Piezoelectric Characteristics of 0.55Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.45Pb(Zr,Ti)O$_3$ Ceramics with Different MnO$_2$ Concentrations for Ultrasound Transducer Applications

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Abstract: In this study, we investigate the piezoelectric characteristics of 0.55Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.45Pb(Zr,Ti)O$_3$ (PNN-PZT) with MnO$_2$ additive (0, 0.25, 0.5, 1, 2, and 3 mol%). We focus on the fabrication of a piezoelectric ceramic for use as both actuator and sensor for ultrasound transducers. The actuator and sensor properties of a piezoelectric ceramic depend on the piezoelectric strain coefficient $d$ and piezoelectric voltage coefficient $g$, related as $g = d/\varepsilon^T$. To increase $g$, the dielectric constant $\varepsilon^T$ must be decreased. PNN-PZT with MnO$_2$ doping is synthesized using the conventional solid-state reaction method. The electrical properties are determined based on the resonant frequencies and vibration modes measured by using an impedance analyzer. The MnO$_2$ addition initially improves the tetragonality of the PNN-PZT ceramic, which then saturates at a MnO$_2$ content of 1 mol%. Therefore, the dielectric constant and piezoelectric coefficient $d_{33}$ steadily decrease, while the mechanical properties ($Q_m$, Young’s modulus), $\tan\delta$, electromechanical coupling coefficient $k$, and piezoelectric voltage coefficient $g$ were improved at 0.5–1 mol% MnO$_2$ content.

Keywords: piezoelectric ceramic; 0.55Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.45Pb(Zr,Ti)O$_3$; MnO$_2$ doping; electrical properties

1. Introduction

Piezoelectric materials have attracted considerable interest for various applications such as multi-layer ceramic actuator, transducer, sensor and actuator applications, and for analyses on fundamental science. Lead-based piezoelectric ceramics such as Pb(Zr,Ti)O$_3$ (PZT) have been extensively used in electrical devices because of their excellent piezoelectric properties [1]. Recently, the policies suggesting lead elimination have triggered studies on alternative compounds such as (K$_{0.44}$Na$_{0.52}$Li$_{0.04}$)-(Nb$_{0.66}$Ta$_{0.10}$Sb$_{0.04}$)O$_3$ (KNL-NTS) [2]. However, the lead-based compositions have exhibited higher piezoelectric performances than those of the lead-free compositions such as KNL-NTS.

Recently, many piezoelectric ceramic compositions of the ternary system have been reported as the ternary system has a larger morphotropic phase boundary (MPB) area than that of a secondary system such as PZT. Lead-based relaxor ferroelectrics have a general formula of Pb(B'+B'')O$_3$ (where B' is Mg$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, Sc$^{3+}$, In$^{3+}$, Mn$^{4+}$, and Sn$^{4+}$ and B'' is Nb$^{5+}$, Ta$^{5+}$, Sb$^{5+}$, and W$^{6+}$) [3,4]. In this ternary system, 0.55Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.45Pb(Zr,Ti)O$_3$ (PNN-PZT) has attracted increasing attention owing to its excellent piezoelectric properties. Modifications of lead-based relaxor ferroelectrics have been extensively investigated to improve the piezoelectric properties. In 1974, Luff et al. [5] investigated a 0.5Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.35PbTiO$_3$-0.15PbZrO$_3$ solid solution in the PNN-PZT ternary
system and observed excellent piezoelectric properties. Vittayakorn et al. [6] reported the phase diagram between PNN and PZT \((1-x)\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{Pb(Zr}_{x}\text{Ti}_{1-x})\text{O}_3 (x = 0.4–0.9)), where the \(Zr/Ti\) composition was fixed close to the MPB of PZT, and new MPB within this system. Cao et al. [7] investigated \(0.3\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbZrO}_3(0.7-x)\text{PbZrO}_3 (x = 0.33–0.43)\) as a function of the content of \(\text{PbTiO}_3\). Nam et al. [8] reported the \(0.35\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.65\text{Pb(Zr}_{x}\text{Ti}_{1-x})\text{O}_3 (x = 0.56–0.63)\) ceramic composition sintered at \(1200^\circ\text{C}\) with good electrical properties including \(d_{33} = 605\ \text{pC/N}, K_p = 0.61,\) and \(\varepsilon_r = 3600\). Du et al. [3] have reported the \(0.55\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.35\text{BiScO}_3-0.6\text{PbTiO}_3-0.05\text{Pb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\) ceramic. Liu et al. [4] investigated \(0.55\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.45\text{Pb(Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3\) with varying MnO\(_2\) additive content and reported high performance \((d_{33} = 1070\ \text{pC/N}, K_p = 0.69, \varepsilon_r = 8710,\) and \(\tan\delta = 26 \times 10^{-3}\). Figure 1 shows the reported compositions of the PNN-PZT ceramics.

