

# The Progress Update of Relaxor Piezoelectric Single Crystals

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**Abstract** —A series of relaxor piezoelectric single crystals, including lead magnesium niobate-lead titanate (PMN-PT) and pure and manganese-doped lead indium niobate-lead magnesium niobate-lead titanate (PIN-PMN-PT and Mn: PIN-PMN-PT), have been developed by a modified Bridgman crystal growth process. These single crystals have been grown along both  $\langle 001 \rangle$  and  $\langle 110 \rangle$  with diameters up to 75mm. PIN-PMN-PT possesses the similar electromechanical properties to PMN-PT, while rhombohedral-to-tetragonal phase transition temperature ( $T_{rt}$ ) and coercive field ( $E_C$ ) increased to higher than 120°C and 4.5kV/cm, respectively. By doping with Mn, mechanical quality factor ( $Q_M$ ) increased above 700 in  $\langle 001 \rangle$ -poled longitudinal mode without compromising electromechanical coupling ( $k_{33}$ ),  $T_{rt}$  and  $E_C$ . This work demonstrated that by composition modification, the electromechanical properties of PMN-PT based crystals can be stabilized with respect to operating temperature and electric field.

**Keywords**- single crystal, piezoelectrics, PMN-PT, PIN-PMN-PT, Mn:PIN-PMN-PT

## I. INTRODUCTION

Lead-based relaxor materials, discovered in the 1950s, are complex perovskites with a general formula  $Pb(B_1B_2)O_3$  ( $B_1 = Mg^{2+}, Zn^{2+}, Ni^{2+}, Sc^{3+}, Fe^{3+}, Yb^{3+}, In^{3+}$ , etc,  $B_2 = Nb^{5+}, Ta^{5+}, W^{6+}$ , etc) [1-2], which exhibit a broad and frequency dispersive dielectric maximum with respect to temperature [3]. It was found that relaxor-PT solid-solution systems with morphotropic phase boundary (MPB) compositions possess superior dielectric and piezoelectric properties compared to that of PZT ceramics [4]. A variety of different Relaxor-PT systems have been extensively studied in the form of single crystals [5-7]. Relaxor-PT single crystals, such as  $Pb(Zn_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$  (PZN-PT) and  $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$  (PMN-PT) have been found to offer significant performance improvements with high electromechanical coupling ( $k_{33} > 90\%$ ) and piezoelectric coefficients ( $d_{33} > 2000pC/N$ ) in contrast to  $Pb(Zr,Ti)O_3$  (PZT) ceramics ( $k_{33} \sim 75\%$ ,  $d_{33} \sim 400-600pC/N$ ). Single crystals are, therefore, promising candidates for medical ultrasonics, sonar transducers and solid-state actuators [4, 8]. Since PZN-PT crystals can only be grown from its high temperature solutions, the crystal size and quality are not sufficient for industrial production. In contrast, PMN-PT melts congruently so that large crystals can be grown in a cost-effective process, such as the Bridgman method. Recently, PMN-PT crystal became the major competitor to PZT

ceramics in high-end medical ultrasound transducer applications.

However, it is known that PMN-PT crystal exhibits low rhombohedral-to-tetragonal phase transition temperature ( $T_{rt} < 100^\circ C$ ), low coercive field ( $E_C < 2.5kV/cm$ ) and low mechanical quality factor ( $Q_M < 160$ ), so its performance is limited by low temperature and low electric field operation. Owing to low  $Q_M$ , heat generation also becomes more problematic for high power, high duty cycle applications. It is necessary to develop new relaxor-PT crystals, which can provide expended operating temperature and electric field driving ranges, while keeping excellent electromechanical properties for transducer and actuator applications. This paper discusses our recent progress on crystal growth and characterization of relaxor-PT crystals, including PMN-PT, PIN-PMN-PT and Mn: PIN-PMN-PT. A comparison study of the piezoelectric and dielectric properties of these crystals at room temperature and at high temperature is summarized.

