

Figures of Merit of (K,Na,Li)(Nb,Ta)O₃ Ceramics with Various Li Contents for a Piezoelectric Energy Harvester

Su Hwan Go*, Dae Su Kim***, Seung Ho Han**, Hyung-Won Kang**,
Hyeung-Gyu Lee**, and Chae Il Cheon*†

*Department of Materials Science and Engineering, Hoseo University, Asan 31499, Korea

**Electronic Materials and Device Research Center, Korea Electronics Technology Institute, Seongnam 13509, Korea

(Received September 20, 2017; Revised October 25, 2017; Accepted October 25, 2017)

ABSTRACT

The figures of merit in the on-resonance and off-resonance conditions (FOM_{on} and FOM_{off}) for the piezoelectric energy harvester (PEH) were measured and compared in $[(K_{0.485}Na_{0.515})_{1-x}Li_x](Nb_{0.99}Ta_{0.01})O_3$ ($x = 0.04 \sim 0.09$) (KNLNT) ceramics with various Li contents. The crystal structure of CuO-doped KNLNT ceramics changes from orthorhombic to tetragonal around the Li fraction of 0.065. The stable temperature range for the tetragonal phase widens to both higher and lower temperatures as Li is substituted. The piezoelectric charge constant (d_{33}), electromechanical coupling factor (k_p) and mechanical quality factor (Q_m) have maximum values at the Li fraction between 0.055 and 0.065 where the phase boundary lies between the orthorhombic and tetragonal phases. Both FOM_{on} and FOM_{off} have peak values around the phase boundary but the peak compositions are not exactly coincided. The optimal Li fraction in the KNLNT ceramic for a PEH application was found to be between 0.055 and 0.065.

Key words : Piezoelectric properties, Sintering, Energy harvester, Figure of merit, (K,Na)NbO₃

1. Introduction

Piezoelectric energy harvesters (PEH) that generate electrical energy from environmental vibrations have been developed for applications such as wireless self-powered sensor nodes.¹⁻⁵⁾ The performance of the PEH is dependent on the energy conversion efficiency of the piezoelectric material.⁴⁻⁶⁾ The energy density produced by the PEH is expressed by the following equation, $U = (1/2)(d_{ij}g_{ij})(F/A)^2$, where d_{ij} is the piezoelectric strain constant, g_{ij} is the piezoelectric voltage constant, F is the applied force and A is the area. The product of d_{ij} and g_{ij} is known as the figure of merit of a piezoelectric material in the off-resonance condition (FOM_{off}) for PEH.⁴⁻⁶⁾ On the other hand, the energy conversion efficiency has been reported to be proportional to $k_{ij}^2Q_m$ in the resonance condition, where k_{ij} is an electro-mechanical coupling factor and Q_m is a mechanical quality factor.⁶⁻⁸⁾ Therefore, the figure of merit of a piezoelectric material in the on-resonance condition (FOM_{on}) can be expressed as $k_{ij}^2Q_m$. The PEH is designed to operate near the resonant frequency of the piezoelectric vibrator because the maximum electric power is generated at the resonant frequency. Both FOM_{on} and FOM_{off} should be considered simultaneously for obtaining a maximum electric power because natural vibrations occur a wide range of frequencies in real circumstances, rather than a fixed value.

Lead-free piezoelectric ceramics have been developed in recent years due to global environmental issues.^{1-3,9-11)} A (K,Na)NbO₃ (KNN)-based ceramic has been reported to show the highest piezoelectric properties among various lead-free piezoelectric candidates.^{2-3,9-11)} Li substitution on a K or Na site changes piezoelectric properties, and show the highest values around the phase boundary between the ferroelectric orthorhombic and the ferroelectric tetragonal phase (morphotropic phase boundary, MPB).^{2-3,9-18)} The phase boundary is often called a polymorphic phase transition (PPT) because the crystal structure also changes with the temperature.^{2,3)} The CuO-doped KNN ceramics have been reported to have a high Q_m and be a good candidate for the PEH.^{6,19-21)}

In this work, the Li content was controlled in a $[(K_{0.485}Na_{0.515})_{1-x}Li_x](Nb_{0.99}Ta_{0.01})O_3$ ($x = 0.04 \sim 0.09$) (KNLNT) ceramic and piezoelectric properties were investigated. Excess alkali oxide of 1 mole % Na₂CO₃ and 0.5 mole % CuO were added to KNLNT ceramics for decreasing the sintering temperature to below 950°C and for improving the mechanical quality factor, respectively. The figures of merit in on-resonance condition and in off-resonance condition (FOM_{on} and FOM_{off}) for the PEH were calculated and compared in KNLNT ceramics with various Li contents for fabricating a PEH with a high performance.

