IEEE, Proceeding of the 2002 13th IEEE, ISAF, Nara, JAPAN, May 28-June 1, 2002, pp 439-442

Domain Engineering of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ Single Crystals and Piezoelectric Related Properties

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Abstract — The domain configuration and the electromechanical related properties have been studied in $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZN-9%PT) single crystals cut along [001] and $[10\bar{1}]$. It was established that soft (with high d) and hard (with lower d) piezoelectric properties are respectively obtained in a multidomain and a single domain configuration. The softer piezoelectric material (d_{33} = 2700 pC/N, s^E_{33} = 180 pN/m^2, k_{33} = 93%) was found in the monoclinic multidomain state after poling with a small field along [001]. Optimal poling process and electromechanical related properties of the single crystals were discussed in term of the field-temperature diagram.

INTRODUCTION

Single crystals of $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZN-9%PT) poled along [001] of the pseudo-cubic axis have been reported to possess much higher piezoelectric and electromechanical coupling constants (k_{33} = 92%, d_{33} = 1570 pC/N) [1] than PMN-PT or PZT ceramics.

For single crystals, we need to introduce a special notation to describe the piezoelectric properties (ij) of a sample poled in a certain direction compared to the field and oriented along a [hkl] cristallographic direction. For example, $d_{33}^{[001]}$ and $d_{33}^{[10\bar{1}]}$ are the piezoelectric constant of a bar sample poled and elongated in [001] and $[10\bar{1}]$ respectively.

According to the poling directions, we introduced in a previous paper [2] some abbreviations indicating the domain configuration of a structural phase at the virgin and poled states (Table I).

Phase	State	Poling direction	
		[001]	$[10\bar{1}]$
Tetragonal (T)	Virgin	6T	6T
	Poled	1T	2T
Monoclinic (M)	Virgin	12M	12M
	Poled	4M	1M

Table I: Abbreviation for the domain configuration of each phase at the virgin and poled states and according to the poling directions

The dipole in each unit cell of the monoclinic phase is along one of the twelve $<10\bar{1}>$ directions. For the tetragonal phase, it is along one of the six <001> directions. Then, for example, 6T means a multidomain structure of the tetragonal phase at the spontaneous state wheareas 2T defines, in this phase poled along $[10\bar{1}]$, two degenerate dipole orientations. These dipolar moments take place in 45° of this direction.

In a recent work, $k_{33}^{[001]}$ of 94% and $d_{33}^{[001]}$ of 2500 pC/N were reported for PZN-8%PT [3]. The origin of these high values is attributed to the existence of a monoclinic multidomain phase. Noheda *et al.* [4] reported, by using X-ray diffraction, that these crystals can adopt a 4M domain state, under high electric field (~2000 kV/m). Cox *et al.* [5] showed that, at the poled state, a crushed powder of PZN-9%PT is orthorhombic 2mm, whose cell comprises two monoclinic unit cell at room temperature. Recent X-ray single crystal diffraction investigations by Renault *et al.* [2] have demonstrated that PZN-9%PT single crystals can comprise either a 2M domain state, or a 4M state. Moreover, they showed that PZN-9%PT single crystals poled along $[10\bar{1}]$ are monoclinic quasi-single domain (1M).

However, the choice of the best poling protocol for these crystals along a given direction is still uncertain. According to several publications, poling is carried out by applying either a strong field of about 1000 kV/m in a field-cooling protocol (FC) [1,6,7], or 2000 kV/m or more at a constant temperature (CF: constant-field protocol) [6,8].

The purpose of this work is to compare the influence of different poling protocols on the domain state and on the electromechanical related properties of PZN-9%PT single crystals poled along [001] and $[10\bar{1}]$.

EXPERIMENTAL METHODS

PZN-9%PT single crystals were prepared by a standard PbO flux method [1,2,3,7,]. Then, two crystals were cut and polished, with orientations [100]/[010]/[001] and [101]/[010]/$[10\bar{1}]$ Their dimensions are respectively 2 x 2 x 4 and 1 x 1 x 2 mm^3.

Thin films of Cr/Au electrodes (~1300 Å) were respectively sputtered on the (001) and $(10\bar{1})$ faces.

Crystals were poled either by the well known FC protocol or by increasing the electric field at a constant temperature, followed by cooling down to room temperature under zero field (IF protocol).

The pyroelectric current I(T) was measured with a programmable electrometer (KEITHLEY 617), during linearly increasing temperature from 200 to 470 K at a rate of 4 K/min, with or without an applied DC field.

