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Piezoelectric Properties of PMN-PNN-PZT Ceramics and the Simulation of Ultrasonic Cleaner

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Abstract: In this paper, for the application of ultrasonic cleaners for cleaning dentures and transparent braces, $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ [PMN-PNN-PZT] system ceramics were manufactured and their dielectric and piezoelectric properties were investigated. Overall the best properties suitable for the device applications such as ultrasonic cleaner were obtained from the ceramics sintered at 920℃: bulk density of 7.8 g/cm^3, the dielectric constant (ε_r) of 1,689, piezoelectric charge constant (d_{33}) of 433 pC/N, planar electromechanical coupling factor (k_p) of 0.64, mechanical quality factor (Qm) of 835, S_{11}^E of 13.37 (10^{-12} N/m^2), and Curie temperature of 315℃ By using the physical properties of this composition, the ultrasonic cleaner was designed and simulated using the commercial ATILA software. For the three-layered ceramics with the dimension of 25 mm × 25 mm × 2.5mm, an excellent displacement of 8.998 (10^{-3} m) and the sound pressure of 147.68 dB were recorded.

Keywords: $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr, Ti)O_3$, Mechanical quality factor (Qm), Ultrasonic cleaner, Piezoelectric properties

Recently, the ultrasonic cleaner has been widely used for the purpose of cleaning eyeglasses, denture, and transparent braces more refreshingly. In general, ultrasonic cleaner generates the ultrasonic wave in order to make fine bubbles in the water. The ultrasonic cleaner has the principle of removing and sterilizing the contaminated substances on the surface with the thermal energy generated when the bubbles burst with a high vibration of 20~40 kHz.

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The numbers of patients requiring orthodontic treatment have been widely increasing. However, there are many cases of hesitation in orthodontic treatment owing to the pain and discomfort that can generate during the orthodontic treatment, and also because of the aesthetic problems caused by the orthodontic device. Therefore, in an effort to overcome these problems, the invisalign system, a transparent orthodontic treatment method using 3D digital technology, have been developed [1,2].

By using this invisalign system, the transparent overlay device with 0.03-inch thickness capable of moving from 0.15 to 0.25 mm step by step using 3D imaging program of malocclusion is replaced for 1~2 weeks and can be sequentially utilized. These transparent braces have the same shape as a thin and transparent mouthpiece. And also, the maintaining it in the oral cavity is advantageous for orthodontic treatment for as long as possible, but it must be removed when eating or brushing teeth. Here, it is necessary to clean the transparent braces, but when using general toothpaste, a problem of wear can be generated. Accordingly, if a transparent braces cleaner using the ultrasonic piezoelectric device is developed, these problems can be solved. The ultrasonic piezoelectric device must be driving under high power source. Accordingly, it is necessary to develop the excellent piezoelectric ceramic device with high Qm and kp for decreasing the heat generation of the ceramics. Ternary component composition ceramics such as $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ have been actively studied in several researchers for the application of ultrasonic device and piezoelectric transformers [3-5].

In general, $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ (abbreviated as PMN-PZT) ceramics with high Qm and kp for the application of high power piezoelectric device were reported by C.Y Chen et al. [6]. In this study, the ceramic specimen and ultrasonic piezoelectric device capable of being used in a transparent braces cleaner was simulated and manufactured using $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ substituted with $Pb(Ni_{1/3}Nb_{2/3})O_3$ piezo-electric materials and then their electrical properties were investigated. By using the physical properties of this composition ceramics with ATILA software, the ultrasonic cleaner was designed and simulated.

