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The Effects of MnO_2 Addition on the Physical Properties of $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$-$Pb(Mg_{1/2}W_{1/2})O_3$-$BiFeO_3$ Ceramics

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Abstract: In this paper, for the application to multi-layer piezoelectric devices capable of being used in piezoelectric speakers, $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$-$BiFeO_3$ ceramics substituted with $Pb(Mg_{1/2}W_{1/2})O_3$ were manufactured according to MnO_2 addition, and their physical properties were studied. At non-doped MnO_2 added specimen, the maximum values of piezoelectric properties were shown, respectively: the ε_r of 2182, d_{33} of 513 pC/N, and k_p of 0.634. When taking into consideration the low dielectric constant and high d_{33} in case of increasing the numbers of multilayer in ceramics, the x = 0.2 composition ceramics was suitable for the device application such as speaker using low-temperature sintering multilayer piezoelectric actuators.

Keywords: low temperature sintering ceramics; d_{33}; k_p; piezoelectric properties

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1. Introduction

Recently, the regulations on hazardous substances have been strengthened. In particular, the manufacture and disposal of environmental pollutants have been severely restricted across all the electrical and electronic products. In the field of electronic ceramics, PZT system ceramics sintered above 1200 °C can cause in general the environmental pollution caused by PbO, which exhibits the rapid volatilization characteristics at around 1000 °C, because the PZT ceramics are composed of PbO over 60–70% [1–4]. Accordingly, in order to solve these problems, it is required to develop the low temperature sintering ceramics with high physical properties which can restrain the deteriorations of dielectric and piezoelectric properties in case of sintering at low temperature. $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ ternary ceramics widely used as a compositions for piezoelectric speakers due to its large piezoelectric d_{33} constant can enhance piezoelectric properties through increasing the kp and d_{33} by the substitution of PMW or PZN instead of PNN [5–8]. Here, it is possible to sinter the ceramics at the temperature below 920 °C through the addition of sintering aids of ZnO, CuO, Li_2CO_3, and $CaCO_3$.

Piezoelectric speakers have high sound pressure levels at high-frequency ranges, while they have low sound pressure levels at low-frequency ranges because of a solid state device. To increase the sound pressure at low frequencies, the frequency constant must be lowered, the number of stacked actuators must be increased in order to improve the generation power. Moreover, the piezoelectric d_{33} constant must be increased to increase the displacement. The composition ceramics applied to the LG G-8 smartphone has a rather high dielectric constant [1]. Such a high dielectric constant (ε_r) has caused a problem that a high power consumption is accompanied by an increase in capacitance (C) when the piezoelectric speaker is manufactured. In particular, when the piezoelectric speaker is made as a multi-layer type, the capacitance C value further can increase in proportion to the number of stacks, and the use of a material with a high dielectric constant can cause restrictions on the number of stacks because capacitance C is proportional to dielectric constant (ε_r). Therefore, to lower the dielectric constant of the ceramics is required. And also, for price competitiveness, pure Ag or Ag rich-Pd electrodes must be utilized [9–11]. Since the sintering temperature of the composition applied to the LG G-8 is currently

950 °C, Ag/Pd = 90/10 is used as an internal electrode. Therefore, the simultaneous firing process with Ag/Pd internal electrode should be applied during the lamination process for manufacturing the multilayer device. However, in this process, in order to use inexpensive pure Ag/Pd = 95/05 as an electrode, the sintering temperature of the ceramic must be 920 °C or less.

In addition, when the applied voltage is increased when driving the multilayer actuator, the sound pressure can increase, so it is good to increase the applied voltage while increasing the number of layers.

However, when the coercive electric field Ec is small, a de-poling problem in the multilayer actuator may occur, and the piezoelectric performance can be decreased.

Therefore, in order to prevent these phenomena, there is urgently required to develop the composition ceramics with a coercive electric field of 11 kV/cm or more.

For manufacturing the ceramics sintered at low temperature for multilayer piezoelectric device application, $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$-$BiFeO_3$ composition ceramics substituted with $Pb(Mg_{1/2}W_{1/2})O_3$ with the piezoelectric d_{33} constant was selected and MnO_2 was added, and their physical properties were studied.