**Figure 1.** Schematic phase diagram of \(\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3-\text{PbZrO}_3\) ceramics.

The doping of proper elements is an effective approach to enhance their properties for targeted applications. Yu et al. [9] investigated the effects of MnO\(_2\) additive on the \(0.12\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.48\text{PbTiO}_3-0.40\text{PbZrO}_3\) ceramic. A 0.15 wt\% MnO\(_2\)-doped sample exhibited enhanced piezoelectric properties, including \(K_p = 0.68, \varepsilon_r = 3069, Q_m = 181,\) and \(\tan\delta = 5.4 \times 10^{-3}\). Bamiere et al. [10] reported that a Sr-doped 0.674\text{Pb,Nd(Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3-Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3 exhibited good ferroelectric properties at low sintering temperatures. Du et al. [11] investigated the effects of small additions of \(x\text{Fe}_2\text{O}_3 (x = 0–1.6\ \text{mol\%})\) on the microstructures and electrical properties of \(0.55\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.45\text{Pb(Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3\) ceramics sintered at \(1200^\circ\text{C}\) for 2 h and reported high piezoelectric performances at 1.2 mol\% of Fe\(_2\)O\(_3\) \((\rho = 7.97\ \text{g/cm}^3, d_{33} = 956\ \text{pC/N}, K_p = 0.74, \varepsilon_r = 6095,\) and \(\tan\delta = 26 \times 10^{-3}\)). Yoo et al. [12] reported high values of piezoelectric properties \((\rho = 7.816\ \text{g/cm}^3, d_{33} = 356\ \text{pC/N}, K_p = 0.597, \varepsilon_r = 920, Q_m = 1186)\) for the 0.2 wt\% MnO\(_2\) \((0.82\text{Pb(Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.12\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.86\text{Pb(Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3\) ceramic. Liao et al. [13] reported that Fe doping largely reduced \(\tan\delta\) and \(d_{33}\), but improved \(Q_m\) and tetragonality of the \(0.35\text{BiScO}_3-0.6\text{PbTiO}_3-0.05\text{Pb(Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3\) ceramic. Liu et al. [4] investigated \(0.55\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.45\text{Pb(Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3\) (PNN-PZT) with varying MnO\(_2\) additive content and reported high performance \((d_{33} = 710\ \text{pC/N}, K_p = 0.595, \varepsilon_r = 3092.25, \tan\delta = 14.9 \times 10^{-3}, Q_m = 176)\) at a MnO\(_2\) content of 1 mol\%. Table 1 shows piezoelectric ceramic and properties according to doping from references.
Most lead-based relaxor ferroelectrics such as PNN-PZT have high dielectric constants and $d_{33}$ values, but low $\varepsilon_{33}$ values and poor mechanical properties ($Q_m$, Young’s modulus) for applications as sensors [13]. Modifications of the properties of the ternary complex systems have not been extensively investigated. The doping of materials such as FeO$_3$ and MnO$_2$ can be used to easily change the properties of ternary complex systems. To improve the $\varepsilon_{33}$ values and mechanical properties of the PNN-PZT systems, Mn can be added to selectively improve sensor characteristics. The MnO$_2$ doping can improve the sinterabilities of lead-based relaxor ceramics owing to the increase in number of oxygen vacancies, generated by the substitutions of the high-valence Ti$^{4+}$ and Zr$^{4+}$ in the perovskite lattice by the low-valence Mn$^{2+}$ and/or Mn$^{3+}$ [4]. The oxygen vacancies in the perovskite lattice can promote lattice diffusion, thus assisting the sintering and grain growth [12], as the grain boundary movement is dragged by these defects. The pores in the lead-based relaxor ceramics easily diffuse through the movement of oxygen vacancies and are eliminated at the grain boundaries. Therefore, the densification of the ceramic originated from the introduction of MnO$_2$ improving the piezoelectric properties [13]. It is possible to adjust the properties of the PNN-PZT ceramic according to the MnO$_2$ content.

