

Cryogenic Behavior of Perovskite Materials

D. S. PAIK*, H. Y. SHIN**, S. J. YOON*, H. J. KIM*, and C. Y. PARK***

Abstract

Dielectric and piezoelectric properties of perovskite materials such as La modified $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 single crystals were investigated for cryogenic capacitor and actuator applications. Enhanced extrinsic contributions resulted in piezoelectric coefficient (d_{33}) as high as 250 pC/N at 30 K, superior to that of PZT ($d_{33} \sim 100$ pC/N). This cryogenic property enhancement was associated with retuning the MPB for cryogenic temperatures. PZN-PT single crystals exhibited dramatic property improvements such as $d_{33} > 500$ pC/N at 30 K as a result of an engineered domain state.

Key Words : Cryogenic temperatures; PLZT Ceramics and PZN-PT Single crystals; MPB tuning; Piezoelectric property; NGST

1. Introduction

Piezoelectric materials with perovskite structure such as BaTiO_3 and $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) have been widely used for capacitor and actuator applications near room temperature. Recently, special devices operated at cryogenic temperatures are demanded in applications such as actuators for adaptive optics (e.g. next generation space telescope, NGST). The room temperature properties of PZT ceramics are optimized by using compositions that correspond to the morphotropic phase boundary (MPB). Both undoped and commercially available hard and soft compositions exhibit poor piezoelectric performance at temperatures below 100 K. For example soft PZT (Navy Type VI) has a $k_{31} \sim 25\%$ and $d_{31} < 50$ pC/N at 30 K compared to $\sim 35\%$ and ~ 250 pC/N, respectively, at room temperature¹⁾. The decrease in properties is attributed to a freezing out of extrinsic contributions (i.e. ferroelectric domain wall motion) to piezoelectricity²⁾. A second possibility is

loss of domain orientation variants due to a shift in the MPB with decreasing temperature. In this paper retuning the composition of soft PZT (through Zr/Ti variation) will be investigated to determine the shift in MPB with decreasing temperature.

Recent developments have shown that relaxor based ferroelectric single crystals such as $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 exhibit extremely high piezoelectric properties such as $k_{33} \sim 94\%$ and $d_{33} > 2500$ pC/N at room temperature. The effect results from an engineered domain state not achievable with conventional PZT ceramics^{3,4)}. The engineered domain state (rhombohedral phase) shows high stability and very high piezoelectric activity at room temperature. From the room temperature properties of PZN-PT crystals, substantial piezoelectricity can be expected to remain at cryogenic temperatures even with large decreases in properties.

It is the objective of this article to explore various materials such as PZT ceramics and PZN-PT single crystals for cryogenic devices. The piezoelectric properties of two representative rhombohedral compositions, PZN-4.5%PT and 8%PT single crystals, were investigated at cryogenic temperatures. The cryogenic

* :KIST, Thin Film Technology Research Center

** :Namseoul Univ., Dept. of Electronics Eng.

***:Yonsei Univ., Dept. of Electrical Eng.

piezoelectric properties of soft PLZT ceramics will be discussed with respect to temperature dependence of the MPB.

2. Experimental Procedures

All ceramic compositions were based on TRS600, a commercially available PLZT⁵⁾ with $T_c \sim 190^\circ\text{C}$. The base composition was modified with different Zr/Ti ratios to locate the MPB at 30 K, the working temperature of the NGST. To prepare the various materials, stoichiometric amounts of constituent powders were first dispersed into a water slurry and mixed by vibratory milling. The powders were then pan dried followed by a high temperature calcination at 950°C to form the desired phase. Sample disks 13 mm in diameter and 1 mm in thickness were pressed at 5000 psi. The samples were then sintered at 1300°C . The PLZT samples were poled by applying 30 kV/cm at 50°C for 5 min. All the properties were measured 24 h after poling. PZN-PT single crystals were grown using the high temperature flux technique. Experimental details are reported elsewhere.⁶⁾ Room temperature dielectric and piezoelectric coefficients (d_{33}) were measured using a Stanford Research LCR meter and a Berlincourt d_{33} meter, respectively. Dielectric, piezoelectric and elastic properties as a function of temperature down to 30 K were measured from lateral (k_{31} , d_{31}) mode resonance using IEEE standard methods.⁷⁾ The sample was placed in an expander module with vacuum

sealed electrical connections. A helium cryostat was used to cool the expander module and sample to 30 K. d_{33} 's at low temperature were estimated using the relationship $d_{33} \sim 2 \text{ to } 2.3 \times |d_{31}|$.