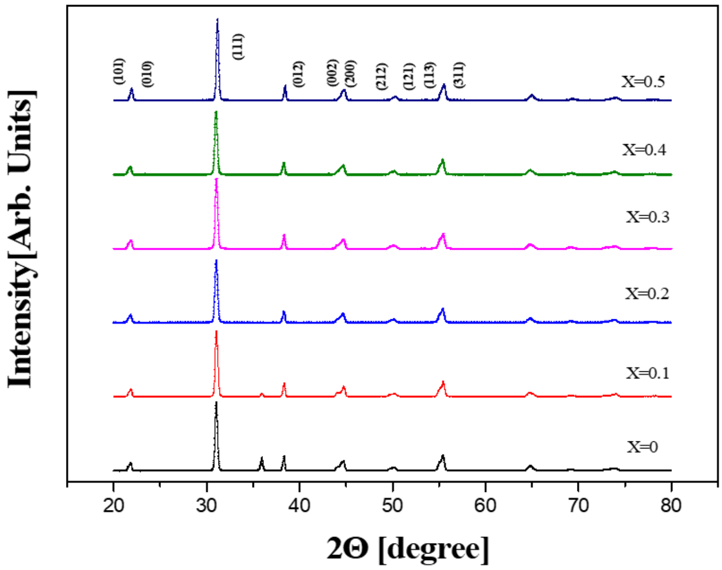
2. Experimental

The samples were fabricated using a conventional mixed oxide process. The composition ceramics used in this experiment were as follows; $0.99[0.03Pb(Mg_{1/2}W_{1/2})O_3$-$0.09Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.88Pb(Zr_{0.5}Ti_{0.5})O_3] + 0.01\ BiFeO_3 + 0.2$ wt%Li_2CO_3 + 0.25wt% $CaCO_3$ + x wt% MnO_2 (x = 0 ~ 0.5).

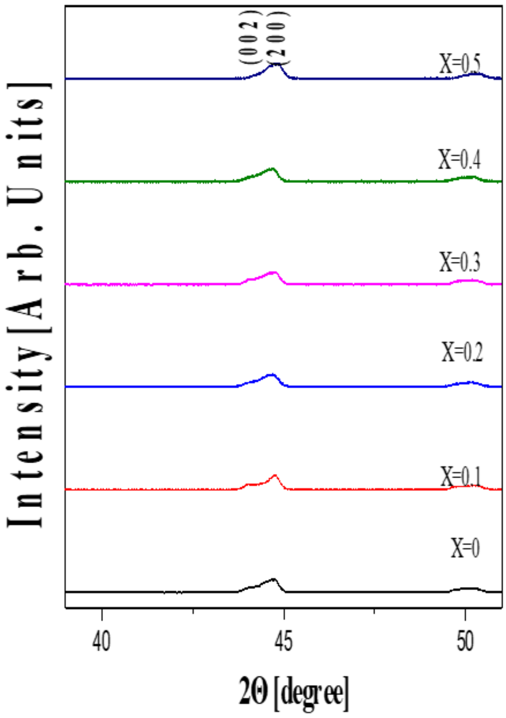
The raw materials like PbO, ZrO_2, TiO_2, NiO, MnO_2, Nb_2O_5, MgO, and WO_3 for the above composition were weighted by mole ratio and the powders were ball-milled for 24 h. After drying, they were calcined at 850 °C for 2 h. And then, sintering aids $CaCO_3$ and Li_2CO_3 were added, ball-milled, and dried. A 5% polyvinyl alcohol was added to the ceramic powders. The powders were molded by the pressure of 1 ton/cm^2 in a mold which has a diameter of 17 millimeters, burned out at 600 °C for 3 h, and then sintered at 920 °C for 2 h. The density was measured using Archimedes method. For measuring the physical properties, the samples were polished and then electrodeposited with Ag paste. The poling was performed at 120 °C in a silicon oil bath by applying DC Electric Fields of 30 kV/cm for 30 min. The microstructure and crystal structure of samples were measured using a scanning electron microscope (SEM: Model Hitachi, S-2400) and X-ray diffraction (XRD: Rigaku, D/MAX-2500H), respectively. For investigating the dielectric properties, capacitance C was measured at 1 kHz using an ANDO AG-4034 LCR meter. For the purpose of investigating the piezoelectric characteristics, by using an impedance analyzer (Agilent 4294A), fr and fa were measured according to IRE standard, and then kp and Qm were calculated.