The aim of this study was to better understand the effects of doping on PZT-based complex ceramics and improve the sensing performances and mechanical properties by using MnO$_2$ as an additive in the 0.55Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.135PbZrO$_3$-0.315PbTiO$_3$ ternary ceramic. The effects of the MnO$_2$ content on the piezoelectric, dielectric, and mechanical properties of the ceramic were investigated.

### 2. Synthesis of the MnO$_2$-Doped PNN-PZT

The ceramics of PNN-PZT + MnO$_2$ (0, 0.25, 0.5, 1, 2, and 3 mol%) were synthesized by using the conventional solid-state method. Raw material powders (PbO, NiO, Nb$_2$O$_5$, ZrO$_2$, and TiO$_2$) (Sigma Aldrich, 99.99%, Gillingham, UK) and MnO$_2$ additive (Sigma Aldrich, 99.99%, Gillingham, UK) were weighed in chemically stoichiometric proportions and ball-milled with distilled water for 24 h. After the ball milling, the slurry was dried at 80 °C, and then calcined at 900 °C (heating rate: 100 °C/h) for 2 h. The calcined powders were ball-milled again for 24 h with a 5 wt% polyvinyl alcohol (PVA) (Sigma Aldrich, 99+%, Gillingham, UK, $M_w = 89000–98000$) solution as a binder for ceramic formation. The mixture was dried and crushed by a high-energy ball mill. The powder was sieved to control the particle size below 5 μm. The sieved powder was pressed into a mold (Φ = 30 mm) under a pressure of 100 MPa. The PVA in the ceramic disk was burnt out at 600 °C (heating rate: 100 °C/h) for 2 h. Subsequently, the ceramic disk was sintered at 1200 °C (heating rate: 100 °C/h) for 2 h with a spacer powder in an alumina crucible [14]. The sintered PNN-PZT ceramic disk was polished and coated with silver paste to obtain electrodes on both surfaces. The samples were polarized by applying a direct-current (DC) electric field of 2.5 kV/mm for 30 min at 50 °C in silicon oil.

