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에너지 하베스팅소자 응용을 위한 $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr\ Ti)O_3$ 계 세라믹스의 유전 및 압전 특성

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Dielectric and Piezoelectric Characteristics of $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr\ Ti)O_3$ System Ceramics for the Application of Energy Harvesting Device

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Abstract In this study, to develop composition ceramics for energy harvesting devices, $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr\ Ti)O_3$ system ceramics substituted with $Pb(Mg_{1/2}W_{1/2})O_3$ were manufactured by conventional mixed oxide method using Li_2CO_3 and Na_2CO_3 (LNCO) as sintering aids. Their microstructure and piezoelectric properties were also investigated. At the specimen sintered at 930℃, high values of piezoelectric properties appeared: the dielectric constant (εr) of 2,522 planar electromechanical coupling factor kp of 0.602, and k_{31} of 0.385, d_{31} = 229 [pC/N], g_{31} = 10.13 [mV.m/N], Qm of 70, respectively. These values were suitable for the application of devices such as energy harvesting devices and ultrasonic devices.

Key words: Energy harvesting device, Li_2CO_3 and Na_2CO_3 (LNCO) piezoelectric properties, Electromechanical coupling factor

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Recently, PZT and ternary ceramics such as PMN-PZT, and PNN-PZT have been widely utilized in level sensors, ultrasonic non-destructive testing, high-power ultrasonic transducers, and energy harvesting devices. In particular, remarkable research is being conducted to utilize them as small power sources for IoT sensors that do not require batteries. Piezoelectric energy harvesting, which can generate power by the environmental vibrations, is very efficient for application as a small power source for IoT sensors. For this purpose, the generated power must be large. In order to increase the power density (W/cm^3), which represents the generated power per unit volume, it is essential to manufacture multilayer type devices using Ag/Pd internal electrodes. Accordingly, for this purpose, low-temperature sintering of the ceramics is essential to increase the Ag portion in Ag/Pd electrodes. In order to develop the high-performance piezoelectric materials for these devices, ternary ceramics have been studied for a long time by adding PZT ceramics to $Pb(Mg,W)O_3$, $Pb(Mg,Nb)O_3$, and $Pb(Ni,Nb)O_3$, because the range of composition selection is very wide [1-3]. However, these PZT system ceramics contain 60-70% PbO. Rapid evaporation of PbO can occur at a sintering temperature of 1,000°C or higher. Therefore, if the sintering temperature of the ceramics is lowered, environmental pollutions due to PbO can be reduced, and energy saving and sintered density improvement effects can be obtained during sintering of the ceramics. In order to develop a composition with a large Ag portion in the Ag/Pd internal electrode, research on low-temperature sintering below 950°C has been conducted for a long time [4]. High piezoelectric charge constant d_{33} and high voltage constant g_{33}, which respectively can reflect the actuation and sensitive capabilities of piezoelectric materials, are very important [5]. In general, piezoelectric energy harvesting devices in the length extensional vibration mode were widely used. Accordingly, in this study, for the manufacture of energy harvesting devices, the value of 31 type must be excellent. Therefore, in this study, in order to develop a low-temperature ceramics with high d_{31} and high g_{31}, the ceramic composition of PNN-PZT ceramics substituted with $Pb(Mg_{1/2}W_{1/2})\ O_3$ was used [6], and also, Li_2CO_3 and Na_2CO_3 proved as excellent sintering aids at the previous studied results were selected [7,8]. Then, the physical properties of the manufactured ceramics were investigated according to the variations of the sintering temperature from 900°C to 990°C. In this study, the following ceramic compositions for the experiment were used : 0.03 $Pb(Mg_{1/2}W_{1/2})O_3$ – 0.09 $Pb(Ni_{1/3}Nb_{2/3})O_3$ – 0.88 $Pb(Zr_{0.5}Ti_{0.5})O_3$ + sintering aids (0.2 wt% Li_2CO_3 – 0.2 wt% Na_2CO_3). The starting materials were PbO, MgO, WO_3, ZrO_2, TiO_2 NiO, and Nb_2O_5, which were weighed and ball milled for 24 h. After drying, the mixture was calcined at 850°C for 2 h. After that, the sintering aids Li_2CO_3-Na_2CO_3 (LNCO) was added and ball milled again. 5 wt% PVA solutions were added to the calcined powder. After the calcined powder was molded using a mold with a diameter of 17 mm at a pressure of 1 ton/cm^2, it was sintered for 2 hours at a sintering temperature ranging from 900°C to 990°C. In order to determine the physical properties of the sample, it was polished to a thickness of 1 mm and then polarized at 120°C under a 30 kV/cm electric field. The dielectric constant (C) was measured using an LCR (inductance capacitance resistance) meter (Instek, LCR = 819) to measure the capacitance of the ceramics, and the dielectric constant (εr) was precisely calculated. The piezoelectric properties of the material were measured by measuring fr (resonant frequency) and fa (anti-resonant frequency) using an impedance analyzer (Agilent4294A), and Qm, k_{31}, kp, and d_{31} were calculated.