The specimens were manufactured using a conventional mixed oxide process. The compositions used in this study were as follows;

$$0.095Pb(Mn_{1/3}Nb_{2/3})O_3\text{-}0.005Pb(Ni_{1/3}Nb_{2/3})O_3\text{-}0.90Pb(Zr_{0.5}Ti_{0.5})O_3 + \text{sintering aids } (Li_2CO_3, Bi_2O_3, CuO)$$

The raw materials, such as PbO, MnO_2, Nb_2O_5, NiO, ZrO_2, and TiO_2 for the given composition were weighed by mole ratio and the powders were ball-milled for 24 h. After adding sintering aids (Li_2CO_3, Bi_2O_3, CuO), they were calcined at 850°C for 2 h. The calcined materials were with ball-milled again. And then, a polyvinyl alcohol (PVA: 5 wt% aqueous solution) was added to the dried powders. The powders were molded by the pressure of 17 MPa in a mold which has a diameter of 17 mm, burned out at 600°C for 3h, and then sintered at 920°C for 2 h. For measurement of the dielectric and piezoelectric characteristics, the specimens were polished to 1.0 mm thickness with 13.45 mm diameter. And then, the Ag paste was screen-printed on the ceramic specimen.

A polarization treatment was performed by applying a voltage of 3 kV/mm in the insulating oil at room temperature for 30 min. The piezoelectric properties of the specimen (13.45 mm diameter × 1 mm thickness) were investigated by the measurement of resonance frequency (fr) and anti-resonance frequency (fa) using an Impedance Analyzer (Agilent 4294A). Electromechanical coupling factor kp were calculated [7]. Then, Qm were calculated according to IRE standard [7].

And also, the entire material constant such as piezoelectric charge constant d_{15}, d_{31} was measured using the specimens of shear mode, length extensional vibration mode, respectively. The elastic compliance such as s_{11}, s_{12}, s_{13}, s_{33}, and s_{44} were also measured using the specimens of IRE standard, respectively.

And also, the ultrasonic cleaner was designed and simulated using the physical properties of this composition ceramics with ATILA software. Here, the total size of ultrasonic cleaner was designed as 90 mm × 90 mm × 50 mm. 200 Vrms voltage was applied to one–layer 2.5 mm thickness piezoelectric ceramics. And also, 66 Vrms voltage was applied to three-layer 2.5 mm thickness piezoelectric ceramics.

Figure 1 shows the X-ray diffraction (XRD) pattern of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics [(a) wide range and (b) narrow range] sintered at 920°C for 2 h. The sample exhibit pure perovskite phase and no secondary phases are observed in the measurement range of XRD. As can be seen in Fig. 1, the ceramic specimens possess a tetragonal phase, which is characterized by the tetragonal (002) and (200) between 42° and 50°. Figure 2 shows the scanning electron microscopy (SEM) of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics. Grain shapes showed relatively dense structure. Average grain size showed 9.51 μm.

Figure 3 shows the temperature dependence of dielectric constant of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics. The temperature dependence of the dielectric constant was measured at a frequency of 1 kHz. Curie temperature relatively showed the high value of 315°C.

In general, the ultrasonic piezoelectric device may be driving under high power source for generating a sufficient

