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Application study of Mn-doped PIN-PMN-PT relaxor ferroelectric crystal grown by Vertical Gradient Freeze method

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ABSTRACT

A 3-inch Mn:PIN-36%PMN-32%PT (Generation III) relaxor ferroelectric crystal was grown using the Vertical Gradient Freeze method. Crystals of [1, 11] and [111] orientations were prepared and studied, evaluating their dielectric constants, piezoelectric coefficients, electromechanical coupling coefficients, loss tangents and pyroelectric coefficients. It is shown that in pyroelectric applications, [111]-poled crystals are particularly suitable for high performance sensors due to a relatively high pyroelectric coefficient, low loss tangent. In addition, the specific heat is lower as compared to LiTaO₃. It is also shown that the alternating current (AC) poling has a more significant effect on the [001]-poled crystal than on the [011]- and [111]-poled crystals due to the lattice distortion induced by a strong electric field along the [001] direction.

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Mn-doped PIN-PMN-PT; crystal; pyroelectricity; ferroelectricity; AC poling

1. Introduction

Manganese-doped Lead Indium Niobate-Lead Magnesium Niobate-Lead Titanate (Mn:PIN-PMN-PT) crystals, also called Generation III relaxor ferroelectric crystals, exhibit a higher rhombohedral-to-tetragonal transition temperature, a higher Curie temperature, and a higher coercive field due to PIN addition, and lower dielectric loss due to manganese doping, as compared to the classical PMN-PT 67/33 system [1]. The benefits of Mn:PIN-PMN-PT crystals are (1) a widened applicable temperature range of up to 100 °C; (2) higher applicable power and voltage levels; and (3) less heat generation in AC operation. These three improvements make the crystal particularly suitable for premium SONAR [2] and infrared applications [3].

Mn:PIN-PMN-PT crystals are difficult to grow, because there is a strong segregation effect of manganese [4]. As a result, production is more expensive, and has a lower yield. The higher fabrication costs were leading to a slow commercialization of these crystals. By controlling multiple close-loop heating systems and rotating crucible at the same time, the Vertical Gradient Freeze (VGF) method proved to enhance yield and uniformity of the crystal and thus allowing for a commercial production level [5].

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One purpose of this research is to assess the crystal properties for pyroelectric applications. The figure of merit includes pyroelectric coefficient, dielectric constant and loss, as well as the specific heat.

Another purpose of this research is to assess the alternating current poling (AC poling) technique for improving key properties of the crystal at different orientations. Recent studies showed that the key properties of the 2-component relaxor system PMN-PT can be enhanced as much as by 20% through AC poling, which influences domain wall density and field induced monoclinic phases (such as M_A) [6]. Furthermore, AC poling might have the potential to allow for a larger portion of the crystal ingot to be qualified despite of Mn segregation at growth. Previous studies had only investigated the [001] oriented relaxor ferroelectric crystal, but not the [011] and [111] orientations; this research will compare AC poling phenomenon on all three orientations.

2. Experiment method

2.1. Crystal growth and sample preparation

0.5%Mn:32.5%PIN-36%PMN-31%PT (atomic % by nominal composition) ceramic precursor powders were molten and directionally solidified into 3 inch cylindrical single crystal ingots along [011] using the VGF method by Innovia Materials (Shanghai). (011)-oriented, 1 mm thick wafers were cut perpendicular to the growth direction, (001) wafers were cut at 45° and (111) wafers were cut at 35.3° to the growth direction, respectively. $7*7*1$ (L*W*T) mm^3 plates were prepared with the T direction along [1, 11] and [111], all of which were taken from the adjacent region to minimize segregation effect on properties. Additionally, $7*7*7$ (L*W*T) mm^3 samples were prepared with the T direction along [011] and W direction along [100] in order to measure the transverse piezoelectric coefficient. All samples were coated with 0.02/0.2 microns of Cr/Au layers on the opposite surfaces of the T directions using a TRP-450 sputter deposition tool from Sky, China. The samples were poled in air by a DC field along the T direction with an electric field of 5.5 kV/cm. For AC poling, a bipolar electric field of 10 kV/cm peak-to-peak at a frequency of 1 Hz was applied for 20 cycles. All samples were relaxed at room temperature for 48 hours before measurement.

