Crystal growth and property characterization for PIN-PMN-PT ternary piezoelectric crystals

Jian Tian* and Pengdi Han
H.C. Materials Corporation

479 Quadrangle Dr., Suite-E, Bolingbrook, IL 60440, USA

*jtian@hcmat.com

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Binary piezoelectric crystal $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) has excellent dielectric and piezoelectric properties, which has led to the commercialization for medical ultrasound imaging. Recently, there is a growing demand for piezoelectric crystals with improved thermal and electrical properties. Ternary piezoelectric crystals $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) have increased depoling temperature and coercive field than binary PMN-PT. To better understand the ternary crystal system and improve crystal properties, we systematically investigated crystal growth of PIN-PMN-PT with modified Bridgman method. Like PMN-PT, PIN-PMN-PT crystals have excellent piezoelectric properties (e.g., $k_{33} \sim 0.87\text{--}0.92$, $d_{33} \sim 1000\text{--}2200$ pm/V). Higher PIN content leads to $\sim 40^\circ\text{C}$ increase in depoling temperature and more than doubling of coercive field (~ 7.0 kV/cm). Such improvements are advantageous for applications where high temperature and/or high-drive are needed.

Keywords: PIN-PMN-PT; ternary crystals; coercive field; thermal stability.

1. Introduction

The excellent dielectric and piezoelectric properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) single crystal have led to a successful commercialization in advanced medical ultrasound.¹ Over the past decade, significant progresses have been achieved on crystal growth and characterization,^{2–6} and new applications^{7–15} for binary PMN-PT crystals.

Despite the excellent properties of PMN-PT single crystals, the relatively low depoling temperature ($T_{\text{R/T}} \sim 75\text{--}97^\circ\text{C}$), low coercive field ($E_{\text{C}} \sim 2.5$ kV/cm) and low mechanical quality factor ($Q_{\text{M}} \sim 80$) remain concerns for many applications especially those require high drive conditions. A low $T_{\text{R/T}}$ limits application temperature and generally leads to a large temperature-dependent variations in crystal property and thus transducer performance. In addition, E_{C} decreases as temperature increases when transducer operates. Low Q_{M} leads to more heat generation and higher temperature rise during transducer operation. Thus, higher coercive field and improved mechanical quality factor of piezocrystals are especially important for high drive applications. Recently, piezocrystals with improved thermal and electrical properties have become active in research.^{16–21} PMN-PT based ternary $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) crystals are attractive because (1) PIN-PMN-PT crystals have improved thermal and electrical properties; and (2) high quality and large-size PIN-PMN-PT crystals can be grown with various compositions/properties.^{21–28}

In this paper, we report crystal growth and property characterization for ternary PIN-PMN-PT crystals. Crystals

of various starting compositions were grown. Dielectric, piezoelectric, and elastic properties were measured on specimens selected along crystal growth direction. The goals are to investigate crystal growth behavior, characterize property variation, and improve understanding of the composition-property relationship for the ternary PIN-PMN-PT crystals.

2. Experimental

Like PMN-PT, ternary PIN-PMN-PT crystals were grown with a modified Bridgman method. Starting compositions for crystal growth were chosen in the rhombohedral phase region close to the morphotropic phase boundary (MPB, Fig. 1) for enhanced piezoelectric properties.^{21–28} Various PIN contents from 12% to 60% for PIN-PMN-PT ternary compositions, as well as the binary composition of PIN-0.31PT, were prepared for crystal growth experiments. Detailed chemicals, precursor preparation and crystal growth information were reported earlier.²³

{001} crystal plates and bars were prepared to characterize crystal properties in [001] direction.^{6,23} Residual stresses from crystal growth and mechanical finishing were relieved by annealing at $\sim 600^\circ\text{C}$. Chromium/gold electrodes were sputter coated on appropriate faces of specimens. Samples were poled at up to 10 kV/cm in air at room temperature.

Properties were measured at room temperature of 24 h after poling. Measurement procedures for crystal properties, including the free and clamped dielectric constants (K_{33}^T and K_{33}^S), electromechanical coupling factors (k_{33} and k_t), elastic

Fig. 1. Starting compositions (1–10) for crystal growth. Arrow indicates the trend of compositional change along crystal growth direction. Line AB is a linear approximation to the MPB composition for ternary PIN–PMN–PT.

compliance (s_{33}^E), ferroelectric hysteresis, field-induced strain, E_C and large-signal piezoelectric strain coefficient (d_{33}), were reported earlier.^{6,23} Measurement of Q_M followed IEEE standard.²⁹ The $T_{R/T}$ and Curie temperature T_C were measured on a custom thermal testing system with 0.1 °C accuracy. The chemical composition of crystal samples were analyzed with an inductively coupled plasma (ICP) method.

3. Results and Discussions

Crystal growth experiments demonstrated that PIN–PMN–PT crystals of various starting compositions can grow directly from stoichiometric melts with modified Bridgman method. High quality and large size (up to 4" diameter) PIN–PMN–PT single crystals of perovskite phase have been successfully grown for PIN content of 12 to 33 mol%. Thus, ternary crystals offer a broad selection of properties for transducer applications that cannot be realized for PMN–PT. For compositions with higher PIN content (>33 mol%), growth flux was needed to obtain perovskite phase single crystals. However, it is more challenging to obtain high quality crystal with flux method because flux can be trapped in the as-grown crystal to form inclusions. In addition, flux dilutes the ions for crystal growth, thus flux method generally has a much slower growth rate than the stoichiometric melt growth. Like PMN–PT, PIN–PMN–PT crystals can grow directly from stoichiometric melt. This is critical for the commercialization of PIN–PMN–PT single crystals.