Figure 1 shows the X-ray diffraction patterns of the specimens according to the variations of sintering temperature from 900°C to 990°C. All samples showed pure perovskite phase, and a secondary phase was observed at 900°C. In addition, the ceramic specimens showed a rombohedral-tetragonal (R-T) phase coexistence, which is characterized by the tetragonal (002) and (200) along with the rhombohedral (200) peak [9].

Figure 2 shows the microstructure of the specimens according to the variations of the sintering temperature from 900°C to 990°C. As shown in Fig. 2, the average grain size

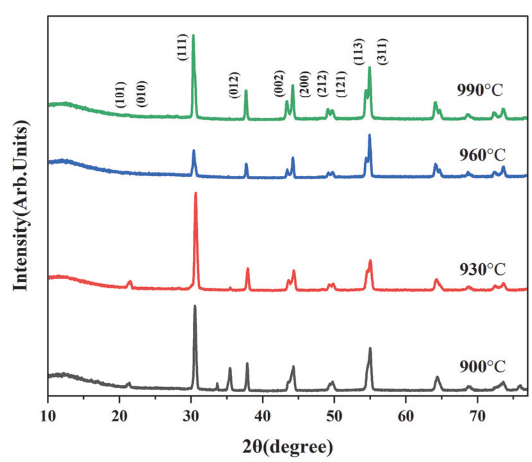
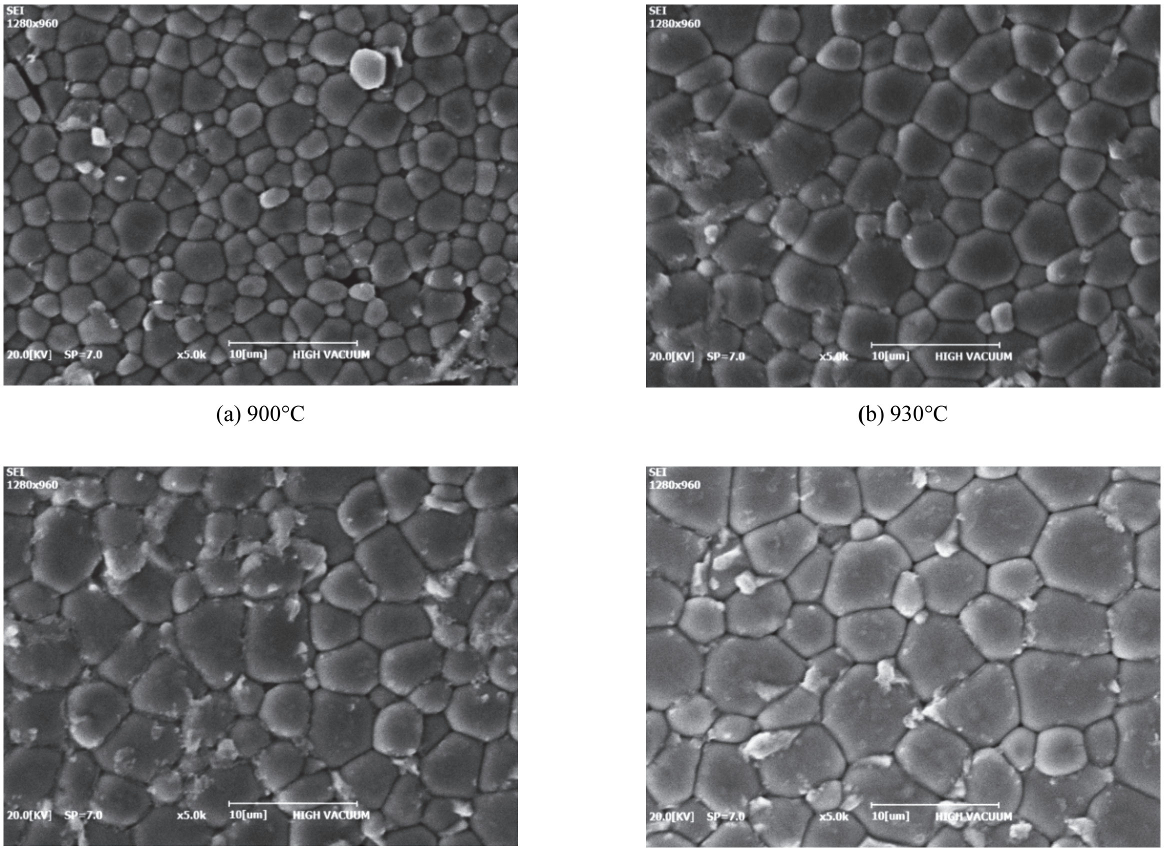