### Table 1. Literature table of piezoelectric ceramic and properties according to doping materials.

| Authors | Piezoelectric Ceramic | Doping | Properties |
|---------|-----------------------|--------|------------|
| Yu et al. [9] | 0.12Pb(Ni$_{1/3}$Sb$_{2/3}$)-0.48PbTiO$_3$-0.4PbZrO$_3$ | MnO$_2$ | $K_p = 0.68$, $\varepsilon_r = 3069$, $Q_m = 181$, $\tan \delta = 5.4 \times 10^{-3}$ |
| Bamieh et al. [10] | 0.67PbNd(Zr, Ti)O$_3$-Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ | SrCO$_3$ (0–4 mol%) | Lower the sintering temperature |
| Du et al. [11] | 0.55Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.45Pb(Zn$_{1/3}$Ti$_{2/3}$)O$_3$ | Fe$_2$O$_3$ (0–1.6 mol%) | $\rho = 7.97 \ g/\ cm^3$, $d_{33} = 956 \ pC/N$, $K_p = 0.74$, $\varepsilon_r = 6905$, $\tan \delta = 26 \times 10^{-3}$ |
| Yoo et al. [12] | 0.02Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.12Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.86Pb(Zn$_{1/3}$Ti$_{2/3}$)O$_3$ | MnO$_2$ | $\rho = 7.816 \ g/\ cm^3$, $d_{33} = 356 \ pC/N$, $K_p = 0.597$, $\varepsilon_r = 920$, $Q_m = 1186$ |
| Liao et al. [13] | 0.35BiScO$_3$-0.6PbTiO$_3$-0.05Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ | Fe$_2$O$_3$ (0–1.6 mol%) | Largely reduced $\tan \delta$ and $d_{33}$, but improved $Q_m$ |
| Liu et al. [4] | 0.55Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.45Pb(Zn$_{1/3}$Ti$_{2/3}$)O$_3$ | MnO$_2$ | $d_{33} = 710 \ pC/N$, $K_p = 0.595$, $\varepsilon_r = 3092.25$, $\tan \delta = 14.9 \times 10^{-3}$, $Q_m = 176$ |
The crystal structures of the sintered samples were characterized by X-ray diffraction (XRD) (X’pert Pro Powder, PANalytical, Netherlands). The surface microstructures of the as-sintered ceramics were observed by using field-emission scanning electron microscopy (SEM) (JSM-5900, JEOL, Akishima City, Japan). Three PNN-PZT specimens were fabricated for each composition. Their properties were measured, and then the average values were calculated. The piezoelectric coefficients (d_{33}) of the piezoelectric ceramics were measured by using a quasi-static piezoelectric d_{33} meter (HY2730, Yangzhou, China). The planar electromechanical coupling coefficients (k_p, k_{31}), piezoelectric coefficient (d_{31}), mechanical factor (Q_m), dielectric constant (\epsilon_r = \epsilon_r^{T33}/\epsilon_0, \epsilon_0 = 8.854 \times 10^{-12} \text{F/m}), piezoelectric voltage coefficients (g_{33}, g_{31}), and Young’s modulus (Y_{11}) were determined according to the method of resonance and antiresonance frequencies by using an impedance analyzer (HP 4194A, Agilent, Santa Clara, CA, USA) based on the Institute of Electrical and Electronics Engineers (IEEE) standards. Length-mode specimens (22 by 4 by 0.8 mm^3) were used to calculate Y_{11}, k_{31}, d_{31}, and g_{31}.

3. Results and Discussion

3.1. Phase and Microstructure

Figure 2 shows XRD patterns of the 0.55PNN-0.45PZT ceramics doped with different MnO_2 contents (0, 0.25, 0.5, 1, 2, and 3 mol%). All samples exhibited typical ABO_3 perovskite structures without the pyrochlore phase. Rhombohedral and tetragonal phases were found to coexist in the PNN-PZT ceramics.

As shown in Figure 3, the XRD patterns were fitted by Gaussian functions in the 2θ range of 44.5–45.5°. The (200) peak consisted of three peaks, tetragonal (200) and (002) diffractions peaks presented in green and blue, respectively, and rhombohedral (200) diffraction peak presented in magenta. The red peak represents the overlap intensities of T(200), T(002), and R(200). Figure 2 shows the apparent changes in diffraction peaks, which indicate a gradual rhombohedral-to-tetragonal phase transition. Tetragonality is a crucial structural parameter of the perovskite lattice because it may affect the material properties. The tetragonality was calculated as \( I_{T(200)}/I_{R(200)} \), where \( I_{T(200)} \) is the T(200) intensity and \( I_{R(200)} \) is the R(200) intensity of the XRD pattern in Figure 3. As shown in Figure 4, with the increase in MnO_2 content, the tetragonality of the PNN-PZT ceramic initially largely increases, and then saturates at MnO_2 contents higher than 1 mol% [13].
Figure 3. XRD patterns of the 0.55PNN-0.45PZT ceramics with different MnO$_2$ contents in the 2θ range of 44.5–45.5°. T represents the tetragonal phase, while R represents the rhombohedral phase.