## II. EXPERIMENTAL

### A. Bridgman growth of Relaxor-PT single crystals

Since the Bridgman method is used to grow relaxor-PT crystals, pre-synthesized pure perovskite-phase raw materials are usually required for keeping the crystal growth interface stable. If there is any amount of secondary phase formed during raw material batching, it may induce spontaneous nucleation and formation of polycrystalline material. In this work, the precursor method was adopted to the batching process to prevent the formation of pyrochlore phase. For preparation of relaxor-PT compounds, both a wolframite precursor,  $InNbO_4$ , and a columbite precursor,  $MgNb_2O_6$ , were first synthesized respectively by calcination of oxides at 1000-1200°C [9-10]. Using these precursors, PMN-PT, PIN-PMN-PT and Mn: PIN-PMN-PT were synthesized by another calcination process at lower temperature (700-950°C). As verified by powder x-ray diffraction (XRD), pure perovskite phase was obtained through this precursor method.

Binary PMN-PT and ternary pure and Mn-doped PIN-PMN-PT single crystals were grown by the seeded Bridgman method using either the same or different kinds of relaxor-PT single crystals as the seeds. The starting composition was selected with 26-36% PIN, 28-32% PT and 0.5-5% Mn. In the Bridgman growth process, the cylindrical Pt crucibles charged with single crystal seeds at the bottom and the binary or ternary starting material above the seeds were placed in a

two-zone multi-crucible furnace. By setting the temperature of the upper zone 80-120°C higher than the melting points and the lower zone 100-300°C lower than the melting point, an axial temperature gradient of 30~50 °C/cm formed between two zones. After the charge and part of the crystal seeds were melted in the upper-zone, the crucibles were lowered down slowly through the temperature gradient to accomplish the unidirectional crystallization process. PMN-PT and PIN-PMN-PT single crystals with diameter up to 75mm were grown along both  $\langle 110 \rangle$  and  $\langle 001 \rangle$  orientations. The Mn: PIN-PMN-PT crystal with diameter up to 50mm was obtained as well. Fig. 1 shows the as-grown binary and ternary relaxor-PT crystal boules and wafers

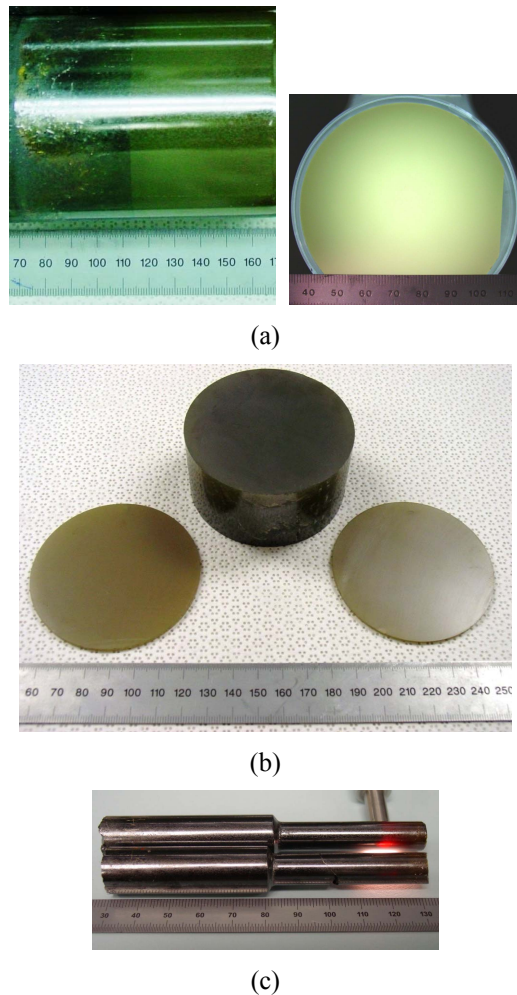


Fig. 1 As-grown binary and ternary relaxor-PT crystals: (a) a boule and a wafer of 75mm diameter and  $\langle 001 \rangle$ -oriented PMN-PT crystal, (b) a boule and two wafers of 75mm diameter and  $\langle 011 \rangle$ -oriented PIN-PMN-PT crystal, and (c) two boules of Mn: PIN-PMN-PT crystal

#### B. Elastic, piezoelectric and dielectric property measurement

The crystals were oriented using real-time Laue X-ray and cut to obtain longitudinal rods with the aspect ratios following IEEE piezoelectric standards [11]. All the samples were oriented along  $\langle 001 \rangle$  and  $\langle 110 \rangle$  directions and vacuum sputtered gold was applied as the electrodes. PMN-PT crystals were poled under 10kV/cm, while pure and Mn-

doped PIN-PMN-PT crystals were poled under 20kV/cm at room temperature. High field polarization and strain measurements were performed on the  $\langle 001 \rangle$  and  $\langle 110 \rangle$  oriented samples at room temperature at a frequency of 1Hz, using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier. Room temperature dielectric, piezoelectric, electromechanical properties and the mechanical quality factor (inverse of mechanical loss) were determined according to IEEE standards, by using HP4194A Impedance-gain/phase analyzer. The dielectric temperature dependence was measured using a multi-frequency LCR meter (HP4284A), connected to a computer controlled temperature chamber. The high temperature piezoelectric and electromechanical characteristics were obtained from an impedance analyzer connected to a temperature chamber. In order to minimize stress effects on the samples during the measurement, thin silver wires were attached on the electrodes using a small amount of high temperature conductive silver.