2. Experimental Procedures

For the synthesis of KNLNT ceramics, K₂CO₃ (Aldrich, 99%), Na₂CO₃ (Aldrich, 99.5%), Li₂CO₃ (Aldrich, 99%), Nb₂O₅

†Corresponding author : Chae Il Cheon

E-mail : cicheon@hoseo.edu

Tel : +82-41-540-5733 Fax : +82-41-548-3502

(Kojundo Chemical Lab., 99.9%), and Ta₂O₅ (Kojundo Chemical Lab., 99.9%) powders were weighed and mixed by ball-milling for 24 h in plastic bottles with anhydrous ethanol and yttria-stabilized zirconia (YSZ) balls. The milled powder was calcined at 800°C for 4 h after drying. 1 mol% Na₂CO₃ and 0.5 mole % CuO (Aldrich, 99%) were added to the calcined powder. They were pulverized by attrition milling at 350 rpm for 3 h and ball-milled again for 24 h with 0.5 wt% polyvinyl butyral (PVB). After drying and granulating the milled powder, disk-type compacts were formed by uniaxial pressing at 150 MPa. The compacts were heat-treated at 600°C for 2 h for binder burn-out and sintered at 920°C for 3 h.

The phase evolution and crystal structure for the calcined powders and sintered samples were examined by X-ray diffraction analysis (XRD-6100, Shimadzu). The densities of the sintered samples were measured using Archimedes' principle. Silver electrodes were printed on the sintered samples and fired at 800°C for 10 minutes for electrical measurements. In order to align dipoles in polycrystalline samples to one direction, a DC electric field about 5 kV/mm was applied for 30 minutes at 100°C in a silicon oil bath. The capacitances and dielectric losses were measured using an impedance analyzer (HP 4294A) and the relative dielectric constants were calculated from the capacitances and sample dimensions. The piezoelectric constant d_{33} was measured using a Berlincourt-type d_{33} meter (YE2730A, APC International Ltd.). Impedances and phases were measured as a function of a frequency with an impedance analyzer. An electromechanical coupling factor (k_p) and a mechanical quality factor (Q_m) for a radial vibration mode were calculated according to the following equations;

$$\frac{1}{k_p^2} 0.395 \frac{f_r}{f_a - f_r} + 0.574, Q_m = \frac{f_a^2}{2\pi f_r Z_r C (f_a^2 - f_r^2)},$$

where f_r , f_a , Z_r , and C are a resonant frequency, an anti-resonant frequency, an impedance at f_r , and a capacitance at 1 kHz, respectively.

3. Results and Discussion

The KNLNT ceramics with Li fractions between 0.04 and 0.09 had high densities of around 95% of the theoretical value after sintering. All samples had similar microstructures with large abnormal grains in small-grained matrix. The X-ray diffraction patterns of the KNLNT ceramics with various Li contents are displayed in Fig. 1. The crystal structure changes from orthorhombic to tetragonal as the Li content increases, and two phases seem to co-exist at Li fraction around 0.065. This agrees with the previous reports in which the phase boundaries have been observed between Li fractions of 0.04 ~ 0.08 in the Li-modified KNN ceramics.^{2, 12-18)}

Figure 2 shows the dielectric constant and loss at room temperature as a function of the Li content. The dielectric constant stays constant between Li fraction between 0.04 to

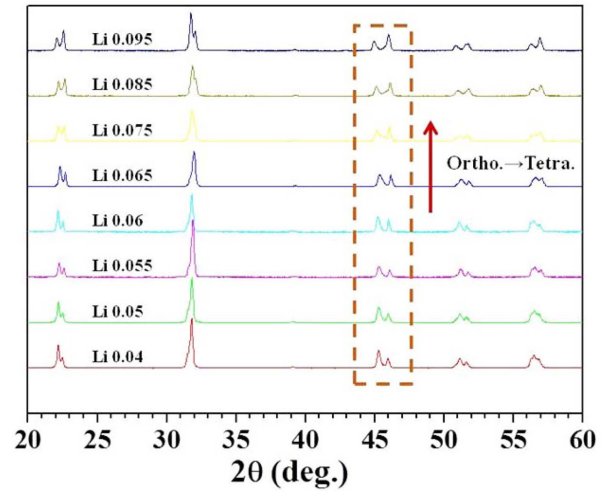


Fig. 1. X-ray diffraction patterns of the KNLNT ceramics with various Li fractions.