3. Results and Discussion

Figure 1 presents X-ray diffraction patterns of samples sintered at 920 °C with MnO_2 addition. Pure perovskite phases were presented at all samples and no secondary phases are observed in the measurement range of XRD except for x = 0 and 0.1. As shown in Fig.1b, the ceramic specimens possess a weak rombohedral-tetragonal (R-T) phase coexistence from (002) and (200) peak along with the rhombohedral (200) peak between 40° and 50° from x = 0 to x = 0.3. Above x = 0.4, rombohedral phase appeared. Figure 2 presents the microstructure of samples sintered at 920 °C according to the amount of MnO_2 addition. As can be seen in Figure 2, the average grain sizes gradually increased up to 6.13 µm at 0.1 wt% MnO_2 with increasing MnO_2 addition and then reduced over 0.2 wt% MnO_2 addition.



(**a**)



(**b**)

Figure 1. XRD pattern with the amount of MnO_2 addition (**a**) Wide range (**b**) Narrow range.

Figure 3 shows density with MnO_2 addition. The highest density of samples was increased up to 7.845 g/cm^3 and 0.4 wt% MnO_2 addition. Thereafter, the density was decreased due to the over addition of MnO_2. These phenomena can be explained by the fact that the Mn^{3+} ion can facilitate the particle diffusion by playing the role of acceptor dopant. Subsequently, the densification of specimens was enhanced [1].

Figure 4 shows k_p according to MnO_2 addition. The k_p of samples increased according to the increase of the amount of MnO_2 addition. The k_p of samples showed the highest value of 0.634 at non doped MnO_2 addition and then decreased due to acceptor dopant Mn^{3+} ion.