Fig. 1. XRD pattern with the variations of sintering temperature.



(a) 900°C (b) 930°C

(c) 960°C (d) 990°C

Fig. 2. The SEM micrographs with the variations of sintering temperature (a) x = 900°C, (b) x = 930°C, (c) x = 960°C, and (d) x = 990°C.

gradually increased to 3.93 μm, 5.06 μm, 6.28 μm, and 6.58 μm, respectively, as the sintering temperature increased. The maximum average grain size of 6.58 μm was observed at 990°C. This phenomenon can be illustrated by the fact that grain growth of the ceramics occurs according to the phenomenological kinetic grain growth equation as the sintering temperature increases [10].

Figure 3 shows the density according to the variations of sintering temperature from 900°C to 990°C. Eutectic temperature of Li_2CO_3 and Na_2CO_3 compound shows 514°C [4]. At the temperature, the liquid phase is started and helps the densification of specimens at low temperature. Accordingly, the maximum density of the specimens appeared as 7.90 g/cm^3 at a low sintering temperature of 930°C. That is, this phenomenon can be explained by the conclusion that the sintering aids (Li_2CO_3-Na_2CO_3) can be properly acted as a liquid phase at 930°C to facilitate sintering of the ceramics. And then, the density of the specimens decreased by the evaporation of sintering aids (Li_2CO_3-Na_2CO_3) due to over-sintering at the sintering temperature above 930°C.

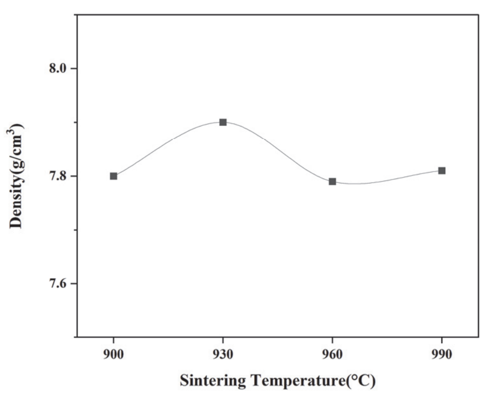


Fig. 3. Density with the variations of sintering temperature.