2.2. Sample testing

The piezoelectric coefficient d_{33} was measured as direct effect using a Berlincourt-type d_{33} meter (ZJ-4B, Institute of Acoustics CAS, Beijing, China), d_{32} was measured with the setup shown in Figure 1. The pyroelectric coefficient was measured with an Aixact TF Analyzer 2000E at 20°C . A Keysight E4990A Impedance Analyzer was used to trace frequency, impedance, capacitance and dielectric loss. In accordance with IEEE Standard on Piezoelectricity 176-1987, electromechanical coupling coefficient is calculated from Equation (1), dielectric constant K_3^T is calculated from Equation (2).

$$k^2 = \frac{\pi f_r}{2 f_a} \tan \left(\frac{\pi f_a - f_r}{2 f_a} \right) \quad (1)$$

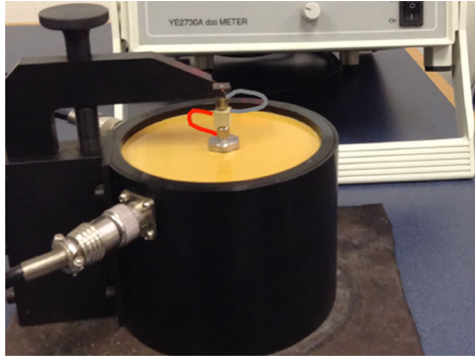


Figure 1. d32 Berlincourt measurement setup, the pins were used to clamp the faces of Direction 2, while electrically wired and soldered to the faces of Direction 3 [10].

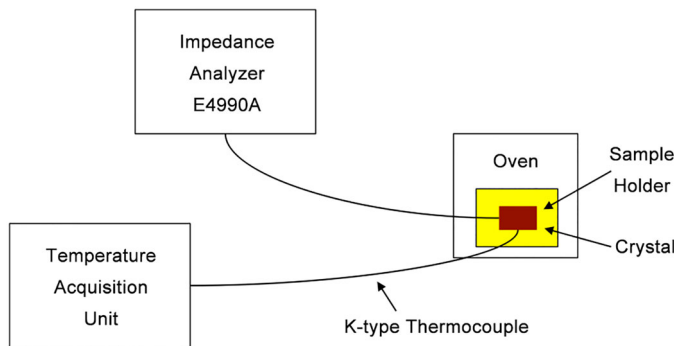


Figure 2. Set up for T_c (Curie temperature) and T_{R-T} measurement.

where k is electromechanical coupling coefficient, f_r is resonance frequency and f_a is anti-resonance frequency.

$$K_3^T = \frac{d \varepsilon_0}{C A} \quad (2)$$

where d is sample thickness, A electrode area, C is capacitance, ε_0 is the vacuum permittivity.

Setup for T_c and T_{R-T} measurement is illustrated in Figure 2. Plate sample is attached to a sample holder which then wired to Impedance Analyzer. Additionally, a K-type thermocouple is attached adjacent to the sample with a temperature acquisition unit. Sample holder is then placed into a programmable oven. Real-time K_3^T -temperature plots are obtained from room temperature to 180 °C at 5 °C/min. All properties were measured three times and an average was taken.

3. Results and discussions

Figure 3 shows a 3-inch ingot and polished wafers. Crystals are brown to black in appearance, with machine-ability close to PMN-PT crystals.

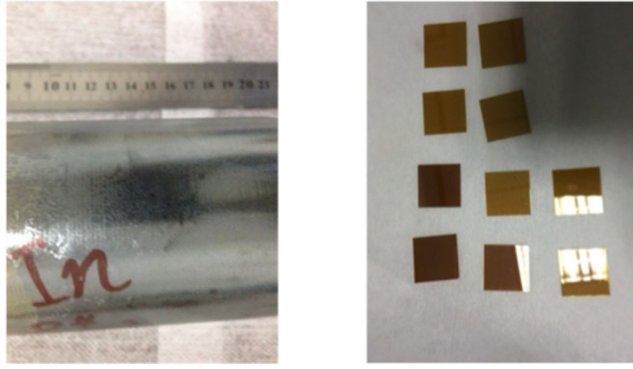


Figure 3. Mn:PIN-36%PMN-32%PT crystal grown by VGF method (left), polished wafers (right).