The polarization current I(E) during IF protocol was measured with an electric field increasing at a rate of 7.7 kV/m/min.

The permittivity ε(T) was measured during FC protocol with a temperature decrease rate of 2 K/min from 480 down to 200 K.

Electromechanical properties were measured according to the IRE standard method with a HP 4192A impedance analyzer. They were focused on the 33 mode of bars. All the measurements were performed in a temperature controlled chamber.

FIELD-TEMPERATURE DIAGRAM

Pyroelectric current under zero field

We measured I(T) of [001]-oriented single crystals poled by FC with E = 100 kV/m.

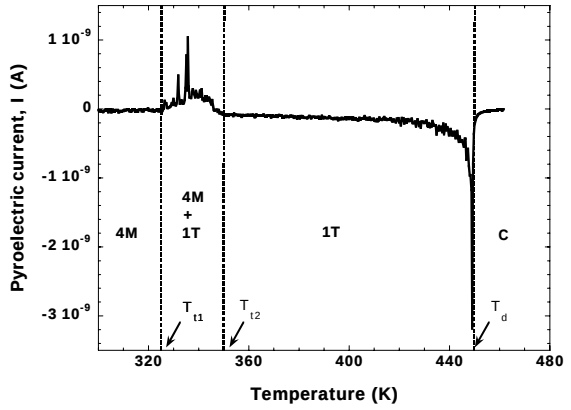

Fig. 1: Pyroelectric curves obtained along a [001] FC poled crystal

We can notice a large positive peak between T_{t1} and T_{t2} and a sharp negative one at T_d (Fig. 1) corresponding respectively to the 4M→1T and 1T→C transitions

In other words, this large positive peak is due to the diffuse thermal hysteresis already observed earlier [1,2] and means that the dipolar moment is first tilted relatively to [001] and then parallel to it.

Pyroelectric current under DC field

We determined the I(T) behaviour under different electric fields between 50 and 450 kV/m. The method was already reported in [9] for PZN.

Figure 2 shows an example of the curves obtained along [001]. At low field ($E_{[001]}$ <~350 kV/m), a broadened positive peak between T_{t1} and T_{t2} is observed. Taking into account the preceding results, it corresponds to a progressive 12M→6T transition accompagnied by a partial polarization. The complete polarization occurs at T_p in the tetragonal phase (6T→1T). Finally, the depolarization occurs at T_d (1T→C transition). Under higher field, the progressive and complete polarization occurs in the M phase region which is followed by the sharp 4M→1T transition.

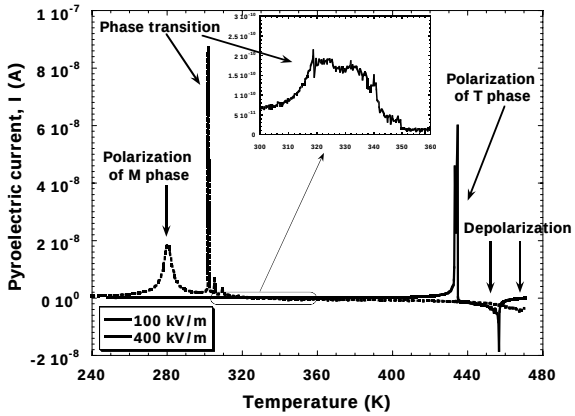

Fig. 2: Pyroelectric current with two different electric fields applied along [001]

Consequently, we can divide the E-T diagram into 6 regions (Fig. 3):

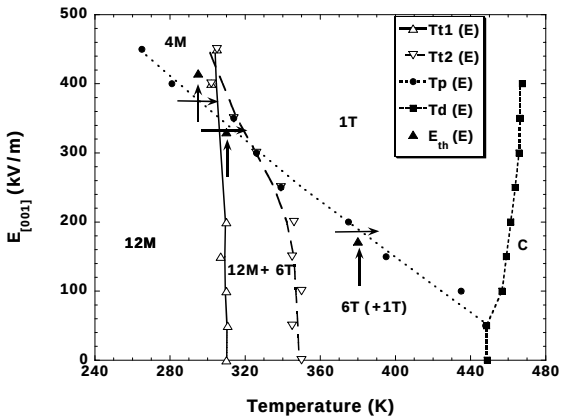

Fig. 3: Field-temperature diagram along [001]

(i) for high temperatures, the crystals remain in a non-polar state, (ii) below the $T_p(E)$ curve, the crystals are partially poled, (iii) above this curve, they are in a 1T state, (iv) on left of $T_{t1}(E)$ curve, the state is 12M, (v) between $T_{t1}(E)$ and $T_{t2}(E)$ curves, it contains a mixture of both 12M and 6T, (vi) between $T_p(E)$ and $T_{t1}(E)$, it is 4M.