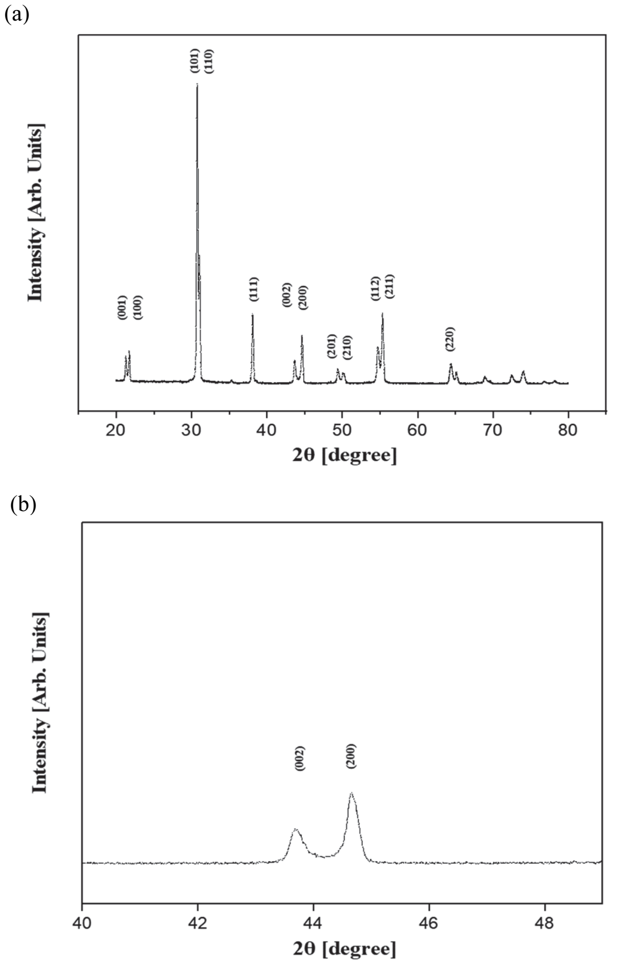

Fig. 1. X-ray diffraction patterns of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics (a) wide range and (b) narrow range.

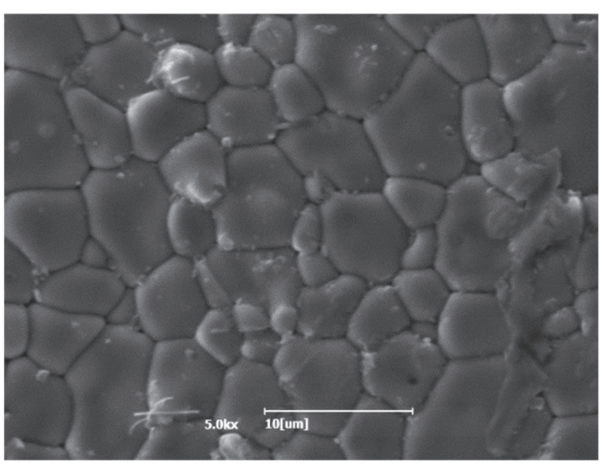

Fig. 2. Scanning electron microscopy (SEM) of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics.

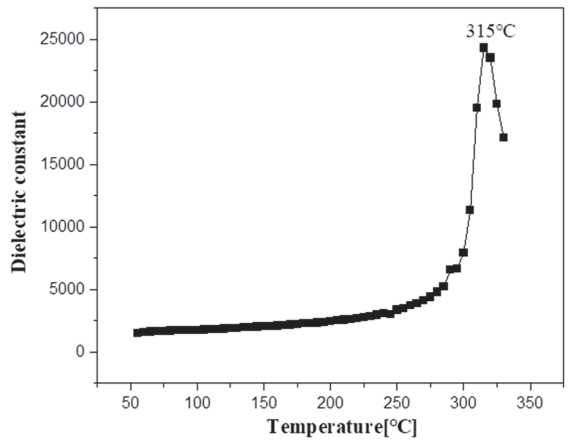

Fig. 3. Temperature dependence of dielectric constant of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics.

ultrasonic wave. It is required to develop the excellent piezoelectric ceramic device with high mechanical quality factor Qm and electromechanical coupling factor kp in order to decrease the heat generation of the ceramics and to increase the efficiency of the ceramics, respectively. The ceramics manufactured in this experiment showed the excellent physical properties of high electromechanical coupling factor k_p of 0.64 and high mechanical quality factor Q_m of 835, suitable for ultrasonic piezoelectric device as shown in Table 1.

Figure 4 shows the specifications of one layer, three layer piezoelectric ceramics (a) and ultrasonic cleaner (b). The dimension of ultrasonic cleaner was designed as 90 mm × 90 mm × 50 mm. Here, the dimension of piezoelectric ceramics were varied as x mm × x mm × 2.5 mm (x=10 mm, 15 mm,

Table 1. Physical properties of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics.