Figure 4 shows the electromechanical coupling coefficient (kp) according to the change in sintering temperature from 900℃ to 990℃. The kp of the specimen sintered at 930℃ showed a maximum value of 0.602, and then decreased by the poor densification due to the over-sintering temperature [11].

Figures 5 and 6 show the electromechanical coupling coefficient (k_{31}), piezoelectric charge constant d_{31}, and piezoelectric voltage constant g_{31} according to the variations of sintering temperature from 900℃ to 990℃. In this study, in order to manufacture the energy harvesting devices as the length extensional vibration mode, the value of 31 types should be excellent. The k_{31}, d_{31}, and g_{31} of the specimen sintered at 930°C showed excellent values of 0.385, 229 [pC/N], and 10.13 [mV.m/N], respectively. These results can be also interpreted as the highest sintered density of the ceramics.

Figure 7 shows the dielectric constant (εr) according to the variations of sintering temperature from 900°C to 990°C. The dielectric constant (εr) of the specimen sintered at 930°C showed the highest value of 2,552, and then also decreased by the poor densification due to the over-sintering temperature. Here, the dielectric constant (εr) of the specimen showed the same trends as d_{31} piezoelectric charge constant.

Figure 8 shows the mechanical quality factor (Qm) according to the variations of sintering temperature from 900°C to 990°C. The value of Qm slightly increased as the sintering temperature increased up to 930°C and then also decreased by the increase of pores due to the over-sintering

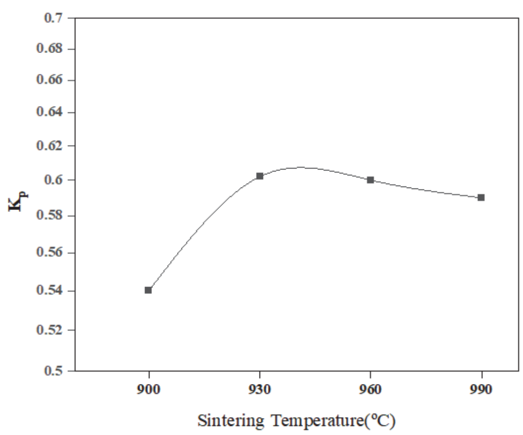


Fig. 4. Electromechanical coupling factor (k_p) with the variations of sintering temperature.

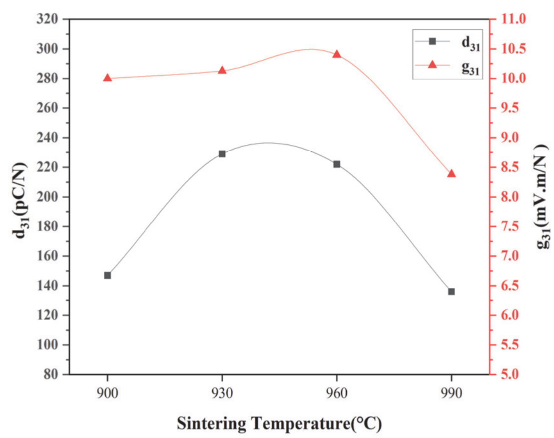


Fig. 6. Piezoelectric charge constant (d_{31}) and voltage constant (g_{31}) with the variations of sintering temperature.

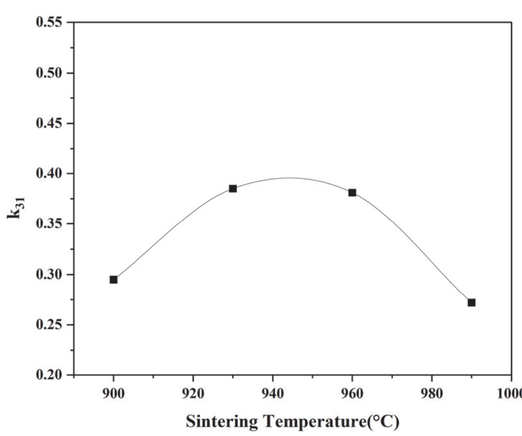


Fig. 5. Electromechanical coupling factor (k_{31}) with the variations of sintering temperature.