In the same way, the E-T diagram (Fig. 4) along $[10\bar{1}]$ is divided into seven regions: an additional region corresponds to a coexistence of monoclinic and tetragonal phases (1M + 2T) in the poled crystal.

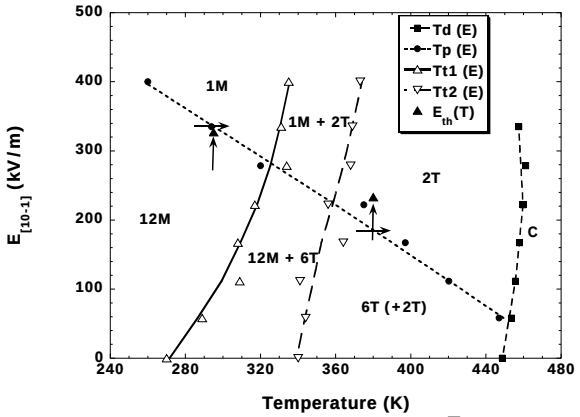

Fig. 4: Field-temperature diagram along $[10\bar{1}]$

Displacement current during IF poling

In order to determine the threshold poling field E_{th} at a given temperature, we measured I(E) during linearly increasing field. This field is given by the maximum of I; it corresponds to the inflexion point of the first polarization curve P=f(E), since:

$$\frac{\partial I}{\partial E}=\frac{\partial}{\partial E}\left(\frac{\partial P}{\partial t}\right)=\frac{\partial}{\partial E}\left(\frac{\partial P}{\partial E}\cdot\frac{\partial E}{\partial t}\right)\propto\frac{\partial^2 P}{\partial E^2}$$

I(E) measurement was carried out at different temperatures with E along [001] and $[10\bar{1}]$. Figure 5 shows that, when the field is parallel to [001], E_{th} decreases with increasing temperature.

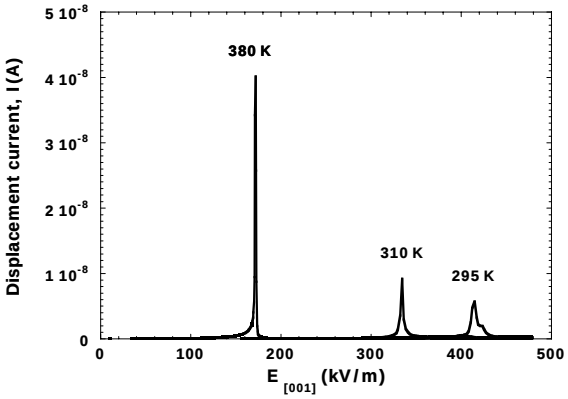

Fig. 5: Displacement current obtained at different temperatures, during a IF run along [001]

At 380 K, the current peak corresponds to the transformation from the unpoled state 6T to the poled single domain state 1T.

We can notice that the transitions observed in $T_p(E)$ and $E_{th}(T)$ measurements are in the same location of the E-T diagram, as indicated by the crossing arrows in figure 3. The values of $E_{th}(T)$ along $[10\bar{1}]$ were reported on figure 4. The E-T diagram allows to predict the value of $E_{th}(T)$ and the domain state of each poled phase at different temperatures and along a given direction.

ELECTROMECHANICAL PROPERTIES AND INTERPRETATION

Table I lists the piezoelectric properties along [001] and $[10\bar{1}]$, and after the two poling protocols.

It is interesting to note that the piezoelectric properties of the room temperature monoclinic phase are very different according to the poling protocol.

On [001] crystals, in IF poling, better results are obtained by poling with low field E and high temperature T than with high E and low T. But still better results are obtained after FC poling with lower field. The tetragonal high temperature phase has much lower properties.

On $[10\bar{1}]$ -crystals, lower elastic compliance and higher Q_{m33} are observed, both in monoclinic and tetragonal phases.

These differences can be explained as follows:
-a soft [001] material with high ε and s (and consequently of d) is obtained after FC poling, during which the poling path goes through a 1T state, without going through a complex 12M state.
-a hard $[10\bar{1}]$ material in 1M state is obtained with a IF poling protocol. The poling path goes through a 12M state. ε_{33}, s and d are lower and Q_{m33} and N are higher.
A FC poling does not give so hard properties, due to the progressive transition between 2T and 1M state, as shown in figure 6. The figure shows that the 2T→1M transition is strongly affected by the electric field. The transition begins at a higher temperature under high field, involving a more narrow region of stability of the tetragonal phase. 1M state gives a small $\varepsilon_{33}^{[10\bar{1}]}$ whereas 2T state gives a much higher value.