0.065, but increases monotonically with the further increase of the Li fraction to 0.09. The dependence of the dielectric constant on the Li content in this CuO-doped KNLNT ceramic is different from the dependence of the dielectric constant in other Li-modified KNN-based ceramics, in which the dielectric constant peaks around the MPB.^{12-14,16)} The dielectric constants in these CuO-doped KNLNT ceramics are also quite low compared with other Li-modified KNN-based ceramics. The CuO doping seems to lead to a different trend in the dependence of the dielectric constant with the Li content. The dielectric loss measured at 1 kHz is lower than 0.015 in the KNLNT ceramics with Li fraction of 0.055 - 0.85, but increases when the Li content of the sample decreases below 0.055 as shown in Fig. 2. The high dielectric loss at 1 kHz decreases to about 0.015 or less when the measured frequency increases to 100 kHz in KNLNT ceramics with Li content of 0.4 - 0.5. It indicates that the high loss in Fig. 2 results from mobile ionic defects. In Li-modified KNN ceramics, some of alkali metals, Na, K, and Li, have been reported to evaporate at the sintering temperature.²²⁾ It is thought that the high dielectric loss at low frequency range in KNLNT ceramics with Li content of

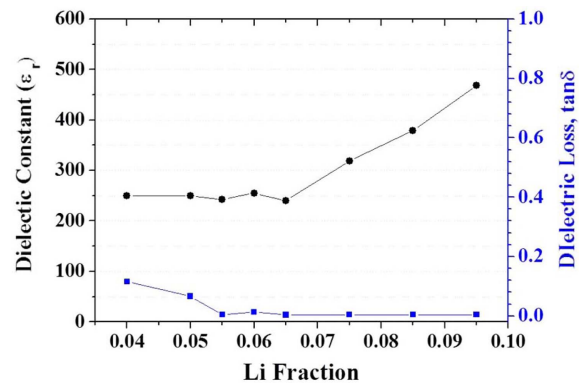


Fig. 2. The changes of the dielectric constants and losses with the Li content in the KNLNT ceramics.

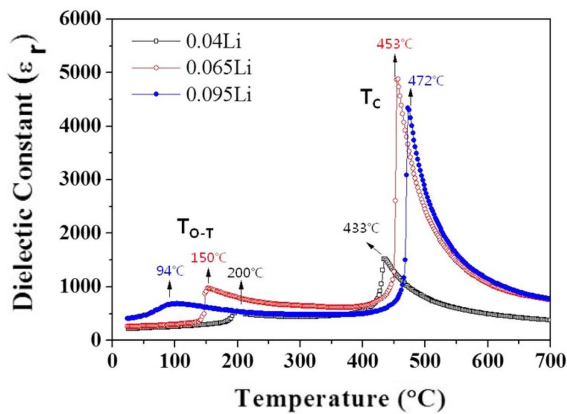


Fig. 3. Temperature-dependent dielectric constants for the KNLNT ceramics with the Li fractions of 0.04, 0.065 and 0.095.

0.4 - 0.5 was caused by the volatilization of alkaline metals.

The temperature-dependent dielectric constants of KNLNT ceramics are displayed in Fig. 3. When the Li fraction increases from 0.04 to 0.09, Curie temperature (T_C) increases from 433°C to 472°C while the transition temperature from orthorhombic to tetragonal (T_{O-T}) continuously drops from 200°C to 94°C as shown in Fig. 3. Therefore, the stable temperature range for the tetragonal phase widens to both higher and lower temperatures as Li is substituted in the KNLNT ceramic. It is consistent with the previous reports on LiNbO_3 or LiTaO_3 -modified KNN-based ceramics^{12,17} but different from the reports on LiSbO_3 -modified KNN ceramics in which Li-doping decreases both T_C and T_{O-T} .^{2,13} The T_{O-T} dependence of the Li content may influence the dielectric constant at room temperature. As shown in Fig. 3, the dielectric constant exhibits the peak value at the T_{O-T} when the measuring temperature increases above room temperature. The dielectric constant is little influenced by the dielectric peak at T_{O-T} in KNLNT ceramics with the Li fraction below 0.065 because T_{O-T} is far away from the room temperature. When the Li fraction increases above 0.065, the dielectric peak at T_{O-T} moves to the room temperature and increases the dielectric constant at room temperature as shown in Fig. 2.