### III. RESULTS AND DISCUSSIONS

#### A. Composition segregation induced longitudinal property variation

Due to the different segregation coefficients of the ions in the solid-solution systems, the as-grown single crystal boules of both PMN-PT and PIN-PMN-PT exhibit composition segregation induced properties variation along the growth direction [12-13]. The composition distribution of the main elements along the crystallization direction was determined by electronic probe microanalysis (EPMA). Except for Pb, all other elements in a PMN-PT crystal exhibit composition segregation during Bridgman growth, with effective segregation coefficient of Nb and Mg larger than 1 and that of Ti is smaller than 1 (see Fig. 2a). Along a PMN-PT crystal boule, dielectric permittivity and piezoelectric coefficient increase along the crystallization direction with the increase of Ti concentration until reaching maximum values near the MPB. Both properties then decrease sharply when the tetragonal phase starts emerging. Studies suggested that a broad MPB region between rhombohedral and tetragonal phases exists with the presence of the mixed phases, including metastable ferroelectric monoclinic ( $FE_m$ ) and ferroelectric orthorhombic ( $FE_o$ ) phases [13-16]. In a PIN-PMN-PT crystal, it was identified that the variation of Ti and Nb followed the same trends along the crystallization direction as in PMN-PT crystal; however, it was observed that the In and Mg concentrations keep nearly constant (only ~1% variation) during the whole crystallization process (see Fig. 2b). Since segregation coefficient of In in PIN-PMN-PT system is close to 1, the composition segregation induced property variation along the crystallization direction in PIN-PMN-PT crystals is quite similar to that in PMN-PT crystals. Fig. 3 compares the piezoelectric coefficient ( $d_{33}$ ) distribution along a PMN-PT and a PMN-PIN-PT crystal boule with the same PT concentration.

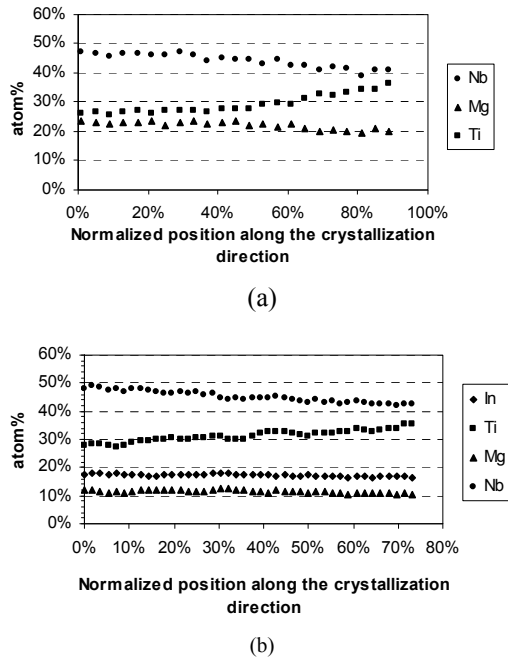


Fig.2 The composition distribution of the main elements along the growth direction of a PMN-PT (a) and a PIN-PMN-PT crystal (b)

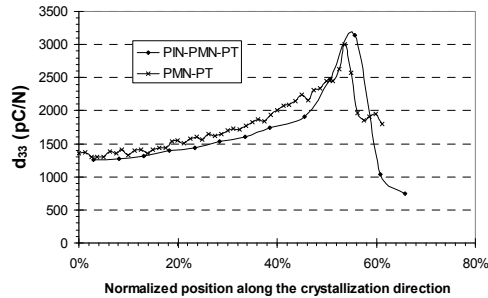


Fig. 3 Piezoelectric coefficient ( $d_{33}$ ) distribution along a PMN-PT and a PMN-PIN-PT crystal boule