Figure 4. Tetragonality of the 0.55Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.45Pb(Zr,Ti)O$_3$ (PNN-PZT) ceramic as a function of the MnO$_2$ content in the range of 0–3 mol%.

Figure 5 shows SEM images of the PNN-PZT ceramics with MnO$_2$ contents of 0–3 mol%. The pure PNN-PZT ceramic exhibited small grain sizes (microstructures) of almost 1.5 µm. When a small amount of MnO$_2$ was added, the grain size of the microstructure was increased. The maximum average grain size of 2.8 µm was observed in PNN-PZT with the MnO$_2$ content of 3 mol%.

Figure 5. SEM images of the PNN-PZT ceramics with 0–3 mol% MnO$_2$ content.
3.2. Dielectric Properties

Figure 6 shows the dielectric constants $\varepsilon_r$ and dielectric losses $\tan\delta$ (%) of the PNN-PZT ceramics with different MnO$_2$ concentrations measured at 1 kHz at room temperature. The dielectric loss largely decreased with the MnO$_2$ content of 1 mol%, and then steadily increased in the MnO$_2$ range of 1 to 3 mol%. The dielectric loss reached the maximum (5.6%) for the undoped PNN-PZT ceramic and minimum (1.6%) for the 1 mol% MnO$_2$ sample. Therefore, the dielectric loss decreased by almost five times upon slight MnO$_2$ doping. This is consistent with the change rate of the tetragonality. The dielectric loss rapidly decreased with the increase in tetragonality from 0 to 1 mol%. The dielectric loss was improved at MnO$_2$ content above 1 mol%, because the tetragonality was saturated at 1 mol%. Figure 6 shows the negative and positive effects on the dielectric constant $\varepsilon_r$ and dielectric loss $\tan\delta$ (%). A negative effect, decrease in dielectric constant, was observed with the increase in tetragonality with the MnO$_2$ content. In terms of the dielectric loss, the minimum value could be explained by the competition between the positive effect (increase in tetragonality) and negative effect of the Mn ions on the motion of the wall domains.

With the increase in MnO$_2$ content, the dielectric constant decreased because the hardener Mn ions affected the domain movement. The decrease in dielectric constant was caused by the oxygen vacancies generated by the substitutions of the high-valence Ti$^{4+}$ and Zr$^{4+}$ in the perovskite lattice by the low-valence Mn$^{2+}$ and/or Mn$^{3+}$. The dielectric constant rapidly decreased up to the MnO$_2$ content of 1 mol%. However, the decrease rate of the dielectric constant was smaller at MnO$_2$ contents of 1 to 3 mol%.

![Figure 6. Dielectric constants $\varepsilon_r$ and dielectric losses $\tan\delta$ (%) of the PNN-PZT ceramics with different MnO$_2$ concentrations measured at 1 kHz at room temperature.](image)

3.3. Mechanical Properties

Figure 7 shows the mechanical properties of the PNN-PZT ceramics with varying MnO$_2$ content (0–3 mol%). The mechanical quality factor $Q_m$ reflects the steepness of the resonance of the mechanical vibration around the resonance frequency. Therefore, $Q_m$ has been considered the main parameter of an ultrasonic actuator. $Q_m$ was improved by approximately five times (from 42.70 to 202.26) with the increase in MnO$_2$ content. In addition, the Young’s modulus $Y^E_{11}$ was improved from 7.14 to 10.56 with the increase in MnO$_2$ content (a similar curve shape was observed). The changes in mechanical properties with the MnO$_2$ content can be attributed to the oxygen vacancies generated by the accepter doping effect. Therefore, the densifications of the ceramics resulted from the introduction of MnO$_2$, which improved the piezoelectric properties [13]. The density was improved from 7771.09 to 7938.41 kg/m$^3$ with the increase in MnO$_2$ content (Table 2). The oxygen vacancies improved the mechanical properties.
3.4. Piezoelectric Properties