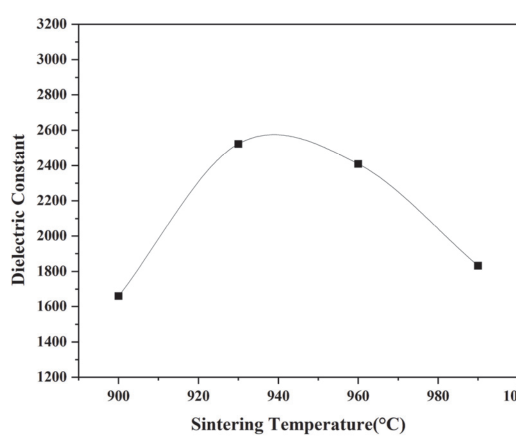


Fig. 7. Dielectric constant (ε_r) with the variations of sintering temperature.

Table 1. The physical properties of the specimens with the variations of sintering.

Sintering temperature (°C)	Density (g/cm^3)	k_p	k_{31}	Qm	Dielectric constant	d_{31} (pC/N)	g_{31} (mV.m/N)
900	7.80	0.540	0.298	70.06	1660	147	10.00
930	7.90	0.602	0.385	70.90	2522	229	10.13
960	7.79	0.600	0.381	61.93	2409	222	10.40
990	7.81	0.590	0.272	58.72	1832	136	8.38

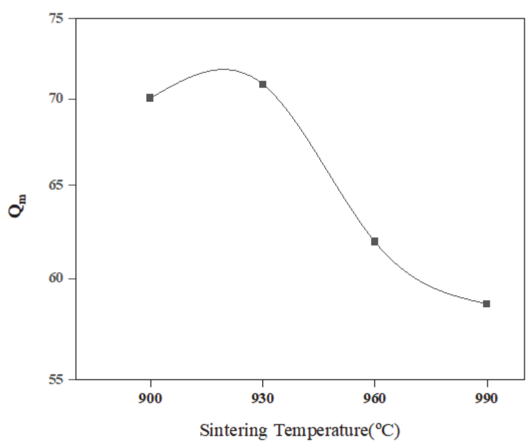


Fig. 8. Mechanical quality factor (Q_m) with the variations of sintering temperature.

temperature. The maximum value of 70.9 appeared at 930°C. Taking into consideration the dielectric and piezoelectric properties of εr = 2,552, k_{31} = 0.385, d_{31} = 229 [pC/N], g_{31} = 10.13 [mV.m/N], Qm = 70.90, kp = 0.602, it was suitable as a length extensional vibration mode energy harvesting device.

Table 1 shows the physical properties of the specimens manufactured by changing the sintering temperature from 900°C to 990°C.

In this study, 0.03 $Pb(Mg_{1/2}W_{1/2})O_3$-0.09 $Pb(Ni_{1/3}Nb_{2/3})O_3$–0.88 $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PMW-PNN-PZT) ceramics were manufactured by the variations of sintering temperature from 900°C to 990°C to develop a composition ceramics for energy harvesting devices. Their dielectric and piezoelectric properties were investigated. The results obtained from the experiment are as follows.

1. The ceramic specimens showed a rombohedral-tetragonal (R-T) phase coexistence phase.

2. The maximum density of the specimens was 7.90 [g/cm^3] in the ceramics sintered at 930°C.

3. Excellent values of dielectric constant = 2,552, density = 7.90 g/cm^3, kp = 0.602, k_{31} = 0.385, d_{31} = 229 [pC/N], g_{31} = 10.13 [mV.m/N], Qm = 70.90 were obtained in the composition ceramics sintered at 930°C. These values were suitable for the application of energy harvesting device and ultrasonic device.

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