Density [g/cm^3]	7.80
k_p	0.64
Dielectric constant	1,689
d_{33} (10^{-12} C/N)	433
Q_m	835
Tc (°C)	315
S_{11}^E (10^{-12} N/m^2)	13.37
S_{13}^E (10^{-12} N/m^2)	-6.3
S_{33}^E (10^{-12} N/m^2)	16.5
S_{44}^E (10^{-12} N/m^2)	40
d_{15}^E (10^{-12} C/N)	360
d_{31}^E (10^{-12} C/N)	-161

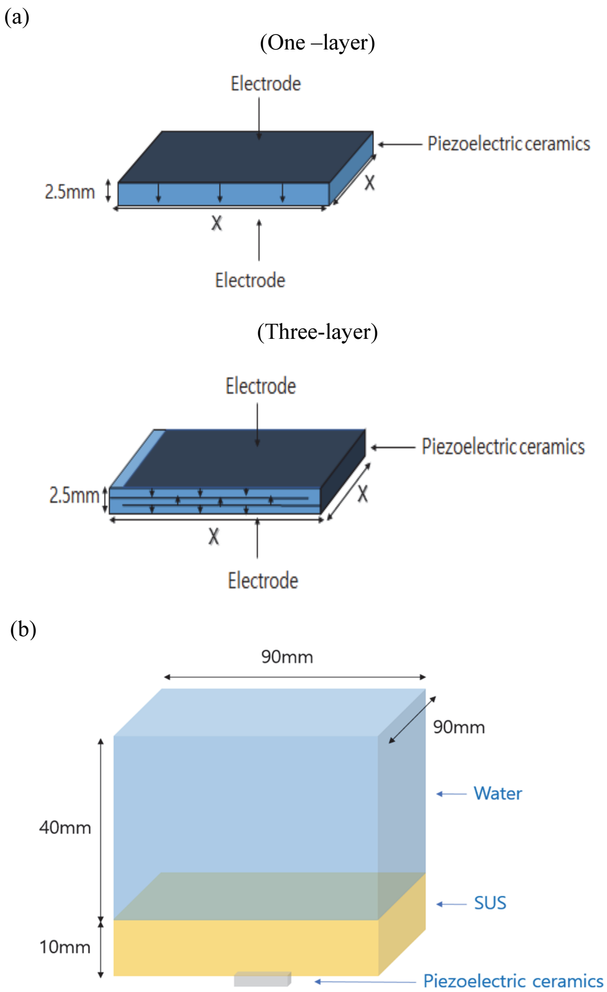

Fig. 4. Specifications of (a) one layer, three layer piezoelectric ceramics and (b) ultrasonic cleaner.

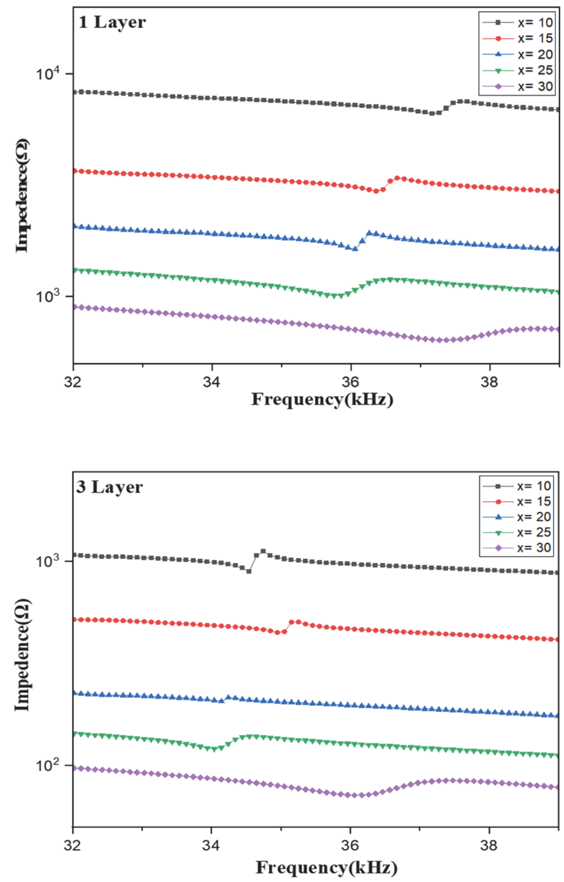

Fig. 5. Impedance characteristic curves of ultrasonic cleaner with the dimension of ceramics.

