Over-poling Study of PMN-PT Crystal Grown by Vertical Gradient Freeze Method

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***Abstract*—3 inch Lead magnesium niobate – lead titanate (PMN-PT) crystal was grown by Vertical Gradient Freeze (VGF) method. Poling reactions of [001]-poled PMN-0.29PT and PMN-0.31PT were studied. DC field 50~1500 V/mm were used to pole along [001] direction, dielectric constant, plate mode coupling coefficient and dielectric loss were recorded. It is shown that piezoelectric properties saturate around 350 kV/mm for PMN-0.29PT and 250 kV/mm for PMN-0.31PT, respectively. Both PMN-0.29PT and PMN-0.31PT experience property degradation due to over-poling over 1300 kV/mm, and PMN-0.31PT is more susceptible to over-poling due to closer vicinity to the Morphotropic Phase Boundary (MPB). The mechanism of over-poling is analyzed by observing dielectric constant against temperature in zero field heating (ZFH) environment. Compared to optimized poled samples, over-poled samples lack rhombohedral-to-tetragonal phase transition, which confirms that over-poling is a field-induced phase transition. Furthermore, over-poling is found reversible by annealing at elevated temperatures. In the case of PMN-0.29PT, over-poling could be reversed by annealing at 300° C for 1 hr. Such discovery could serve as potential remedy for over-poled PMN-PT crystals, although a more comprehensive study must be carried out to verify microscopic phase change and macroscopic property restoration before and after annealing. Above all, it is recommended to impose a DC poling limit of 1000 V/mm anytime for [001] oriented PMN-PT to avoid over-poling. Similar study is to be carried out on PIN-PMN-PT tertiary crystal system.**

Keywords—PMN-PT; Overpoling; Phase transition

I. INTRODUCTION

In recent years, relaxor ferroelectric crystal Lead Magnesium Niobate – Lead Titanate (PMN-PT) crystal products have been used on various application such as medical ultrasound imaging, SONAR, micro-actuation and energy harvesting applications due to high electromechanical coupling coefficient and high piezoelectric coefficient [1]. Larger diameter and significant property improvement has been achieved through Vertical Gradient Freeze (VGF) method [2]. However, the properties of PMN-PT crystal are sensitive to poling conditions and can be degraded due to over-poling. Hence, it is important for device manufacturers to understand over-poling mechanism and design against over-poling.

Previous studies have shown that, melt-grown PMN-PT crystal is generally resistant to over-poling up to 1 kV/mm. Over-poling, once induced, can have negative effects on dielectric and piezoelectric properties such as dielectric constant, piezoelectric constant and coupling coefficient [3]. Such over-poling effects also hold true for other piezoelectric crystal systems such as PZN-PT [4]. Some mechanisms of over-poling can be explained by field induced phase change near MPB: in particular, from rhombohedral to orthorhombic in the case of [011] poled PMN-PT and PZN-PT crystals [5, 6].

To further understand over-poling, the following issues need to be addressed:

a) [001] poled PMN-PT crystal is the most common crystal product for medical ultrasound and non-destructive testing (NDT) applications whose over-poling behavior and mechanisms remain to be explored.
b) Whether degradation caused by over-poling is recoverable.
c) Vertical Gradient Freeze (VGF) method is a novel method to growth more uniform PMN-PT crystal, poling behaviors of crystal grown by this method need to be studied.

The purpose of this paper is to address the above three issues.

II. EXPERIMENT

A 3 inch diameter PMN-PT ingot was grown using Vertical Gradient Freeze (VGF) method in platinum crucible with (001) faced seed crystal and precursor ceramic. From the ingot, a wafer PMN-0.29PT and a wafer PMN-0.31PT were selected with faces oriented within 0.5° of the (001) planes, from each wafer 5 plate samples of $10\times10\times0.7$(H) mm^3 were separated so that H direction is parallel to the [001] direction. Each sample was sputtered with Cr/Au on both faces normal to the [001] direction, followed by poling in air along [001] with DC electric field of 50 V/mm to 1500 V/mm with interval of 50 V/mm in the between. After each poling, a Keysight E4990A Impedance Analyzer was used to trace impedance from 2 MHz to 4 MHz, and measure resonance frequency, antiresonance frequency; capacitance was also measured at frequency of 1 kHz at 25° C.

In accordance with IEEE Standard on Piezoelectricity 176-1987, electromechanical coupling coefficient is calculated from Eq. 1, dielectric constant K_3^T is calculated from Eq. 2.

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

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

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

where d is sample thickness, A electrode area, C is capacitance, ε_0 is permittivity of space.