Table 1. Property values of 0.5%Mn:PIN-36%PMN-32%PT crystals dc poled along different orientations.

Properties	DC poled at different orientations		
	[001]-poled	[011]-poled	[111]-poled
Dielectric Constant K_3^T	4800	1700	520
Piezoelectric coefficient (pC/N)	1500 (d_{33})	-1300 (d_{32})	-
Loss Tangent (%)	0.5	0.1	0.05
Pyroelectric Coefficient $\mu\text{C}/\text{m}^2/\text{K}$	470	-	800
Transition Temperature (T_{R-T}) ($^\circ\text{C}$)	128	128	128

Table 1 shows measured property values of Mn:PIN-PMN-PT crystals which are DC poled along different orientations. Overall, the [001]-poled crystal has the highest values for thickness mode piezoelectric applications such as dielectric constant K_3^T and the piezoelectric coefficient d_{33} . The [011]-poled crystal has the highest transverse mode piezoelectric coefficient d_{32} , suitable for certain SONAR applications. [111]-poled crystal has the highest pyroelectric coefficient of 800 $\mu\text{C}/\text{m}^2/\text{K}$, highly desirable for pyroelectric applications. Overall, the Mn doping has decreased the loss tangent for all three poling directions. The lowest value of 0.05% was achieved at the [111]-poled sample, which is excellent for pyroelectric and high-power applications. The rhombohedral-to-tetragonal transition temperatures (T_{R-T}) were measured at 128 $^\circ\text{C}$, and Curie Temperature at around 162 $^\circ\text{C}$ for the [111]-poled crystal (Figure 4). The rise of critical temperature with regard to PMN-PT is due to the addition of PIN [1]. The applicable temperature is thus higher in this generation III relaxor.

3.1. pyroelectric applications

The essential characteristics of pyroelectric detectors are voltage responsivity S_v , the noise equivalent power NEP and the specific detectivity D^* . The corresponding figures of merit (F_V , F_D , respectively) for the pyroelectric material are:

$$F_V = \frac{P}{\varepsilon_0 K_3^T c_p'} \quad (3)$$

$$F_D = \frac{P}{c_p' \sqrt{\varepsilon_0 K_3^T \tan \delta}} \quad (4)$$

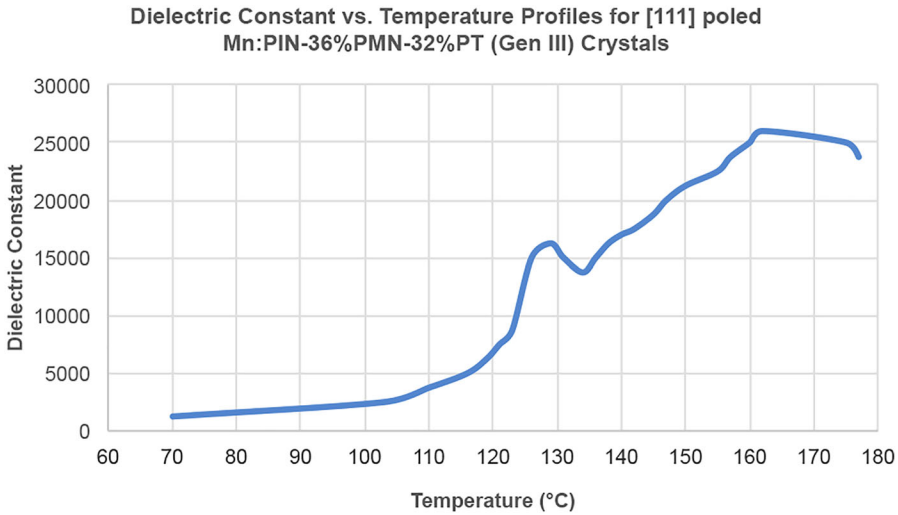


Figure 4. Dielectric Constant vs. Temperature profiles for [111] poled Mn:PIN-36%PMN-32%PT relaxor ferroelectric crystal, with T_{R-T} around 128 °C and T_C around 162 °C.