20 mm, 25 mm, and 30 mm). Figure 5 shows the impedance characteristic curves of ultrasonic cleaner with the dimension of ceramics. 200 Vrms voltage was applied to thickness direction of one layer 2.5 mm thickness ceramics, and also, 66 Vrms voltage was applied to three-layer 2.5 mm thickness ceramics and the driving frequency was kept constant at resonance frequency.

As shown in Fig. 5. and Table 2, the effective electromechanical coupling factor (k_{eff}) is only calculated as the difference between resonance frequency (fr) and anti-resonance frequency (fa). Here, highest k_{eff} was obtained when x=30.

However, the impedance at anti-resonance frequency was relatively lowered at x=30 as shown in Table 2. Piezoelectric resonator can be strongly driven when the resonator has high impedance at anti-resonance frequency and high dynamic range [8].

The impedance at resonance frequency (Z_{min}) was decreased with increasing the number of multi-layer. It is considered that Z_{min} decreased according to the increase of parallel capacitance due to the number of multi-layer. Figures 6 and 7 show the displacement and the sound pressure of ultrasonic cleaner with the dimension of ceramics. When x=25, the excellent displacement and sound pressure appeared at one–layer and three-layer. These results can be explained by the fact that the dimension of ultrasonic cleaner was most proper at x=25 in spite of showing the excellent k_{eff} at x=30. It is illustrated by the fact that x=25 ceramics is best for generating the excellent displacement and sound pressure at the dimension of ultrasonic cleaner of 90 mm × 90 mm × 50 mm. And also, although the same electric field E (=80 V/mm)

Table 2. Electrical properties of ultrasonic cleaner with the dimension of ceramics.

One–layer							
x	Fr (kHz)	Fa (kHz)	Displacement (10^{-3}m)	Sound pressure (dB)	$Z_{min\ (\Omega)}$	$Z_{max\ (\Omega)}$	k_{eff}
10	37.1717	37.5758	2.293	129.532	6,648	7,515	0.1479
15	36.3636	36.6667	4.982	133.88	2,980	3,413	0.1294
20	36.0606	36.2626	8.378	134.801	1,635	1,924	0.1060
25	35.7576	36.5657	7.461	136.911	1,011	1,195	0.2138
30	37.3737	38.6869	6.903	128.177	638	718	0.2674

Three-layer							
x	Fr (kHz)	Fa (kHz)	Displacement (10^{-3}m)	Sound pressure (dB)	$Z_{min(\Omega)}$	$Z_{max(\Omega)}$	k_{eff}
10	34.5454	34.7475	5.453	140.82	889	1,116	0.1083
15	34.9495	35.2525	5.875	142.65	448	504	0.1320
20	34.1414	34.2424	7.808	140.735	206	214	0.0770
25	34.0404	34.5454	8.998	147.68	120	139	0.1729
30	36.0606	37.4748	6.420	146.867	71	84	0.2828

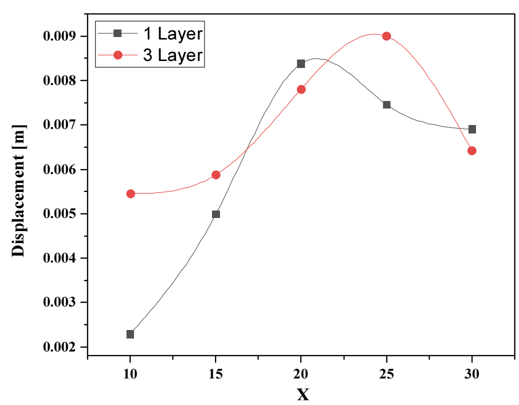

Fig. 6. Displacement of ultrasonic cleaner with the dimension of ceramics.