To further understand the mechanism of over-poling and the potential recovery method, dielectric constant K_3^T vs. temperature profiles were obtained at different stages: a) optimized poled, b) over-poled, c) furnace annealing at 170 °C for 1 hr of the over-poled and d) furnace annealing at 300°C for 1 hr of the over-poled. The set up for such measurement is illustrated in Fig. 1: plate sample is attached to a sample holder which is then wired to Impedance Analyzer. Additionally, a K-type thermocouple with a temperature acquisition unit is attached adjacent to the sample. Sample holder is then placed into a programmable oven. Real-time K_3^T-temperature plot is obtained from room temperature to 180 ° C at heating rate of 5° C/min.

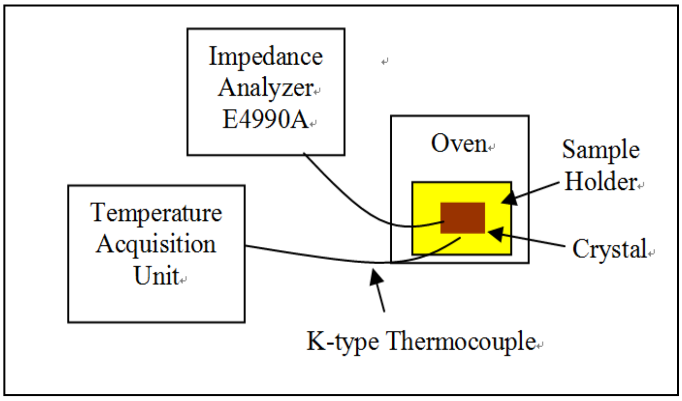

Fig. 1: Set up for phase transition measurement

III. RESULTS AND DISCUSSION

A. Poling Effects on Dielectric Constant and Coupling

Figure 2(a), 2(b) and 2(c) show the effect of poling field on plate mode coupling coefficient k_t, dielectric constant K_3^T and dielectric loss tan δ of [001] poled PMN-0.29PT and PMN-0.31PT crystals, respectively.

For PMN-0.29PT, k_t, K_3^T and tan δ gradually reach a plateau at around 350 V/mm where complete poling is reached. Below 350 V/mm, the crystal is under-poled. At 1350 V/mm, k_t starts to show slight degradation while tan δ and K_3^T remain at the same level as of fully poled. Degradation in k_t indicates the onset of over-poling.

For PMN-0.31PT, k_t, K_3^T and tan δ gradually reach a plateau at around 250 V/mm where complete poling is reached. Below 250 V/mm, the crystal is under-poled. Unlike PMN-0.29PT, both k_t and K_3^T show continuous degradation beyond poling field of 1350 V/mm, while tan δ shows slight increase at poling field of 1500 V/mm.

From the above observation, it is concluded that PMN-0.31PT crystal has lower coercive field than PMN-0.29PT due to its closer vicinity to the Morphotropic Phase Boundary (MPB) [7,8]. Such phenomenon happens on the same ingot because of segregation of titanium during crystal growth [2]. As a result, [001] poled PMN-0.31PT has higher k_t, higher K_3^T and lower tan δ than those of PMN-0.29PT.

Both PMN-0.29PT and PMN-0.31PT are reasonably resistant to DC over-poling up till 1250 V/mm. As device designer, however, it is recommended to set a safety DC application and poling voltage limit of 1000 V/mm as a safety precaution against over-poling for all grades of [001] poled PMN-PT under room temperature.