3. Results and Discussion

3.1 PLZT Ceramics

The Curie temperature (T_c) of the PLZT ceramics synthesized in this study ranged from 175°C to 200°C , lower than most commercial PZT's with $T_c > 200^\circ\text{C}$. Dopants that shift the Curie point closer to room temperature are often used in PZT ceramics for high strain actuator applications. Lower Curie point materials tend to have a severe temperature dependence of piezoelectric properties and are susceptible to depoling. However, if the material is used at cryogenic temperatures the Curie point can be shifted well below 200°C with no detrimental effects. Lower T_c indicates softer piezoelectrics, resulting in increased extrinsic contributions to piezoelectricity.⁸⁾ Fig. 1 and 2 present dielectric constant and d_{33} as a function of Zr content, respectively. At room temperature the MPB was located at 57 mol% as evidenced by the peak at this composition. As shown in Fig. 1 and 2, there is an apparent shift of 2 mol% in the MPB location on cooling to 30 K. The estimated d_{33} value of 250 pC/N at 30 K approaches the room temperature value for commercial hard PZT's (Navy Type I & III). Fig. 3 and 4 show the

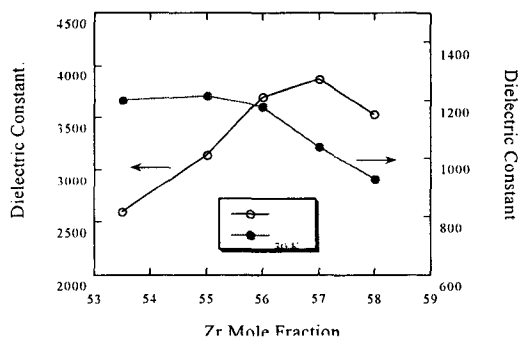


Fig. 1. Dielectric constant vs. Zr content for PLZT ceramics.

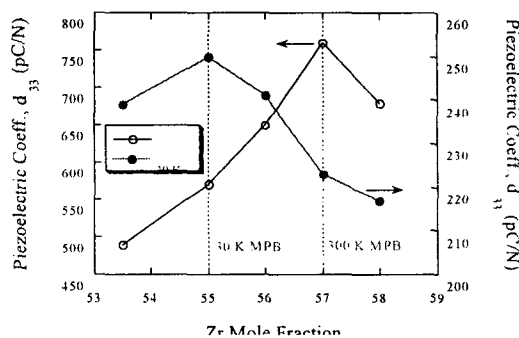


Fig. 2. d_{33} vs. Zr content for PLZT ceramics

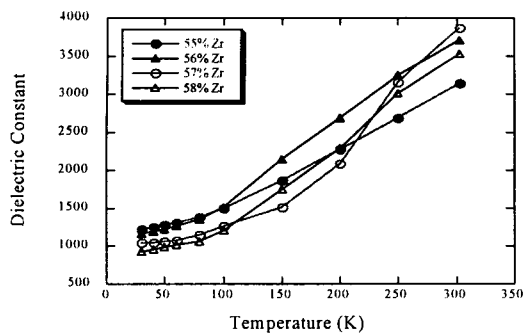


Fig. 3. Temperature dependence of dielectric constant for PLZT ceramics

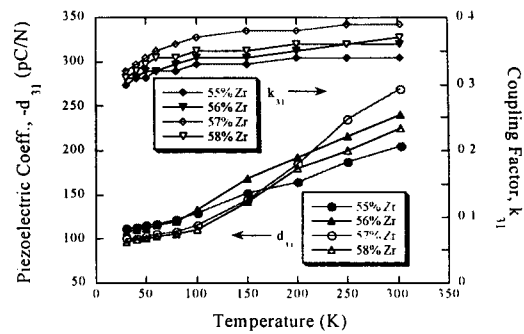


Fig. 4. Temperature dependence of piezoelectric properties for PLZT ceramics

temperature dependence of dielectric constant, electromechanical coupling factor and transverse piezoelectric coefficient for several PLZT compositions from 300 to 30 K.

As shown in Fig. 3, ceramics close to the cryogenic MPB composition (Zr 55 mol%) had a less severe change in dielectric constant with temperature than did the samples close to the room temperature MPB. Materials compositionally engineered to lie on the MPB at room temperature have both rhombohedral and tetragonal phases coexisting, resulting in maximum polarization. Upon cooling the temperature to 30 K, a phase transition occurs from the mixed phase to rhombohedral phase with a subsequent shift of the MPB into the Ti-rich side of the phase diagram.