Figure 4 shows the dependence of the piezoelectric charge constant (d_{33}), electromechanical coupling factor (k_p) and mechanical quality factor (Q_m) on the Li content. The k_p and d_{33} have maximum values at the Li fraction of 0.055 ~ 0.065 where the MPB lies, as confirmed by the X-ray diffraction. A maximum piezoelectric activity is observed at the MPB in many piezoelectric solid solutions including $\text{Pb}(\text{Zr,Ti})\text{O}_3$ -based and KNN-based ceramics.^{2,3} The peak values for k_p and d_{33} in Fig. 4 indicate that the MPB effect is also present in this CuO-doped KNN ceramic. The compositions for the peak values of k_p and d_{33} are slightly different in this KNLNT ceramic; 0.065 Li for k_p and 0.055 Li for d_{33} . The increase of d_{33} at Li fraction above 0.065 is thought to be caused by the increase of the dielectric constant in that composition range. The mechanical quality factor exhibits the

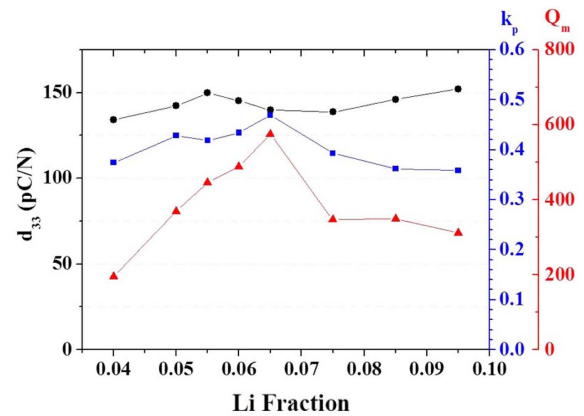


Fig. 4. The changes of a piezoelectric constant (d_{33}), an electromechanical coupling factor (k_p), and a mechanical quality factor (Q_m) with the Li content in the KNLNT ceramics.

peak value at the Li fraction for the peak of k_p as shown in Fig. 4. The Q_m has been reported to have a minimum value around the MPB in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ -based ceramics and soft KNN-based ceramics with low Q_m .^{16,23} Fig. 4 presents that the CuO-doped KNN ceramics with a high Q_m may cause the change of Q_m with the Li content in a different way.

The figures of merit for the PEH in on-resonance and in off-resonance conditions were calculated and displayed in Fig. 5. The maximum value for the FOM_{on} is observed at the Li fraction of 0.065 and it is expected from the fact that the piezoelectric properties measured in the resonance conditions, k_p and Q_m , had peak values at that composition. Fig. 5 shows that the FOM_{off} has the peak value at the Li fraction of 0.055 and it is also expected from the maximum d_{33} at that composition which is measured in the off-resonance condition. The noticeable fact is that both FOM_{on} and FOM_{off} have maximum values around the MPB, but the peak compositions are not exactly coincided. Fig. 5 demonstrates that the most suitable composition in the KNLNT ceramic for the PEH is that with the Li fraction between 0.055 and 0.065.

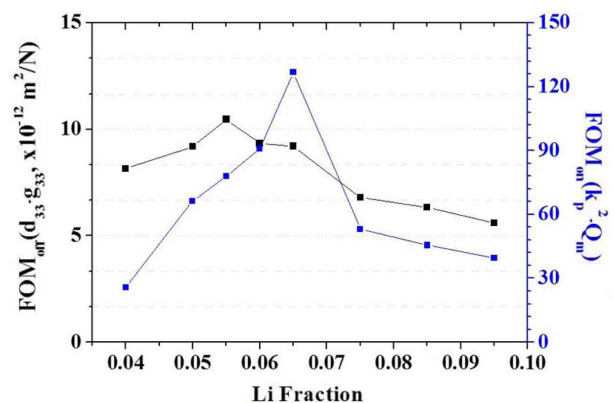


Fig. 5. The figures of merit in the resonance condition (FOM_{on}) and in the off-resonance condition (FOM_{off}) in the KNLNT ceramics with various Li fractions.