### B. Comparison of room temperature properties

Table I summarizes the  $\langle 001 \rangle$ -poled longitudinal mode piezoelectric and dielectric properties of PMN-PT, PIN-PMN-PT and Mn: PIN-PMN-PT crystals with the same PT content (28-30%PT). The electromechanical coupling ( $k_{33}$ ) for all three types of crystals are equal or higher than 0.90. Thus, the extremely high electromechanical coupling of single crystal piezoelectrics may be enhanced by the perfect periodical structure the crystals, which allows dipoles to align perfectly along the poling field in a domain engineered configuration, regardless of composition differences. Of particular significance was the coercive field ( $E_c$ ) being greater than 4.5kV/cm for both undoped and doped PIN-PMN-PT crystals, more than twice the values of PMN-PT. This will allow PIN-PMN-PT to be driven at higher AC field without depoling. By doping Mn into PIN-PMN-PT crystals, mechanical quality factor ( $Q_M$ ) increased dramatically; meanwhile, the dielectric permittivity ( $K$ ) and  $d_{33}$  dropped slightly, which means that Mn affects PIN-PMN-PT crystal properties similarly to PZT ceramics by

making both of them “harder”. It has to be pointed out that, the decrease of  $d_{33}$  in Mn doped PIN-PMN-PT crystals is small compared to that in acceptor-doped PZT ceramics. Mn: PIN-PMN-PT possesses  $d_{33}$  between 1080 and 1700pC/N, which is still 2-4 times higher than that of “soft” PZT ceramics. For  $\langle 001 \rangle$ -poled Mn: PIN-PMN-PT crystals,  $Q_M$  reaches 700, which is quite close to that of Navy Type I and III “hard” PZT ceramics (500-1000).

### C. Anisotropy of relaxor-PT crystals

As shown in Table I as well, for the longitudinal mode,  $\langle 001 \rangle$ -poled crystals exhibit higher dielectric permittivity ( $K$ ) and  $d_{33}$  than  $\langle 110 \rangle$ -poled crystals; however,  $\langle 110 \rangle$ -poled crystals still possessed electromechanical coupling ( $k_{33}$ ) close or equal to 0.9. Of particular significance was the  $Q_M$ , being greater than 400, 500 and 1030 for  $\langle 110 \rangle$  poled PMN-PT, PIN-PMN-PT and Mn: PIN-PMN-PT crystals, respectively, much higher than that of crystals poled along  $\langle 001 \rangle$ . Mn-doped PIN-PMN-PT crystals also exhibit significantly higher  $E_c$  ( $\geq 8$ kV/cm) along  $\langle 110 \rangle$ , making the potential of this crystal for high power resonant transducer applications.

Table I: A summary of the  $\langle 001 \rangle$ - and  $\langle 110 \rangle$ -poled longitudinal mode piezoelectric and dielectric properties relaxor-PT crystals

Crystals	Poling	Free K	Loss (%)	$k_{33}$	$D_{33}$ (pC/N)	$T_r$ ( $^{\circ}$ C)	$E_c$ (kV/cm)	$Q_M$
PMN-PT	$\langle 001 \rangle$	$\geq 5000$	$\leq 0.6$	$\geq 0.90$	1500-2200	$\geq 85$	$\geq 1.8$	$\geq 80$
PIN-PMN-PT		$\geq 4000$	$\leq 0.6$	$\geq 0.90$	1300-2000	$\geq 120$	$\geq 4.5$	$\geq 100$
Mn: PIN-PMN-PT		$\geq 2900$	$\leq 0.2$	$\geq 0.90$	1080-1700	$\geq 120$	$\geq 4.5$	$\geq 700$
PMN-PT	$\langle 110 \rangle$	$\geq 3500$	$\leq 0.6$	$\geq 0.87$	1000-1500	$\geq 75$	$\geq 1.8$	$\geq 400$
PIN-PMN-PT		$\geq 3100$	$\leq 0.6$	$\geq 0.87$	900-1300	$\geq 110$	$\geq 4.5$	$\geq 500$
Mn: PIN-PMN-PT		$\geq 2600$	$\leq 0.2$	$\geq 0.87$	800-1100	$\geq 110$	$\geq 8.0$	$\geq 1030$