3.2 PZN-PT Single Crystals

Fig. 5 and 6 depict dielectric and piezoelectric properties of rhombohedral PZN-PT single crystals measured as a function of temperature from 300 K to 30 K. Large coupling coefficients ($k_{33} > 94\%$) and large piezoelectric coefficients ($d_{33} \sim 2500$ pC/N) were found at room temperature. PZN-4.5%PT and 8%PT crystals were also found to possess high d_{31} values of ~ 800 and ~ 1200 pC/N, respectively, at room temperature. Since the MPB of PZN-PT crystals is more dependent upon temperature, rhombohedral PZN-PT crystals are further away from the MPB at low temperature than is the case for PZT ceramics. Rhombohedral single crystals, therefore, exhibit no phase transition under cooling from room temperature because the

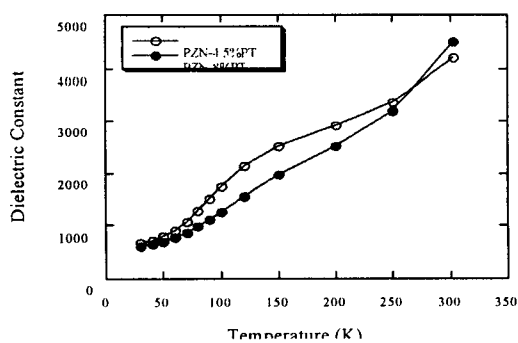


Fig. 5. Temperature dependence of dielectric constant for PZN-PT single crystals

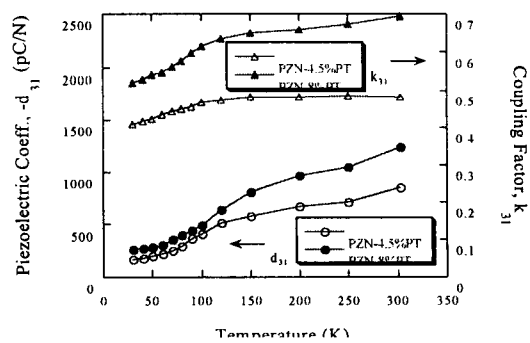


Fig. 6. Temperature dependence of piezoelectric properties for PZN-PT single crystals

low temperature form of crystal is rhombohedral structure. For cryogenic temperatures large decreases in properties were observed for both of compositions compared to the room temperature properties. Despite the decreases substantial piezoelectricity remains at cryogenic temperatures. The estimated d_{33} 's of ~ 700 and 500 pC/N for PZN- 8%PT and 4.5%PT crystals, respectively, are substantially larger than those of most room temperature PZT's. Although domain wall motion of single crystals was frozen out by cooling, there is still significant piezoelectricity because domain wall motion is not believed to contribute to the piezoelectric effect in the same manner as in PLZT ceramics.⁹⁾ High piezoelectric properties of PZN-PT single crystals at cryogenic temperatures are very important to investigate the origin of ultrahigh piezoelectricity of engineered rhombohedral PZN-PT single crystals.

4. Summary

Compositionally, PZT's were engineered to increase extrinsic contributions to piezoelectricity at cryogenic temperatures by T_c below 200°C and returning Zr/Ti ratios to locate the cryogenic MPB. The cryogenic MPB composition (55 mol% Zr) exhibited high piezoelectric properties such as

$d_{33} \sim 250$ pC/N corresponding to hard PZT's at room temperature. Dramatic performance was observed in the PZN-PT single crystals that had domain engineered rhombohedral structure.

References

1. X. L. Zhang, Z. X. Chen, L. E. Cross and W. A. Schulze, *J. Mater. Sci.*, 18, 968 (1983).
2. R. Gerson, *J. Appl. Phys.*, 33 (3), 830 (1962).
3. S.-E. Park and T. R. Shrout, *J. Appl. Phys.*, 82 (4), 1804 (1977).
4. S.-E. Park and T. R. Shrout, *IEEE Trans. Ultras. Ferroelectric and Freq. Cont.*, 44 (5) 1140 (1997).
5. G. H. Haertling and C. E. Land, *J. Am. Ceram. Soc.*, 54 (1), 1 (1971).
6. M. L. Mulvihill, S.-E. Park, G. Risch, Z. Li, K. Uchino and T. R. Shrout, *Jpn. J. Appl. Phys. I*, 35, 51 (1996).
7. IEEE Standard on Piezoelectricity (American National Standards Institute, Washington, DC, 1976).
8. G. H. Haertling, *Ferroelectrics*, 75, 25 (1987).
9. S. Wada, S.-E. Park, L. E. Cross, T. R. Shrout, *Proceedings of 8th US-Japan Seminar*, 11 (1997).