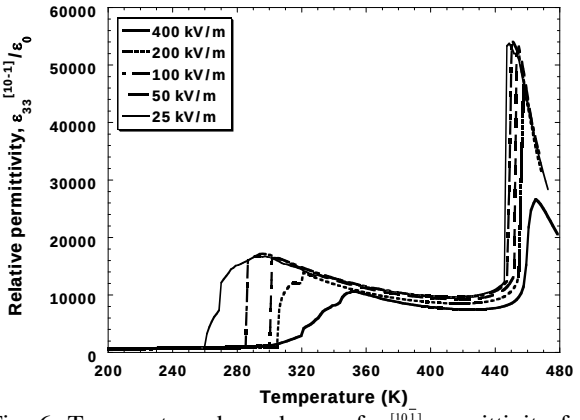

Fig. 6: Temperature dependence of $\varepsilon_{33}^{[10\bar{1}]}$ permittivity for several fields applied in a FC run along $[10\bar{1}]$

On the other hand, it is instructive to compare the properties of M phase to those of T phase. For a given direction, ε_{33}^{T}, s_{33}^{E} and d_{33} of a 4M state are much larger than those of the corresponding 1T state. In the same way, 2T state exhibits higher piezoelectric properties than 1M state. Therefore, for a given poling direction, a multidomain state is always more piezoelectric and compliant than a single domain state.

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Orientation	**[001]**					**[10$\bar{1}$]**	
Poling protocol	***FC (100 kV/m)***	***IF (380 K)***	***IF (295 K)***	***FC (100 kV/m)***	***FC (1000 kV/m)***	***IF (295K)***	
Phase At T (Domain Structure)	***Monoclinic 295 K (4M)***			***Tetragonal 360 K (1T)***	***? 295 K*** (Kuwata et al. [1])	***Monoclinic 295 K (1M)***	***Tetragonal 360 K (2T)***
ε_{33}^T	5300	4500	3480	2300	2200	1000	11000
$N=2lf_a$ (m/s)	2200	2300	2090	2550	*	3200	2600
s_{33}^E (pN/m^2)	184	162	133	52	143	18	20
d_{33} (pC/N)	2730	2540	1800	830	1570	250	550
k_{33} (%)	93	92	89	80	92	60	40
Q_{m33}	61	81	90	160	*	300	560

Table I: Electromechanical properties of PZN-9%PT single crystals obtained from different poling conditions

Moreover, the results reveal that k_{33} is higher in monoclinic structures than in tetragonal ones, both for [001] and [10$\bar{1}$] crystals. But the reasons could be very different. In 4M structure, the polarization is not parallel to the field, so it can both stretch and tilt towards the direction of the field, leading to higher coupling than in 1T structure. In 1M structure, the polarization is almost parallel to the [10$\bar{1}$] direction of the field, so the origin of the high coupling is not clear.

Whatever the domain structures may be and particularly along [10$\bar{1}$], a highest Q_{m33} is found in the single crystals having the lowest k_{33}.

SUMMARY AND CONCLUSION

After FC (field cooling under constant field) or IF (increasing field at constant temperature) poling, the electromechanical properties of PZN-9%PT single crystals in the 33 mode were measured by using the IRE method. Coupling $k_{33}^{[001]}$ and strain $d_{33}^{[001]}$ coefficients higher than in previous works were found. They can be obtained by getting a monoclinic-polydomain phase 4M by going through a tetragonal-single domain 1T phase.

The field-temperature diagrams offer the possibility to optimize, for a given crystal orientation, the path followed by the sample during the poling procedure. The polarization can be made with a lower field than previously assumed. Conditions are found to obtain either soft single crystals (with high ε and s) using low field and low temperature, or hard single crystals (with lower ε and lower s). Whatever the structural phase is - tetragonal or monoclinic- the soft and hard crystals have respectively a multidomain and a single domain state.

[001]-oriented single crystals have relatively low mechanical quality factors Q_{m33}, but higher Q_{m33} have been found in [10$\bar{1}$], related to a lower coupling factor.

ACKNOWLEDGEMENTS

The authors are grateful to A. Marx for assistance in crystal growth, to M. Gramond for helping during electric measurements.

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