4. Conclusions

The crystal structure of CuO-doped KNLNT ceramics changes from orthorhombic to tetragonal at the Li fraction around 0.065. The dielectric constant exhibits the peak value at the transition temperature from orthorhombic to tetragonal ($T_{O,T}$) when the measuring temperature increases above room temperature. Curie temperature (T_C) increase from 433°C to 472°C while $T_{O,T}$ decreases from 200°C to 94°C continuously as the Li fraction increases from 0.04 to 0.09. The dielectric constant at room temperature increases as the dielectric peak at $T_{O,T}$ closes to the room temperature at the Li fraction above 0.065. A piezoelectric charge constant (d_{33}), an electromechanical coupling factor (k_p) and a mechanical quality factor (Q_m) have maximum values at the MPB. The compositions for the peak values of k_p and Q_m , and d_{33} are a little different in this KNLNT ceramic; 0.065 Li for k_p and Q_m , and 0.055 Li for d_{33} , respectively. Both the figures of merits for the PEH in on-resonance (FOM_{on}) and in off-resonance condition (FOM_{off}) have maximum values around the MPB, but the peak compositions are not exactly coincided; 0.065 Li for FOM_{on} , and 0.055 Li for FOM_{off} . The optimal composition of the KNLNT ceramic for a PEH application has Li fraction between 0.055 and 0.065.

Acknowledgments

This work was supported by the Materials and Components Technology Development Program of MOTIE/KEIT, Republic of Korea [10050958, Development of 1mW self-powered module for driving system prognosis sensor using piezoelectric composite].