Table 2. Typical property values of MN:PIN-PMN-PT crystals dc poled along different orientations.

Properties	DC poled at different orientations	
	Commercial LiTaO ₃ Crystal	[111]-poled Mn:PIN-PMN-PT
Dielectric constant K_3^T	45	520
Pyroelectric coefficient p $\mu\text{C}/\text{m}^2/\text{K}$	170	800
Loss tangent (%)	0.1	0.05
Specific heat c_p' $\text{MJ}^{-3}\text{K}^{-1}$	3.2 ^a	2.5 ^b
$\frac{p}{c_p}$ (10^{-11} m/V)	5.3	32.0
F_V (m^2/C)	0.133	0.070
F_D (10^{-5} Pa ^{-1/2})	8.4	21.1

where c_p' is volume of specific heat, ϵ_0 is the vacuum permittivity, K_3^T is dielectric constant, $\tan\delta$ the dielectric loss tangent, and p is pyroelectric coefficient.

To single out material properties in Equations (3) and (4), Table 2 tabulates the figure of merits of Mn:PIN-PMN-PT in comparison to commercial LiTaO₃ crystals used for infrared sensors [7, 8]. Through calculation, [111]-poled Mn:PIN-PMN-PT shows clear advantage over LiTaO₃ in terms of current responsivity, which is proportional to $\frac{p}{c_p}$. However, for the voltage response Gen III crystal's advantage is diminished. For the detectivity, which is accounting also for the noise, the Gen III crystal is again better. Indeed, it was reported that the Gen III crystal is currently applied in high performance infrared sensors, but not necessarily a great choice for low end sensors [7].

3.2. AC poling

Figure 5 shows the effects of AC poling on dielectric constants K_3^T for all crystal orientations. AC poling has significantly increased the K_3^T value of the [001]-poled crystal by 20% (from 4,879 to 5,997), whereas no appreciable increase was observed for [011] and [111]-poled crystals.

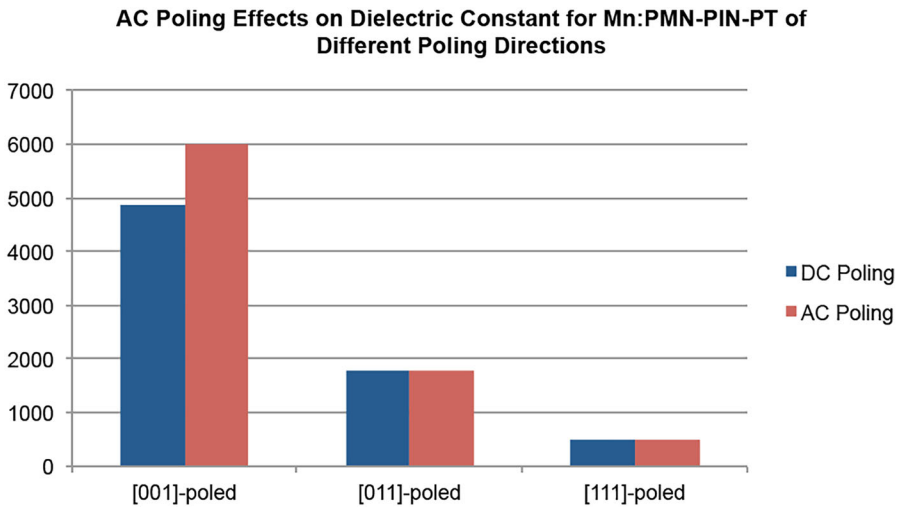


Figure 5. AC poling's effects on [001]-poled, [011]-poled and [111]-poled Mn:PIN-36%PMN-32%PT crystals.