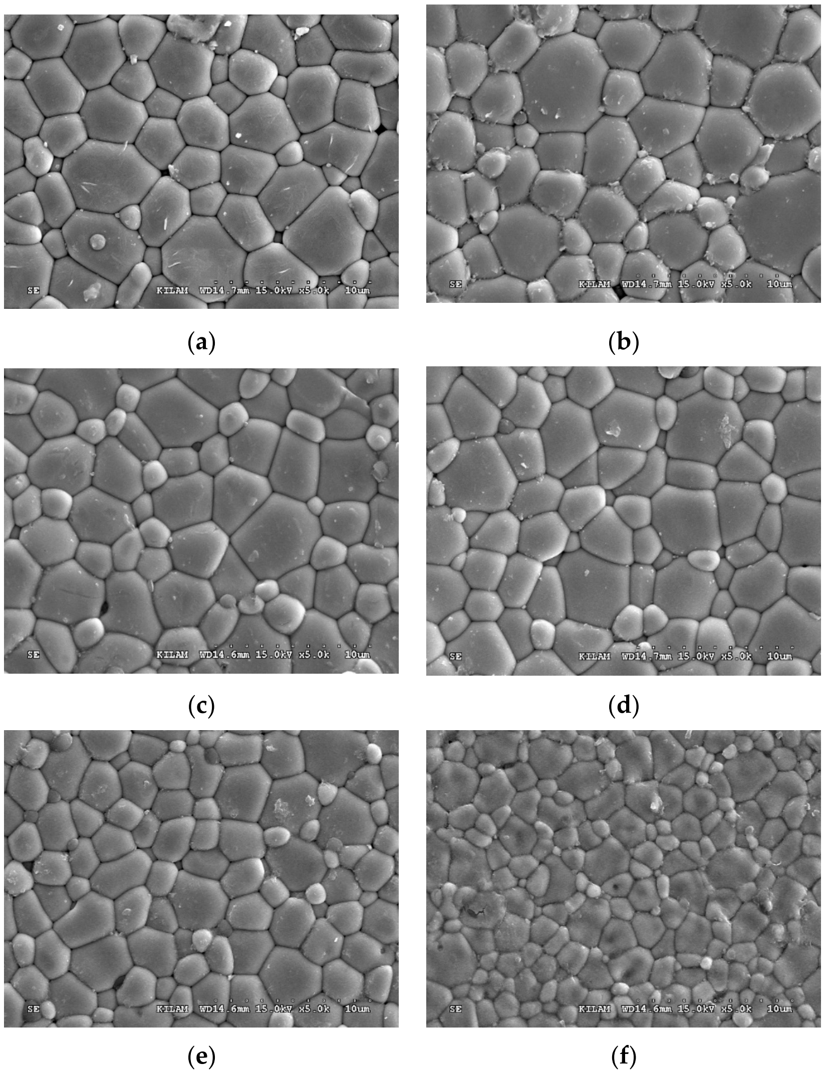


Figure 2. The SEM micrographs of the PMW-PNN-PZT with MnO_2 addition (**a**) x = 0 wt% (**b**) x = 0.1 wt% (**c**) x = 0.2 wt% (**d**) x = 0.3 wt% (**e**) x = 0.4 wt% (**f**) x = 0.5 wt%.

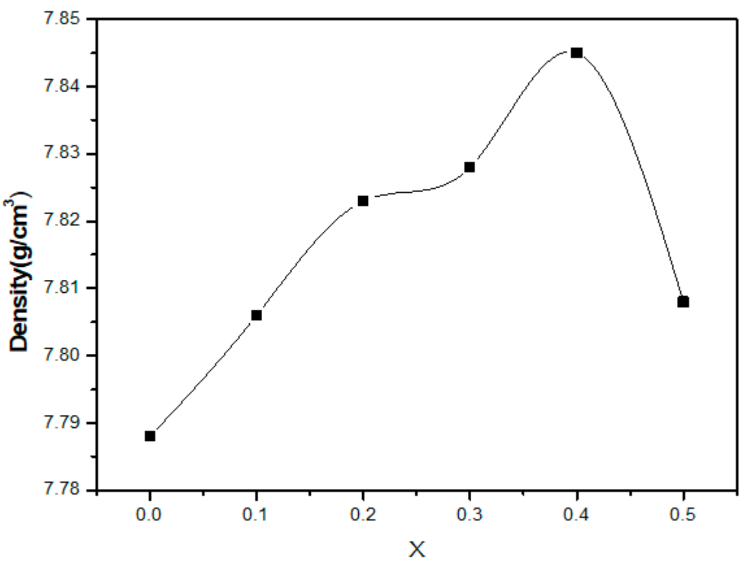


Figure 3. Density with MnO_2 addition.

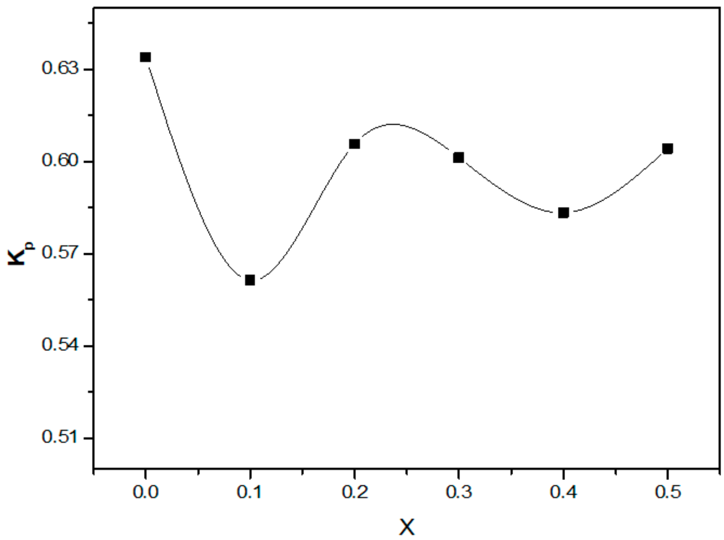


Figure 4. Electromechanical coupling factor (k_p) with MnO_2 addition.

Figure 5 presents d_{33} according to MnO_2 addition. The d_{33} of samples decreased according to the increase of the amount of MnO_2 addition. The d_{33} of samples showed the highest value of 513 (pC/N) at non doped MnO_2 addition. It is considered that the Mn^{3+} ion can play a role of acceptor dopant by the substitution of Zr^{4+} and Ti^{4+} ion sites.