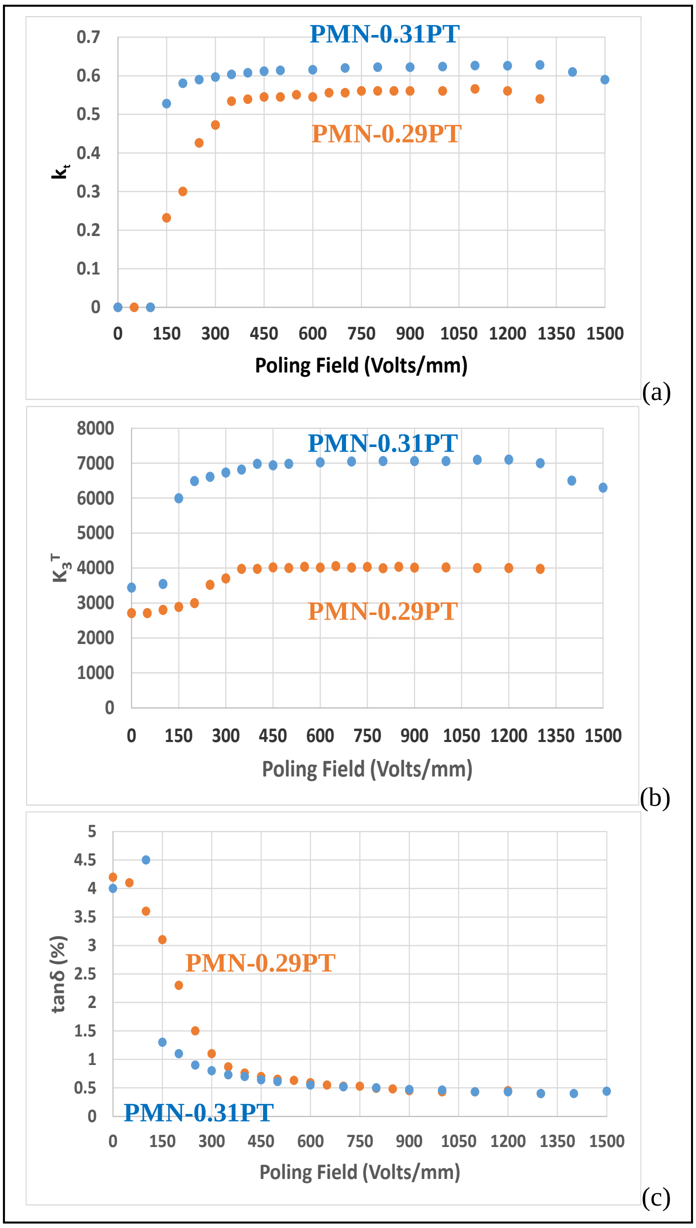

Figure 2: Poling Effects on (a) Plate-mode Electromechanical Coupling Coefficient k_t, (b) Dielectric Constant K_3^T, and (c) Dielectric Loss tan δ of PMN-0.29PT and PMN-0.31PT Crystals

B. *Mechanism of Over-poling*

Fig. 3(a) shows the dielectric constant K_3^T vs. temperature profile of a PMN-0.29PT plate sample optimized poled at 400 V/mm. The first peak appears at around 115 ˚C, indicating rhombohedral to tetragonal phase transition temperature (T_{R-T}); the second peak appears at around 150 ˚C, indicating tetragonal to cubic phase transition temperature, or Curie temperature (T_c). Fig. 3(b) shows K_3^T vs. temperature profile of the same sample over-poled by a DC field of 1500 V/mm. It is observed that K_3^T increases from room temperature to 125 ˚C, then plateaus out without apparent T_{R-T} or T_c. Fig. 3 (c) shows K_3^T vs. temperature profile of the same sample over-poled by a DC field of 1500 V/mm, annealed at 170 ˚C for 1 hr and then re-poled at 400 V/mm. It is observed a steady increase of K_3^T from room temperature to 100 ˚C followed a sharp increase of K_3^T from 100 ˚C to 120 ˚C without apparent T_{R-T}; however, T_c is apparent at 150 ˚C. Fig. 3(d) shows K_3^T vs. temperature profile of the same sample over-poled by a DC field of 1500 V/mm, annealed at 300 ˚C for 1 hr, then re-poled at 400 V/mm. It is observed that, similar to Fig. 3 (a), T_{R-T} is restored at 115 ˚C and T_c is restored at 150 ˚C.

Based on the above observations, it is thought that the mechanism of over-poling is field-induced phase transition. Such transition may be rhombohedral to orthorhombic, or rhombohedral to cubic transition, owing to the absence of T_{R-T} after over-poling. However, over-poling could be reversed by annealing at elevated temperature for some time; and in the case of PMN-0.29PT crystal, at 300 ˚C for 1 hr. Whether such reversal could be applied as an over-poling remedy in transducer design requires further confirmation which includes phase determination by XRD profile or polarized light microscopy and comprehensive property comparison before and after the overpoling-annealing cycle.

IV. CONCLUSION

3 inch PMN-PT crystal ingot was grown using Vertical Gradient Freeze (VGF) method. Over-poling behavior of [001] poled PMN-0.29PT and PMN-0.31PT samples were studied. It is shown that PMN-0.29PT is fully poled around 350 V/mm and PMN-0.31PT is fully poled around 250 V/mm. Both PMN-0.29PT and PMN-0.31PT are resistant to DC overpoling up to 1250 V/mm at room temperature; beyond 1300 V/mm, both show degradation in coupling, dielectric constant and dielectric loss, with PMN-0.31PT being more susceptible to over-poling due to closer vicinity to MBP.