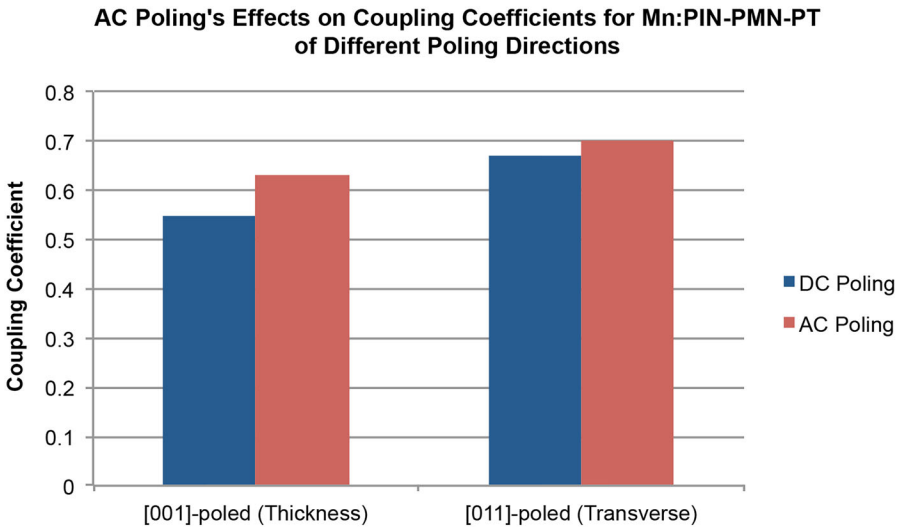


Figure 6. AC poling's effects on [001]-poled and [011]-poled Mn:PIN-36%PMN-32%PT crystals in terms of thickness mode coupling and transverse mode coupling.

Figure 6 shows the effects of AC poling on the thickness mode coupling of [001]-poled and transverse mode coupling of [011]-poled crystal. AC poling leads to a 15% of increase of the former (k_t increased from 0.55 to 0.63), whereas the latter does not change much (k_{32} increased from 0.67 to 0.70).

Figure 7 shows the effects of AC poling on piezoelectric coefficients' absolute values of d_{33} on [001]-poled, of d_{32} on [011]-poled and of d_{33} on [111]-poled Mn:PIN-PMN-PT crystals, respectively. Again, AC poling has significant increased piezoelectric coefficient only on [001]-poled crystals (d_{33} increased from 1200 to 1380), but not so on either [011]-poled or [111]-poled ones.

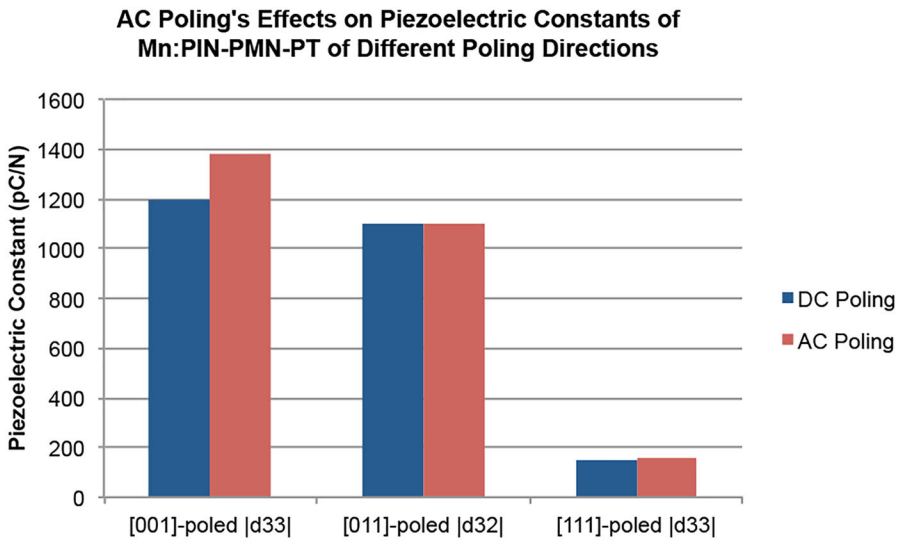


Figure 7. AC poling's effects on [001]-poled and [011]-poled Mn:PIN-36%PMN-32%PT crystals in terms of thickness mode coupling and transverse mode coupling.

