Comparative study of the Bi(Ni$_{0.5}$Zr$_{0.5}$)O$_3$–PbTiO$_3$ and Bi(Mg$_{0.5}$Zr$_{0.5}$)O$_3$–PbTiO$_3$ piezoelectric materials for energy harvesters

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1. Introduction

The depletion of fossil fuels has highlighted the importance of renewable energy. Among the various renewable energy technologies, piezoelectric energy harvesting based on mechanical vibration energy is a robust renewable energy source that can convert mechanical energy into electrical energy. To present, lead-free piezoelectric ceramics have been intensively studied for industrial applications. However, owing to the environmental issues, studies on lead-free or reduced-lead-content piezoelectric ceramics for piezoelectric devices are being conducted. Therefore, the world is now focusing on energy harvesting as a new energy source [1–3]. Energy harvesting refers to the technology of harvesting energy from natural energy sources, such as light, magnetism, vibration (piezoelectric), thermal energy, and radio frequency energy. Energy harvesting technology involves the conversion of various types of energies into usable electrical energy. Unlike other types of renewable energy sources, such as solar cells or wind power and fuel cells, piezoelectric energy harvesters are based on mechanical vibration energy. Mechanical vibration energy can be converted into electrical energy using electrostatic, electromagnetic, and piezoelectric effects [4,5]. The conversion efficiency and output property of energy harvesting devices are affected by environmental conditions. The piezoelectric energy harvesters are semi-permanent because they are less limited to environmental factors as long as the ambient vibrations are present. Therefore, piezoelectric energy harvesting is relatively less constrained by external factors than other energy harvesting technologies. In addition, it can be used wherever kinetic energy is available.

Lead zirconate titanate (Pb,Zr)TiO$_3$ (PZT) ceramics are widely used in various fields, such as piezoelectric sensors and actuators [6–8]. Owing to their excellent electrical and mechanical properties, PZT ceramic-based actuators and transducers have attracted significant attention in industrial applications. In addition, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN)-based ceramics, such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbZrO$_3$–PbTiO$_3$ (PMN–PZT) and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbO$_3$ (PMN–PT), are well-known relaxor ferroelectrics, which have broad diffuse and dispersive phase transition. These relaxor ferroelectric ceramics exhibit high dielectric constant and piezoelectric charge coefficient [9,10]. However, recently, there has been an increasing demand for more eco-friendly materials with reduced lead content [11]. Meanwhile, the large ferroelectric property of Bi-based BiMO$_3$ (where M = Sc, Fe, and In, and among others) has been investigated. Moreover, high-temperature ferroelectric ceramics based on (1-x)BiMO$_3$–xBaTiO$_3$, such as BiScO$_3$–PbTiO$_3$, BiFeO$_3$–PbTiO$_3$, and BiInO$_3$–PbTiO$_3$, have been intensively studied [12–14]. However, these materials are not cost-effective due to the need of rare-earth metals such as scandium or indium. There is a strong demand to replace PZT materials with alternative lead-free materials. However, completely lead-free piezoelectric materials have demerits in the piezoelectric charge coefficient. Therefore, reduced lead-content
piezoelectric materials have emerged as potential materials for replacing PZT.

For the first time, piezoelectric 0.4Bi(Ni0.5Zr0.5)O3–0.6PbTiO3 (BNZ-PT) and 0.4Bi(Mg0.5Zr0.5)O3–0.6PbTiO3 (BMZ-PT) ceramics were selected and compared for sensor and actuator applications. By comparing the mol% of lead, it was found that the lead composition of 0.4BNZ-0.6PT piezoelectric ceramics was 40% less than that of PZT. Thus, this piezoelectric material can be considered less harmful than PZT. In addition, 0.4BNZ-0.6PT ceramics showed similar piezoelectric properties to those of PZT ceramics. Therefore, in this study, potential piezoelectric applications, including energy harvesters of BNZ-PT and BMZ-PT ceramics, were presented. BNZ-PT and BMZ-PT piezoelectric ceramics were investigated in this study for the first time. Also, they are considered as alternatives to PZT ceramics [15,16]. BNZ-PT and BMZ-PT have improved dielectric and piezoelectric properties compared to those of other PZT-based piezoelectric materials. However, to date, only limited research has been conducted on this material. In this study, the sintering conditions of BNZ-PT and BMZ-PT were varied to determine the optimized sintering conditions. Then, the piezoelectric and dielectric properties were investigated. Furthermore, we confirmed that the optimized sintering conditions of BNZ-PT and BMZ-PT can result in improved piezoelectric and dielectric properties.