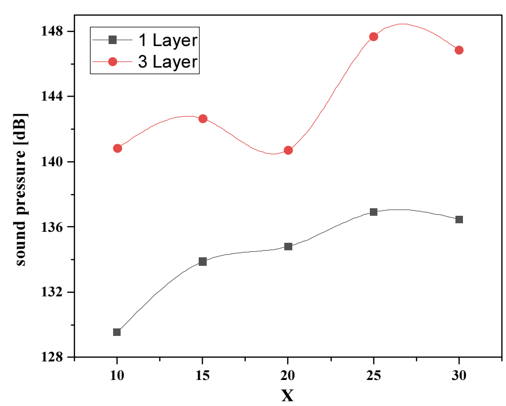

Fig. 7. Sound pressure of ultrasonic cleaner with the dimension of ceramics.

as one layer was applied to the three-layer piezoelectric device, the excellent displacement of 8.998 (10^{-3} m) and the sound pressure of 147.68 dB appeared, respectively. This can be also illustrated by the fact that the generating force of piezoelectric device is increased by the increase of the number of multi-layer. In this study, 2.5 mm thickness ceramics with one–layer and three-layer was used for simulation. It is thought that the ceramic devices with many multi-layer numbers must be used for further-decreasing the driving voltage.

In this study, for application of ultrasonic cleaner for cleaning denture and transparent braces, the 0.095Pb $(Mn_{1/3}Nb_{2/3})O_3$-0.005Pb$(Ni_{1/3}Nb_{2/3})O_3$-0.90Pb$(Zr_{0.5}Ti_{0.5})O_3$ ceramics were manufactured and the their dielectric and piezoelectric properties were investigated. By using the physical properties of this composition ceramics with ATILA software, the ultrasonic cleaner was designed and simulated.

1) At the ceramics sintered at 920℃, the high values of piezoelectric properties were appeared, respectively: bulk density of 7.8 g/cm^3, the dielectric constant (εr) of 1,689, piezoelectric charge constant (d_{33}) of 433 pC/N, electromechanical coupling factor (kp) of 0.64,

mechanical quality factor (Qm) of 835, S_{11}^{E} of 13.37 (10^{-12} N/m^2), and Curie temperature of 315°C, were suitable for the device application such as ultrasonic cleaner.

2) The impedance at resonance frequency (Z_{min}) was decreased with increasing the number of multi-layer.
3) At the dimension of x=25 three-layer ceramics, the excellent displacement of 8.998 (10^{-3} m) and sound pressure of 147.68 dB appeared, respectively.
4) For further-decreasing the driving voltage of the ceramics, many multilayer-structured ceramic must be used.

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REFERENCES

[1] H. S. Kim, J. H. Ahn, and R. L. Boyd, *Korean J. Orthod.*, **33**, 21 (2003).

[2] A. Papadimitriou, S. Mousoulea, N. Gkantidis, and D. Kloukos, *Prog. Orthod.*, **19**, 37 (2018). [DOI: https://doi.org/10.1186/s40510-018-0235-z]

[3] R. A. Islam and S. Priya, *J. Am. Ceram. Soc.*, **89**, 3147 (2006). [DOI: https://doi.org/10.1111/j.1551-2916.2006.01205.x]

[4] H. W. Kim, A. Batra, S. Priya, K. Uchino, D. Markley, R. E. Newnham, and H. F. Hofmann, *Jpn. J. Appl. Phys.*, **43**, 6178 (2004). [DOI: https://doi.org/10.1143/JJAP.43.6178]

[5] J. Yoo, K. Yoon, Y. Lee, S. Suh, J. Kim, and C. Yoo, *Jpn. J. Appl. Phys.*, **39**, 2680 (2000). [DOI: https://doi.org/10.1143/JJAP.39.2680]

[6] C. Y. Chen and H. L. Lin, *Ceram. Int.*, **30**, 2075 (2004). [DOI: https://doi.org/10.1016/j.ceramint.2003.11.010]

[7] S. Kang, J. Lee, J. Yoo, S. A. Whang, S. Lee, S. Kee, I. Im, and C. Oh, *Crystals*, **12**, 738 (2022). [DOI: https://doi.org/10.3390/cryst12050738]

[8] J. Yoo, S. Min, C. Park, S. Suh, H. Yoon, J. Kim, and S. Lee, *Jpn. J. Appl. Phys.*, **41**, 7011 (2002). [DOI: https://doi.org/10.1143/JJAP.41.7011]