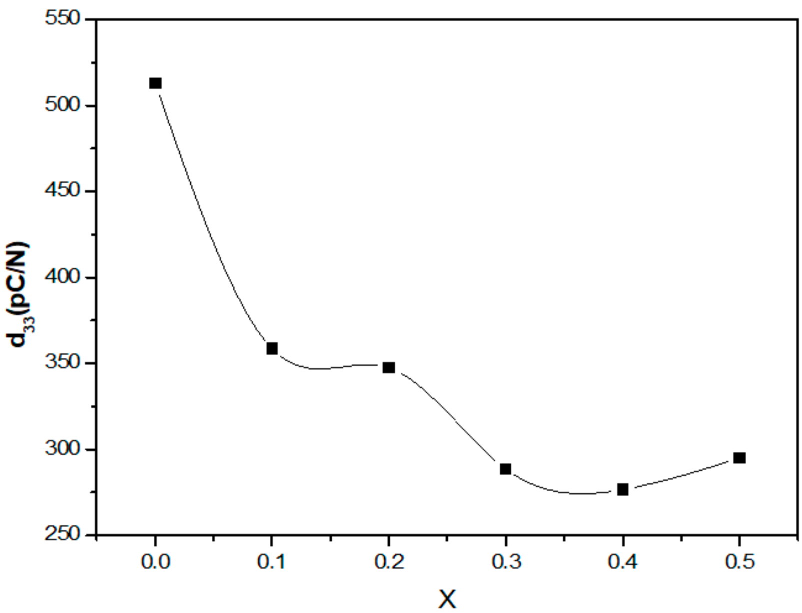


Figure 5. Piezoelectric constant (d_{33}) with MnO_2 addition.

Figure 6 presents Q_m according to MnO_2 addition. The behavior of Q_m showed opposite trends with k_p. That is, as the amount of MnO_2 addition increased, the value of Q_m increased because the substitution of Mn^{3+} ion for Zr^{4+}, Ti^{4+} ion sites can increase the oxygen vacancy of the ceramics.

Figure 7 presents ε_r according to MnO_2 addition. The ε_r of specimens decreased according to the increase of the amount of MnO_2 addition and was nearly consistent with the trends of piezoelectric constant d_{33}.

Figure 8 presents the temperature dependence of dielectric constant (ε_r) according to MnO_2 addition. The Curie of specimens slowly decreased with the increase of the amount of MnO_2 addition.

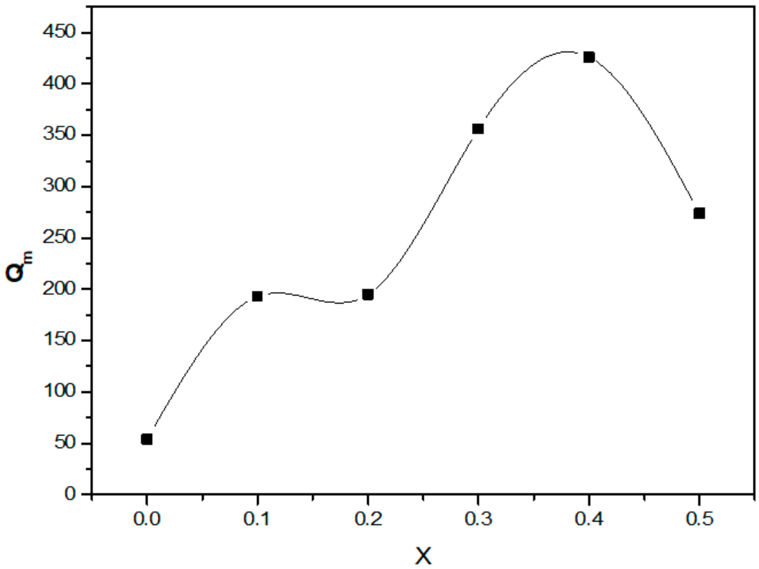


Figure 6. Mechanical quality factor (Q_m) with MnO_2 addition.