2. Experimental methods

The 0.4Bi(Ni0.5Zr0.5)O3–0.6PbTiO3 (BNZ-PT) and 0.4Bi(Mg0.5Zr0.5)O3–0.6PbTiO3 (BMZ-PT) ceramics were prepared using a conventional solid state reaction process. To produce BNZ-PT powders, Bi2O3 (99.9%, Sigma-Aldrich Co. Ltd.), NiO (99.97%, Kojundo), ZrO2 (99.0%, Sigma-Aldrich Co. Ltd.), PbO (99.0%, Sigma-Aldrich Co. Ltd.), and TiO2 (99.9%, Kojundo) powders were prepared as starting materials. To produce BMZ-PT powders, Bi2O3, 4MgCO3-Mg(OH)2 · SH2O (BioXtra, Sigma-Aldrich Co. Ltd.), ZrO2, PbO, and TiO2 powders were prepared. These powders were ball-milled in ethyl alcohol with zirconia balls for 24 h and dried at 100 °C for 24 h. The dried powders of BNZ-PT and BMZ-PT were calcined at 780°C for 2 h in air. The calcination process was conducted at 700–900°C. After calcination, the powders had a different particle size. The powder calcined at 780°C was small and uniform. These calcined powders were mixed with 5 wt.% poly vinyl alcohol and uniaxially pressed into discs, with a diameter of 12 mm and under a pressure of 300 MPa. Then, the pressed discs were sintered in air at 1050–1200°C for 2 h. At 25°C intervals. The obtained specimens were polished to a thickness of 1 mm and silver paste was applied on both the sides. These specimens were fired at 700°C for 10 min. The volume density of the sintered specimens was measured using the Archimedes method using deionized water as medium. The crystalline structures of the sintered samples were investigated using X-ray diffraction (XRD, Bruker-AXS; New D8-Advance) analysis. The microstructures were observed using field emission scanning electron microscopy (FE-SEM, Carl Zeiss; SIGMA). The frequency-dependent dielectric constant (εr) and dielectric loss tangent of the specimens were measured using an impedance analyzer (Agilent 4294A precision) from 1 kHz to 1 MHz. The samples were poled under a DC electric field for 30 min in a silicon oil bath by employing a high voltage power supply (Hantech poling M/C). The electromechanical coupling coefficient (kp) was estimated by measuring resonance-antiresonance frequencies (Agilent 4294A precision), following IEEE standards at room temperature. The poling temperature and electric field were varied from 20 to 100°C and 1 to 5 kV, respectively. The piezoelectric coefficient (d33) values were measured using a Berlincourt quasi-static d33 meter (YE 2730A).

3. Results and discussion

3.1. Crystalline properties

Figure 1 shows X-ray diffraction patterns of the 0.4Bi(Ni0.5Zr0.5)O3–0.6PbTiO3 and 0.4Bi(Mg0.5Zr0.5)O3–0.6PbTiO3 ceramics sintered at different temperatures in the range from 1050 to 1200°C. The structural characteristics of 0.4BNZ-0.6PT and 0.4BMZ-0.6PT were observed from the XRD analysis results. Figure 1(a) shows the (00 l) and (hk0) peaks for the 0.4BNZ-0.6PT ceramics. In addition, by analyzing the XRD 2θ data, the lattice parameters of c and a, for both the materials, were calculated. For the 0.4Bi(Ni0.5Zr0.5)O3–0.6(Pb,Ti)O3 ceramics, the lattice parameters a and c were 4.173 and 4.272 Å, respectively, whereas for the 0.4Bi(Mg0.5Zr0.5)O3–0.6(Pb,Ti)O3 ceramics, the lattice parameters a and c were 3.998 and 4.124 Å, respectively. Therefore, we can argue that both 0.4Bi(Ni0.5 Zr0.5)O3–0.6PbTiO3 and 0.4Bi(Mg0.5Zr0.5)O3–0.6PbTiO3 ceramics have similar tetragonality.

In particular, (100)/(010) and (200)/(002) peaks gradually split with increasing sintering temperatures. This indicates a phase transition of the 0.4BNZ-0.6PT ceramics from rhombohedral to tetragonal [17–19]. Similarly, for the 0.4BMZ-0.6PT ceramics in Figure 1(b), the splitting peaks were appeared at approximately 22° and 45° with increasing sintering temperature due to a phase transition from rhombohedral to tetragonal.

Also, the XRD patterns show that both 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics were well formed with a perovskite structure. A weak pyrochlore phase peak was observed at approximately 2θ = 28°, according to the XRD JCPDS card (No. 5–543). This secondary peak
Figure 1. X-ray diffraction (XRD) patterns of the 0.4Bi(Ni0.5Zr0.5)O3–0.6PbTiO3 and 0.4Bi(Mg0.5Zr0.5)O3–0.6PbTiO3 ceramics sintered at different temperatures in the range from 1050 to 1200°C.

was attributed to a Zr-rich phase, caused by the evaporation of Bi at high sintering temperatures. As shown in Figure 1(a,b), (002) and (200) peaks were clearly observed by increasing the sintering temperature. This means that the tetragonal structure was more clearly formed by increasing the sintering temperature for 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics. We believe that with enough thermal energy, both BNZ-PT and BMZ-PT ceramics can settle at their optimized phase structure.