To determine the growth behavior of ternary PIN–PMN–PT single crystals, samples were selected along crystal growth direction for ICP analyses. Chemical composition of crystal samples were then calculated from the ICP data. Figure 2 showed variation in the end-member components for 0.24PIN–PMN–PT and 0.33PIN–PMN–PT crystals. Both

Fig. 2. (Color online) Changes in composition along growth direction for ternary crystals of PIN24–PMN–PT (blue color) and PIN33–PMN–PT (black color). Specimens are 1 mm apart with No. 1 from crystal base.

crystals show similar trend, with increasing PT and decreasing PMN along crystal growth direction. The increase in PT can be largely accounted by the decrease in PMN. In contrast, PIN content only had a slightly decreasing trend for both crystals, suggesting that PIN is least sensitive to chemical segregation during crystal growth. In addition, changes in PIN content do not seem to affect much of the segregation behavior in PMN and PT. This is important for the composition/property optimization of ternary PIN–PMN–PT single crystals.

As PIN content increases, the $T_{R/T}$ of PIN–PMN–PT crystals generally increase. Figure 3 illustrates the relationship between the maximum $T_{R/T}$ value and PIN content of different crystals. The $T_{R/T}$ –PIN% relationship fits well to exponential growth ($R^2 > 0.99$). $T_{R/T}$ increased noticeably for PIN–PMN–PT crystals of high PIN content. The

Fig. 3. Relationship between maximum $T_{R/T}$ in a crystal boule and PIN content in starting composition. Dotted line is an exponential fit.

Fig. 4. Relationship of average E_C in a crystal boule and PIN content in starting composition. Error bars show standard deviation of E_C . Dotted line is a linear fit to E_C -PIN%.

maximum $T_{R/T}$ of 0.33PIN-PMN-PT is 137°C, which is 20°C over 0.24PIN-PMN-PT and 40°C over PMN-PT. For both PMN-PT and PIN-PMN-PT single crystals, $T_{R/T}$ is the upper temperature limit for piezoelectric application. Crystal will depole at temperatures above $T_{R/T}$ and properties degrade rapidly. Higher $T_{R/T}$ improves allows crystal application at a higher temperature without risking of thermal depoling. Thus, reliability of crystal transducers is enhanced with increased $T_{R/T}$. Furthermore, increased $T_{R/T}$ also improves transducer performance since temperature induced variation in crystal property is significantly reduced.

Similar to the $T_{R/T}$, E_C values of PIN-PMN-PT crystals increase with PIN content. Average value of E_C was plot (Fig. 4) since E_C is relatively stable within a crystal. E_C exhibits a good linear relationship with PIN mol% ($R^2 > 0.99$). Higher E_C allows a greater driving electric field in high power transducer application. In addition, enhanced E_C eliminates/reduces the need for a bias voltage that is commonly required for binary PMN-PT crystal in high drive application, which improves the robustness of crystal transducers. E_C is relatively stable within a crystal boule for PIN-PMN-PT crystals of different PIN contents (e.g., 12, 24, 28 and 33 mol%). The moderately steady PIN content along crystal growth direction (Fig. 2) likely led to the stable coercivity for both 0.24PIN-PMN-PT and 0.33PIN-PMN-PT crystals. This is likely true for PIN-PMN-PT crystals of other PIN contents. In contrast, variations in PMN and PT contents had little effect on coercivity of ternary PIN-PMN-PT crystals, consistent with the binary PMN-PT single crystal.

Other key piezoelectric properties of ternary PIN-PMN-PT crystals, such as electromechanical coupling factors k_{33} and k_t , and piezoelectric strain coefficient d_{33} , remain excellent. On the other hand, PIN-PMN-PT crystals generally have lower dielectric values than PMN-PT, with decreasing dielectric values with increasing PIN content. Improvements

Fig. 5. Ferroelectric hysteresis and piezoelectric strain response for Mn modified PIN-PMN-PT single.

in $T_{R/T}$ and E_C of PIN-PMN-PT crystals further expands operating conditions and enhanced reliability for crystal transducers.

The coercive field of Mn modified PIN-PMN-PT crystal increased (Fig. 5). The E_C value based on the first hysteresis measurement is ~ 11 kV/cm. The E_C value after 10 hysteresis measurements is ~ 8 kV/cm. Both values are higher than those of unmodified PIN-PMN-PT crystal. In addition, Mn modified ternary PIN-PMN-PT crystals show improvement in Q_M , with values up to 700. However, other important properties including coupling factors, piezoelectric coefficient and dielectric constant were noticeably degraded.

ICP analyses revealed significant compositional segregation of Mn for Mn modified PIN-PMN-PT crystals. As shown in Fig. 6, the segregation of Mn is more than twice of the PT, which presents a challenge for crystal growth. New crystal growth technique with continuous material feeding

Fig. 6. Composition segregation along crystal growth direction for Mn modified PIN-PMN-PT single. Samples 1–7 were selected from a crystal boule along growth direction, with sample 1 from base and 7 near top.

during crystal growth is needed to improve the control of compositional segregation for Mn modified PIN–PMN–PT crystals.

4. Conclusion

Ternary PIN–PMN–PT crystals with PIN content up to 33 mol% can be grown directly from stoichiometric melt with modified Bridgman method. PIN–PMN–PT crystals have improved depoling temperature and coercive field, with $T_{R/T}$ up to 137°C and E_C up to 7.0 kV/cm for PIN33–PMN–PT. Other key piezoelectric properties including coupling factors k_{33} , k_t and piezoelectric coefficient d_{33} remain excellent. These improvements are important especially for high-drive transducers.

Mn-modified PIN–PMN–PT crystals show improved coercive field and mechanical quality factor at the expense of degraded electromechanical coupling, piezoelectric and dielectric properties. In addition, Mn has significant segregation during crystal growth.

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