### D. Comparison of high temperature properties

Fig. 4 shows the dielectric permittivity as a function of temperature for rhombohedral PMN-PT, PIN-PMN-PT and Mn: PIN-PMN-PT crystal samples with the similar PT content ( $\sim 29\%$ PT). Of particular interest is that both undoped and doped PIN-PMN-PT crystals possess much higher Curie temperature ( $T_C$ ) and rhombohedral-to-tetragonal phase transition temperature ( $T_r$ ) than PMN-PT crystals. For these specific doped and undoped PIN-PMN-PT crystal samples,  $T_r$  is 120  $^{\circ}$ C and 138  $^{\circ}$ C, respectively; 24 $^{\circ}$ C and 42 $^{\circ}$ C higher than that of PMN-PT. The dielectric permittivity variation for doped and undoped PIN-PMN-PT in the range of room temperature to 60 $^{\circ}$ C was found to be on the order of 34% and 38%, respectively; much lower when compared to PMNT crystal ( $\sim 67\%$ ).

Fig. 5 compares the temperature dependence of electromechanical coupling ( $k_{33}$ ) and piezoelectric coefficient ( $d_{33}$ ) among Mn: PIN-PMN-PT, PIN-PMN-PT and PMN-PT crystals. The  $\langle 001 \rangle$ -poled longitudinal mode rod samples used in the test all have the same dimension, while the composition has similar PT and PIN concentrations to make the results comparable. It was observed that  $k_{33}$  maintained similar values with increasing temperature, but decreased sharply above  $T_r$  due to the

rhombohedral to tetragonal phase transition. The values of  $d_{33}$  were found to increase with increasing temperature and reach their maxima at the phase transition temperature, whereupon they decreased significantly. It is shown that for both Mn: PIN-PMN-PT and PIN-PMN-PT crystals, phase transition started around 125°C, while for PMN-PT, it started around 90°C. It was also found that all the tested samples maintained the original  $k_{33}$  and  $d_{33}$  values after they are cooled down to room temperature, which means depoling did not happen even though they were heated over the rhombohedral-to-tetragonal phase transition temperature.

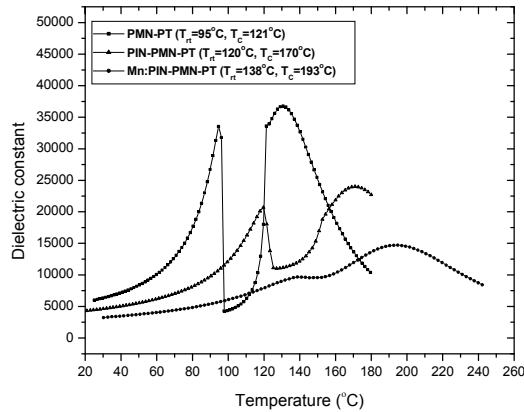


Fig. 4 The dielectric permittivity as a function of temperature for rhombohedral relaxor-PT crystal samples

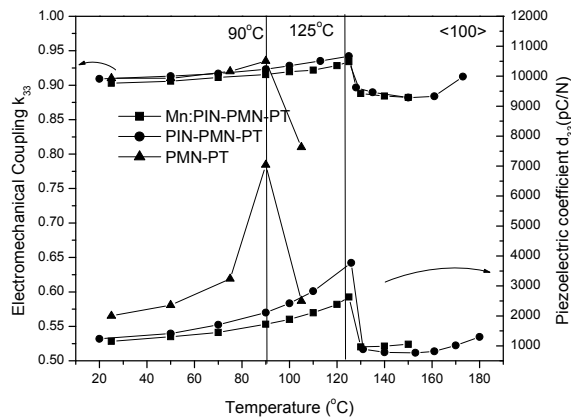


Fig. 5 A comparison of the temperature dependence of electromechanical coupling ( $k_{33}$ ) and piezoelectric coefficient ( $d_{33}$ ) among relaxor-PT crystals

#### IV. CONCLUSIONS

By composition modification of PMN-PT single crystals, ternary PIN-PMN-PT crystals have been successfully developed by the Bridgman method. Ternary crystals exhibited the same excellent electromechanical performance, but significantly improved thermal stability and expanded operating temperature range and driving electric field.

Furthermore, by doping acceptor Mn into ternary PIN-PMN-PT crystal, the mechanical quality factor of the crystal increased dramatically with further improved thermal stability. It is demonstrated that by composition modification, the electromechanical properties of relaxor-PT crystals can be optimized for the high power output and high duty cycle applications.

#### ACKNOWLEDGMENT

This work was supported by the ONR under SBIR and STTR programs.

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