REFERENCES

1. J. Rödel, K. G. Webber, R. Dittmer, W. Jo, M. Kimurac, and D. Damjanovic, "Transferring Lead-Free Piezoelectric Ceramics into Application," *J. Eur. Ceram. Soc.*, **35** [6] 1659-81 (2015).
2. J.-F. Li, K. Wang, F.-Y. Zhu, L.-Q. Cheng, and F.-Z. Yao, "(K,Na)NbO₃-Based Lead-Free Piezoceramics: Fundamental Aspects, Processing Technologies, and Remaining Challenges," *J. Am. Ceram. Soc.*, **96** [12] 3677-96 (2013).
3. J. Rödel, W. Jo, K. T. P. Seifert, E.-M. Anton, and T. Granzow, "Perspective on the Development of Lead-Free Piezoceramics," *J. Am. Ceram. Soc.*, **92** [6] 1153-77 (2009).
4. T. Rüdiger, A. Schönecker, and G. Gerlach, "A Survey on Piezoelectric Ceramics for Generator Applications," *J. Am. Ceram. Soc.*, **93** [4] 901-12 (2010).
5. S. Priya, "Advances in Energy Harvesting Using Low Profile Piezoelectric Transducers," *J. Electroceram.*, **19** [1] 165-82 (2007).
6. I.-T. Seo, C.-H. Choi, D. Song, M.-S. Jang, B.-Y. Kim, S. Nahm, Y.-S. Kim, T.-H. Sung, and H.-C. Song, "Piezoelectric Properties of Lead-free Piezoelectric Ceramics and Their Energy Harvester Characteristics," *J. Am. Ceram. Soc.*, **96** [4] 1024-28 (2013).
7. C. D. Richards, M. J. Anderson, D. F. Bahr, and R. F. Richard, "Efficiency of Energy Conversion for Devices Containing a Piezoelectric Component," *J. Micromech. Microeng.*, **14** [5] 717-21 (2004).
8. M. Umeda, D. Nakamura, and S. Ueha, "Analysis of the Transformation of Mechanical Impact Energy to Electric Energy Using Piezoelectric Vibrator," *Jpn. J. Appl. Phys.*, **35** [5B] 3267-73 (1996).
9. Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, "Lead-Free Piezoceramics," *Nature*, **432** [4] 84-7 (2004).
10. T. R. Shrout and S. J. Zhang, "Lead-Free Piezoelectric Ceramics: Alternatives for PZT?," *J. Electroceram.*, **19** [1] 111-24 (2007).
11. J. Rödel, W. Jo, K. T. P. Seifert, E. M. Anton, T. Granzow, and D. Damjanovic, "Perspective on the Development of Lead-Free Piezoceramics," *J. Am. Ceram. Soc.*, **92** [6] 1153-77 (2009).
12. Y. Guo, K. Kakimoto, and H. Ohsato, "(Na_{0.5}K_{0.5})NbO₃-LiTaO₃ Lead-Free Piezoelectric Ceramics," *Mater. Lett.*, **59** 241-44 (2005).
13. J. Wua, D. Xiao, Y. Wang, J. Zhu, P. Yu, and Y. Jiang, "Compositional Dependence of Phase Structure and Electrical Properties in (K_{0.42}Na_{0.58})NbO₃-LiSbO₃ Lead-Free Ceramics," *J. Appl. Phys.*, **102** [11] 114113 (2007).
14. J. Wu, T. Peng, Y. Wang, D. Xiao, J. Zhu, Y. Jin, J. Zhu, P. Yu, L. Wu, and Y. Jiang, "Phase Structure and Electrical Properties of (K_{0.48}Na_{0.52})(Nb_{0.95}Ta_{0.05})O₃-LiSbO₃ Lead-Free Piezoelectric Ceramics," *J. Am. Ceram. Soc.*, **91** [1] 319-21 (2008).
15. D. Liu, H. Du, F. Tang, F. Luo, D. Zhu, and W. Zhou, "Effect of Heating Rate on the Structure Evolution of (K_{0.5}Na_{0.5})NbO₃-LiNbO₃ Lead-Free Piezoelectric Ceramics," *J. Electroceram.*, **20** [2] 107-11 (2008).
16. Z.-Y. Shen, J.-F. Li, K. Wang, S. Xu, W. Jiang, and Q. Deng, "Electrical and Mechanical Properties of Fine-Grained Li/Ta-Modified (Na,K)NbO₃-Based Piezoceramics Prepared by Spark Plasma Sintering," *J. Am. Ceram. Soc.*, **93** [5] 1378-83 (2010).
17. N. Klein, E. Hollenstein, D. Damjanovic, H. J. Trodahl, N. Setter, and M. Kuball, "A Study of the Phase Diagram of (K,Na,Li)NbO₃ Determined by Dielectric and Piezoelectric Measurements, and Raman Spectroscopy," *J. Appl. Phys.*, **102** [1] 014112 (2007).
18. K. Wang, J.-F. Li, and N. Liu, "Piezoelectric Properties of Low-Temperature Sintered Li-Modified (Na, K)NbO₃ Lead-Free Ceramics," *Appl. Phys. Lett.*, **93** [9] 092904 (2008).
19. J. B. Lim, S. Zhang, J.-H. Jeon, and T. R. Shrout, "(K,Na)NbO₃-Based Ceramics for Piezoelectric "Hard" Lead-Free Materials," *J. Am. Ceram. Soc.*, **93** [5] 1218-20 (2010).
20. R. Huang, Y. Zhao, X. Zhang, Y. Zhao, R. Liu, and H. Zhou, "Low-Temperature Sintering of CuO-Doped 0.94(K_{0.48}Na_{0.535})NbO₃-0.06LiNbO₃ Lead-Free Piezoelectric Ceramics," *J. Am. Ceram. Soc.*, **93** [12] 4018-21 (2010).
21. J. H. Kim, J. S. Kim, S. H. Han, H.-W. Kang, H.-G. Lee, and C. I. Cheon, "Low-Temperature Sintering and Piezoelectric Properties of CuO-Doped (K,Na)NbO₃ Ceramics," *Mater. Res. Bull.*, **96** [2] 121-25 (2017).
22. J. H. Kim, J. S. Kim, S. H. Han, H.-W. Kang, H.-G. Lee,

- and C. I. Cheon, "(K,Na)NbO₃-Based Ceramics with Excess Alkali Oxide for Piezoelectric Energy Harvester," *Mater. Res. Bull.*, **42** [4] 5226-30 (2016).
23. T. Kudo, T. Yazaki, F. Naito, and S. Sugaya, "Dielectric and Piezoelectric Properties of Pb(Co_{1/3}Nb_{2/3})O₃-PbTiO₃-PbZrO₃ Solid Solution Ceramics," *J. Am. Ceram. Soc.*, **53** [6] 326-28 (1970).