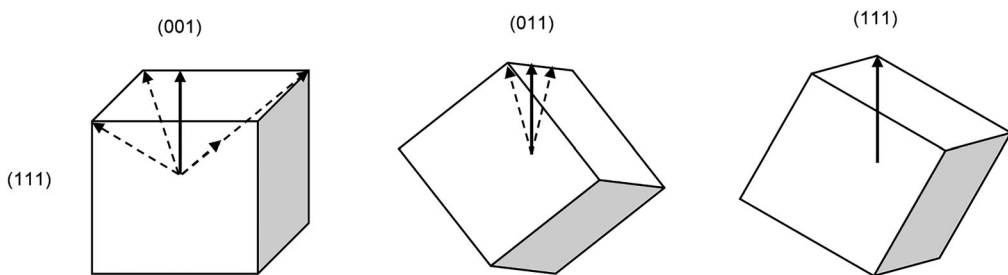


Figure 8. Domain states engineered in three configurations. Crystal lattice under 4 mm (left) is easier to be shifted by AC poling than mm^2 (middle) and 3 m (right), making M_A phase easier to be induced in [001]-poled crystals.

While the origin of AC poling needs further exploration, a recent study showed that AC poling induced a lattice extension along the [001] poling direction, and it was proposed that the higher domain wall density formation and a field induced formation of a monoclinic phase (M_A) might be the causes for the enhancement of properties [9]. Based on such assumption, it is reasonable to deduce that along [111] and [011] poling directions, lattice parameters are more difficult to be shifted by AC poling because the existing domain symmetries (3m for the [111]-poled and mm^2 for the [011]-poled crystals) are more resistant against lattice distortions than the 4mm symmetry of [001] poled crystals. In Figure 8, it is shown that in 4mm symmetry (left), AC poling along [001] may exercise the lattice by changing spontaneous polarization along 4 different directions inclined by 55 degrees from the poling direction; in mm^2 configuration (center), AC poling along [011] may exercise the lattice by changing spontaneous polarization in 2 different possibilities, with each possibility 45 degrees from the poling direction; in 3m configuration (right), the AC poling along [111] only one domain has

lowest energy as the poling direction is parallel its spontaneous polarization. Hence, M_A phases are more difficult to be induced by AC poling along [111].

4. Conclusion

A giant 0.5%Mn:32.5%PIN-36%PMN-31%PT crystal was grown along the [011] crystallographic direction using the VGF method. Plate samples with poling directions of [1, 11] and [111] were taken from the same ingot region and tested for their key ferroelectric material properties. Loss tangents of [001]-, [011]- and [111]-poled crystals were measured at 0.5%, 0.1% and 0.05%, respectively. The pyroelectric coefficient of the [111]-poled crystal was measured as $800\mu\text{C}/\text{m}^2/\text{K}$, while T_{R-T} and T_C were measured at 128°C and 162°C , respectively.

Figures of merits for pyroelectric responsivity mean that the Gen III crystal allows for a higher current responsivity, and a higher detectivity than LiTaO_3 crystals, while the voltage responsivity is expected to be lower. This clearly indicates that the new crystals are suitable for high performance infrared sensors at this stage.

The effects of AC poling were studied on [001]-, [011]- and [111]-poled crystals, respectively. It is shown that AC poling can increase the dielectric constant K_3^T , piezoelectric coefficient and plate-mode coupling k_t of [001]-poled crystals. However, such effect is not apparent on K_3^T , transverse piezoelectric coefficient d_{32} and transverse coupling k_{32} of the [011]-poled crystal, nor on K_3^T and k_t values of the [111]-poled crystal. Such disparity could be explained by different degrees of AC poling effects exerted on crystal's different states of configuration: while the configuration of 4mm symmetry associated with the [001]-poled crystal is more susceptible to field-induced distortion, [011]-poled crystal is less susceptible, and [111]-poled crystal is not susceptible at all. As a result, [001]-poled Mn:PIN-PMN-PT crystals could benefit the most from AC poling in terms of enhancement in dielectric, piezoelectric and ferroelectric properties.

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