The mechanism of over-poling is thought to be field induced phase transition from rhombohedral to orthorhombic, or rhombohedral to cubic, owing to the absence of T_{R-T}. Such transition could be reversed by annealing at elevated temperature; and in the case for PMN-0.29PT, at 300 ˚C for 1 hr. This discovery could be a potential remedy to recover key properties of over-poled PMN-PT crystal, although further study is required to confirm complete restoration in microscopic structure and macroscopic properties. As a precaution, it is advised to set a DC poling and driving field limit of 1000 V/mm to avoid over-poling at all times.

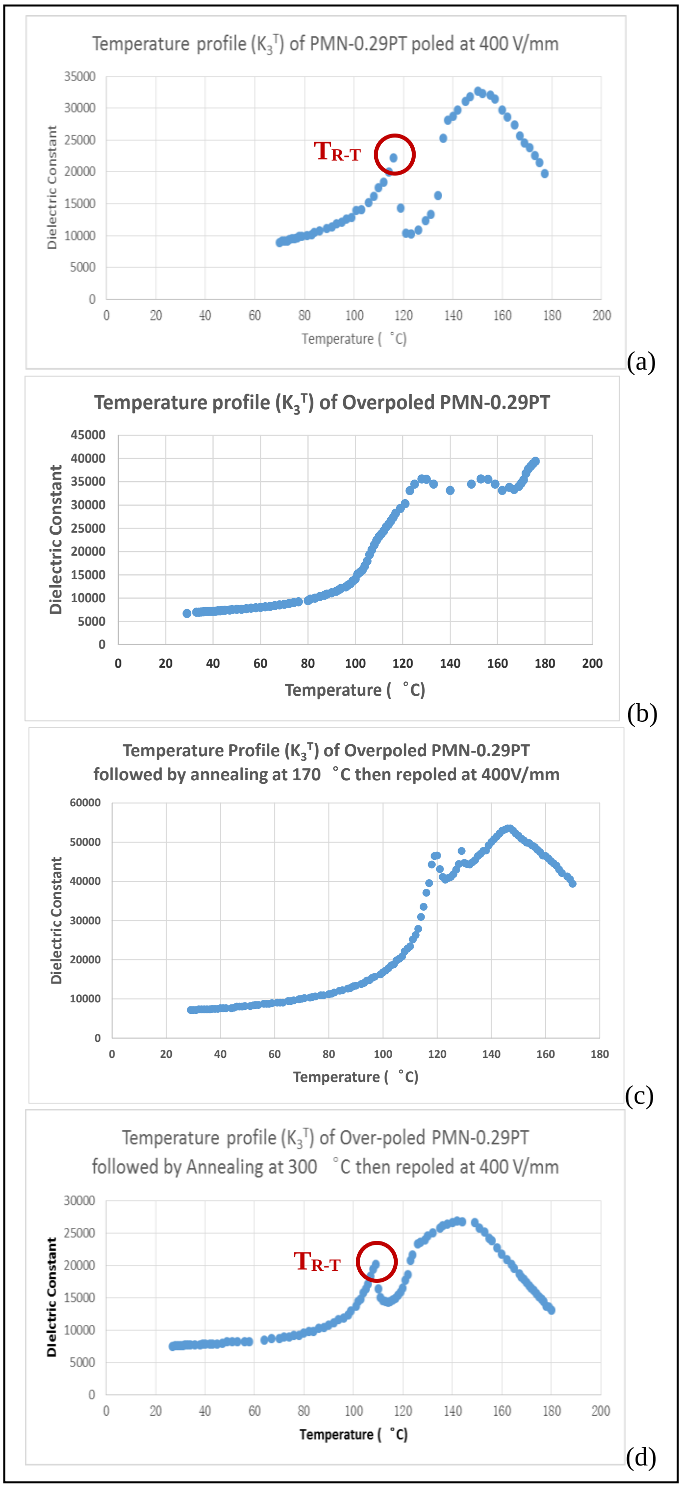

Figure 3: Dielectric Constant vs. Temperature profile of a PMN-0.29PT plate sample (a) poled at 400 V/mm; (b) over-poled at 1500 V/mm; (c) over-poled at 1500 V/mm, annealed at 170 ˚C for 1 hr, then re-poled at 400 V/mm; (d) over-poled at 1500 V/mm, annealed at 300 ˚C for 1 hr, then re-poled at 400 V/mm.

V. FUTURE WORK

Future work includes studying poling behavior of PMN-PT crystal at elevated temperatures and under alternative current (AC) to serve as guide to transducer design and the actual application. Over-poling research of the ternary PIN-PMN-PT crystal will also be carried out.

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