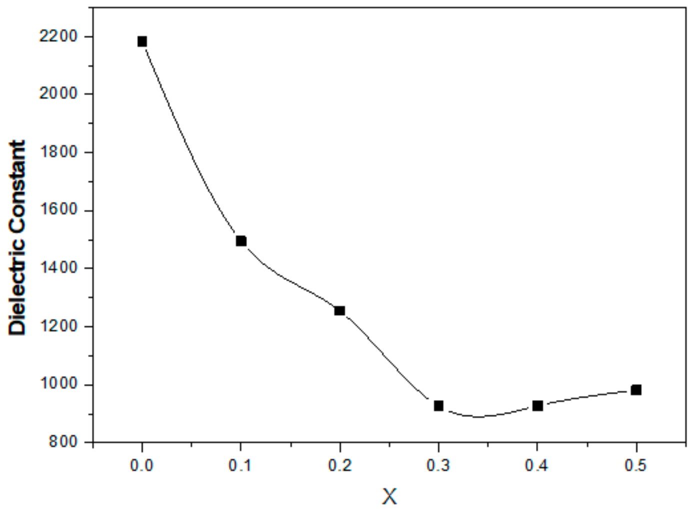


Figure 7. Dielectric constant (ε_r) with MnO_2 addition.

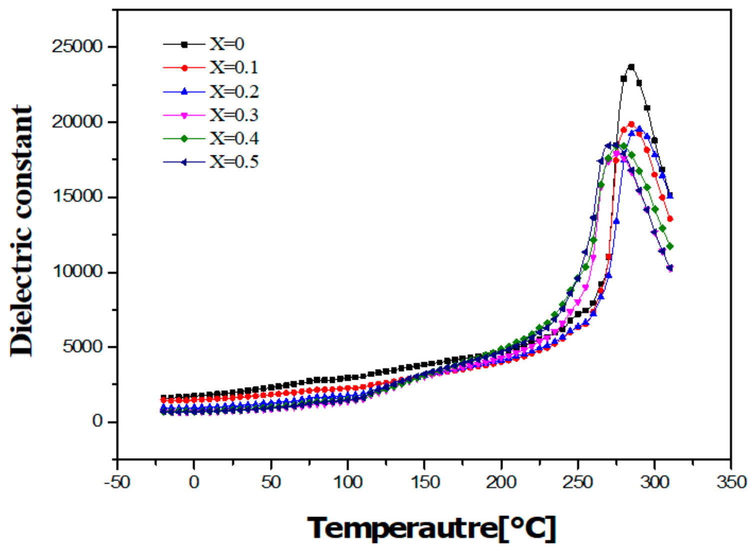


Figure 8. Temperature dependence of dielectric constant (ε_r) with MnO_2 addition.

Taking into consideration the physical properties of ε_r = 1250, d_{33} = 347 pC/N, and k_p = 0.605 were suitable for the device application such as speaker using low-temperature sintering multilayer piezoelectric actuators [1].

Table 1 shows the physical properties of specimens manufactured according to the amount of MnO_2 addition.

Table 1. Physical properties with MnO_2 addition.

X	Density [g/cm^3]	k_p	Dielectric Constant	d_{33} [pC/N]	g_{33} [mV·m/N]	Q_m	Tc (°C)
0	7.788	0.634	2182	513	26.55	54	285
0.1	7.806	0.561	1495	358	27.04	193	285
0.2	7.823	0.605	1250	347	31.25	195	290
0.3	7.828	0.601	926	288	35.12	356	280
0.4	7.845	0.583	927	276	33.60	426	275
0.5	7.808	0.604	982	295	33.90	274	275

4. Conclusions

For the application to multi-layer piezoelectric devices capable of being used in piezoelectric speakers, $Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$-$BiFeO_3$ ceramics substituted with $Pb(Mg_{1/2}W_{1/2})O_3$ were manufactured according to MnO_2 addition, and their physical properties were studied. The results obtained from the experiments are as follows:

The ceramic composition showed weak rombohedral-tetragonal (R-T) phase coexistence from x = 0 to x = 0.3.

At non-doped MnO_2 added specimen, the maximum values of piezoelectric properties were shown, respectively: the ε_r of 2182, d_{33} of 513 pC/N, and k_p of 0.634. In case of increasing the numbers of multilayer in ceramics.

At x = 0.2 compositions, the ε_r of 1250, d_{33} of 347 pC/N, and k_p of 0.605 were suitable for the device application such as speaker using low-temperature sintering multilayer piezoelectric actuators.

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