The electromechanical coupling coefficient \( k_p, -k_{31} \) is a constant representing the piezoelectric efficiency of a piezoelectric ceramic, i.e., it represents the efficiency of conversion of electrical energy into mechanical energy. As shown in Figure 8, \( k_p \) decreased with the increase in MnO\(_2\) content to 0.25 mol\%. However, it was largely increased at MnO\(_2\) contents of 0.25 and 1 mol\%, where it reached the maximum of 0.41. Above this concentration, it steadily decreased in the MnO\(_2\) content range of 1 to 3 mol\%.

\[
d_{3x} = k_{3x} \sqrt{\frac{\varepsilon_{33}^{T}}{Y_{xx}^{E}}}
\]  

(1)

The curve shape of \(-k_{31}\) was different. It had the maximum value for the undoped PNN-PZT ceramic, and then steadily decreased with the increase in MnO\(_2\) content. The \(-k_{31}\) values at 0.25–1 mol\% were similar. At MnO\(_2\) concentrations less than 1 mol\%, the changes may be attributed to the relatively large increase in tetragonality. Above this concentration, \( k_p \) and \(-k_{31}\) decreased owing to the hardener doping effect (acceptor substitution inducing point defects) [12,13]. The piezoelectric coefficients \((-d_{31}, d_{33})\) reflect the distortion originating from the application of an electric field having a uniform strength without stress. Therefore, the piezoelectric coefficients \((-d_{31}, d_{33})\) have been considered the primary parameters of actuators. The piezoelectric coefficient was calculated by using \(-k_{31}, Y_{11}^{E},\) and \(\varepsilon_{33}^{T}\):
Figure 9 shows the piezoelectric coefficients (\(-d_{31}, d_{33}\)) of the PNN-PZT ceramics with varying MnO₂ content (0–3 mol%). \(-d_{31}\) and \(d_{33}\) exhibited similar curve shapes; they decreased with the increase in MnO₂ content because the decrease rate of \(\varepsilon^{T}_{33}\) was considerably higher than the increase rates of \(k_{31}\) and \(Y_{E11}\). The piezoelectric coefficient exhibited the minimum decrease rate between 0.5 and 1 mol% MnO₂, because of the relatively significant increase in tetragonality at 0.5–1 mol%.

![Piezoelectric Voltage Coefficient](image)

Figure 9. Piezoelectric coefficients \(d_{33}\) and \(-d_{31}\) of the PNN-PZT ceramics with different MnO₂ concentrations in the range of 0–3 mol%.

The piezoelectric voltage coefficients (\(-g_{31}, g_{33}\)) reflect the field strength, originating from a uniform applied stress without electrical displacement, and thus they represent the sensor properties. The values of \(-g_{31}\) and \(g_{33}\) were calculated by using the relationship between the piezoelectric coefficient \(d\) and dielectric constant, \(g = d/\varepsilon^{T}\). \(-g_{31}\) exhibited a similar tendency to that of \(k_{31}\) (Figure 10). \(g_{33}\) steadily increased to a high value of \(20.31 \times 10^{-3}\) Vm/N at 1 mol%. However, it was decreased at 2 mol%, and then largely increased to the maximum of \(21.13 \times 10^{-3}\) Vm/N at 3 mol%, as the decrease rate of \(d_{33}\) was smaller than the rate of decrease in \(\varepsilon^{T}_{33}\). Table 2 shows the densities and dielectric, mechanical, and piezoelectric properties of the PNN-PZT samples with different MnO₂ contents (0, 0.25, 0.5, 1, 2, and 3 mol%).

![Piezoelectric Voltage Coefficient](image)

Figure 10. Piezoelectric voltage coefficients \(g_{33}\) and \(-g_{31}\) of the PNN-PZT ceramics with different MnO₂ concentrations in the range of 0–3 mol%.

