Piezoelectric Properties of $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.09\text{PbTiO}_3$ single crystals, *Jpn J. Appl. Phys.*, 1982, **21** (9), 1298-1302
- 2 Zhang, R., Jiang, B., Jiang, W., Cao, W., Anisotropy in Domain Engineered $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.08\text{PbTiO}_3$ Single Crystal and Analysis of Its Property Fluctuation, *IEEE Trans. On Ultra. Ferro. And Freq. Cont.*, 2002, **49** (12), 1622-1627
- 3 Lebrun, L., Sebald, G., Guiffard, B., Richard, C., Guyomar, D., Pleska, E., Investigations on ferroelectric PMN-PT and PZN-PT single crystals ability for power or resonant actuators, *Ultrasonics*, 2004, **42**, 501-505

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- 4 Zhao, X., Fang, B., Cao, H., Guo, Y., Luo, H., Dielectric and piezoelectric performance of PMN-PT single crystals with compositions around the MPB: influence of composition, poling field and crystal orientation, *Materials Science and Engineering*,
- 5 IEEE standard on piezoelectricity, ANSI/IEEE Std., *US : IEEE*, 176, 1987, 54p
- 6 Gupta, S.-M., Viehland, D., Tetragonal to rhombohedral transformation in the lead zirconium titanate lead magnesium niobate-lead titanate crystalline solution, *J. Appl. Phys.*, 1998, **83** (1), 407-414
- 7 Zawilski, K. , Custodio, C., DeMattei, R., Lee, S-G., Monteiro, R., Odagawa, H., Feigelson, R., Segregation during the vertical Bridgman growth of lead magnesium niobate-lead titanate single crystals, *Journal of Crystal Growth*, 2003, **258**, 353-367
- 8 Zhang, R., Jiang. B., Cao, W., Orientation dependence of piezoelectric properties of single domain $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.33\text{PbTiO}_3$ crystals, *Appl. Phys. Letters*, 2003, **82** (21), 3737-3739
- 9 Yin, J., Jiang, B., Cao, W., Elastic, Piezoelectric, and Dielectric Properties of $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.045\text{PbTiO}_3$ Single Crystal with Designed Multidomains, *IEEE Trans. On Ultra. Ferro. And Freq. Cont.*, 2000, **47** (1), 285-290
- 10 Priya, S., Viehland, D., Ryu, J., Uchino, K., Yamashita, Y. ,Luo, H., Investigation of elastic nonlinearities in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single crystals, *Jpn. J. Appl. Phys*, 2002, **40**, 6487-6495
- 11 Uchino, K., Seiji, H., Loss mechanisms in piezoelectrics: How to measure different losses separately, *IEEE Trans. On Ultra. Ferro. and Freq. Cont.*, 2001, **48** (1), 307-321