The MnO₂ doping can affect the PNN-PZT ceramic properties owing to the increase in number of oxygen vacancies generated by the substitutions of the high-valence Ti⁴⁺ and Zr⁴⁺ in the perovskite lattice by the low-valence Mn²⁺ and/or Mn³⁺, as mentioned above [4]. The oxygen vacancies improved the mechanical properties (Young's modulus, \(Q_m\)). The Young's modulus and \(Q_m\) exhibited similar curve shapes. Initially, they were rapidly improved, but their increase rates were reduced at MnO₂.
contents above 1 mol%. The phase of PNN-PZT transformed from rhombohedral to tetragonal with the increase in MnO₂ content. The phase transition is attributed to the enhancements in electrical properties, which led to the piezoelectric property changes. Therefore, the dielectric constant, Young’s modulus, electromechanical coupling coefficients ($k_p$, $g_{31}$, and $g_{33}$) of PNN-PZT changed with the density of MnO₂ [4].

| MnO₂ Content | Density (kg/m³) | $\varepsilon_r$ at 1 kHz | tanδ (%) at 1 kHz | $Q_m$ | $Y_{E_{11}}$ (× 10¹⁰ N/m²) | $K_{31}$ | $k_p$ | $−d_{31}$ (pC/N) | $d_{33}$ (pC/N) | $−g_{31}$ (× 10⁻³ V·m/N) | $g_{33}$ (× 10⁻³ V·m/N) |
|--------------|----------------|--------------------------|-------------------|-------|-----------------------------|---------|------|----------------|----------------|------------------|------------------|
| 0 mol%       | 7771.09        | 4925.51                  | 5.6               | 42.70 | 7.14                        | 0.35    | 0.36 | 243.40         | 746            | 6.40             | 17.10            |
| 0.25 mol%    | 7782.96        | 3772.38                  | 2.85              | 50.99 | 7.70                        | 0.26    | 0.27 | 167.07         | 592            | 5.40             | 17.71            |
| 0.5 mol%     | 7864.18        | 3177.74                  | 1.6               | 63.49 | 8.70                        | 0.27    | 0.32 | 140.40         | 538            | 6.06             | 19.13            |
| 1 mol%       | 7936.33        | 2965.10                  | 1.6               | 139.70| 9.56                        | 0.26    | 0.41 | 115.01         | 533            | 5.99             | 20.31            |
| 2 mol%       | 7938.13        | 2408.93                  | 2.4               | 173.50| 10.11                       | 0.21    | 0.34 | 78.51          | 396            | 5.33             | 18.55            |
| 3 mol%       | 7938.41        | 1826.92                  | 4.5               | 202.26| 10.56                       | 0.18    | 0.28 | 68.98          | 342            | 5.24             | 21.13            |

4. Conclusions

In this study, we investigated the piezoelectric characteristics of 0.55Pb(Ni1/3Nb2/3)O3-0.45Pb(Zr,Ti)O3 according to the MnO₂ additive content (0, 0.25, 0.5, 1, 2, and 3 mol%). We measured $\varepsilon_r$, tanδ, $Q_m$, $Y_{E_{11}}$, $d_{31}$, $d_{33}$, $g_{31}$, and $g_{33}$ as functions of the MnO₂ concentration. The MnO₂ addition initially improved the tetragonality of the PNN-PZT ceramic, which then saturated at a MnO₂ content of 1 mol%.

$Q_m$ and Young’s modulus ($Y_{E_{11}}$) also increased with the MnO₂ content owing to the oxygen vacancies generated by the MnO₂ doping. The dielectric properties and electromechanical coupling coefficient $k$ were optimal at MnO₂ contents of 0.5–1 mol%, where tanδ and $k_p$ had the maximum values. The changes in electrical properties were attributed to the increased tetragonality. PNN-PZT is a soft piezoelectric material more suitable for actuator applications. The addition of MnO₂ to PNN-PZT showed its potentials for use in sensory actuators. In following studies, we aim to investigate vibration control and nondestructive testing applications based on the enhanced PNN-PZT ceramics.

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