Figure 2 displays the bulk densities of the 0.4Bi(Ni0.5Zr0.5)O3–0.6PbTiO3 and 0.4Bi(Mg0.5Zr0.5)O3–0.6PbTiO3 piezoelectric ceramics, which were sintered from 1050 to 1200°C. As shown in Figure 2(a), the density increased with an increase in the sintering temperature, up to 1100°C. When the sintering temperature reached 1100°C, the highest density of 7.16 g/cm³ was observed, and then the density decreased with further increase in the sintering temperature. We believe that this decrease in density was caused by the over-sintering phenomenon. The bulk densities of 0.4BMZ-0.6PT are shown in Figure 2(b). Similar to the 0.4BNZ-0.6PT ceramics, the bulk density of the 0.4BMZ-0.6PT ceramics also increased as the sintering temperature was increased to 1100°C. When the sintering temperature was 1100°C, the highest bulk density value of 7.01 g/cm³ was obtained. As the sintering temperature was increased above 1100°C and reached 1200°C, the bulk density of the 0.4BMZ-0.6PT ceramics decreased, reaching its lowest value of 6.408 g/cm³.

3.2. Dielectric characteristics and Curie temperature

Figure 3(a,b) show the frequency-dependent dielectric constant and dielectric loss of the 0.4Bi(Ni0.5Zr0.5)O3–0.6PbTiO3 and 0.4Bi(Mg0.5Zr0.5)O3–0.6PbTiO3 piezoelectric ceramics, sintered at different temperature from 1050 to 1200°C. As the frequency was varied from 1 kHz to 1 MHz, the dielectric constant εr decreased monotonically for both 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics. As shown in Figure 3(a), for the case of 0.4BNZ-0.6PT, as the sintering temperature range was increased, the dielectric constant also increased up to 1100°C. The highest dielectric constant of 1977 was observed for the 0.4BNZ-0.6PT ceramics sintered at 1100°C, which then decreased as the sintering temperature increased. In contrast, the specimens sintered at 1200°C showed the lowest dielectric constant, with the lowest dielectric loss tangent than that of other specimens.

As shown in Figure 3(b), for the case of the 0.4BMZ-0.6PT ceramics, the frequency-dependent dielectric constant increased as the sintering temperature was increased up to 1100°C. In general, the poling
processes were conducted to increase the dielectric polarization process. However, the main purpose for the polarization process was to obtain the piezoelectric charge coefficient, as shown in Figure 6. The dielectric constants were also strongly related with the charge coefficient. The highest dielectric constant of the 0.4BMZ-0.6PT ceramics was 1397, achieved at 1 kHz. As the sintering temperature increased, the dielectric constant also increased up to 1100 °C. The samples sintered at 1100°C showed a dielectric constant of 1397 at 1 kHz, the highest measured value. Overall, as the sintering temperature was further increased, the dielectric constant decreased. For example, the sample sintered at 1050°C showed a dielectric constant of 957, which was the lowest dielectric constant value at 1 kHz. This occurred because the sample was not sufficiently sintered.

Figure 4 displays the temperature-dependent dielectric constant of the 0.4Bi(Ni0.5Zr0.5)O3-0.6PbTiO3 and 0.4Bi(Mg0.5Zr0.5)O3-0.6PbTiO3 piezoelectric ceramics sintered at different temperatures from 1050 to 1200°C.

3.3. Microstructure of ceramics

Figure 5 shows surface images taken using field emission scanning electron microscopy (FE-SEM) obtained from the 0.4Bi(Ni0.5Zr0.5)O3-0.6PbTiO3 ceramics and 0.4Bi(Mg0.5Zr0.5)O3-0.6PbTiO3 ceramics sintered at different temperatures from 1050 to 1200°C. As shown in Figure 5(a), the 0.4BNZ-0.6PT ceramics have high porosity with very small grains, when sintered at 1050°C. The sintering mechanism and grain growth started at a temperature near 1050°C. As the sintering temperature was increased up to 1100°C, the grain size increased and became uniform. However, as the sintering temperature was further increased above 1100°C, the grains became distorted and turned to an over-sintered phase. As shown in the SEM image at 1200°C, the microstructure appears dense and free from voids at some point. However, this SEM image shows irregular grain sizes, which indicates the over-growth of grain caused by over-sintering. Therefore, we believe that the irregular grain growth with increasing sintering temperature results in a decrease in densification. As shown in Figure 5(b), as the sintering temperature was increased up to 1100°C, the grain size gradually increased, and the grain size became uniform. These images also show that the porosity disappeared. However, when the sintering temperature exceeded 1100°C, the grain size tended to become distorted and unbalanced, which also seems to be due to over-sintering, similar to the case for 0.4BNZ-0.6PT.

3.4. Piezoelectric properties

Figure 6 illustrates the piezoelectric charge coefficient (d33) of the 0.4Bi(Ni0.5Zr0.5)O3-0.6PbTiO3 and 0.4Bi(Mg0.5Zr0.5)O3-0.6PbTiO3 piezoelectric ceramics.
at different sintering temperatures from 1050 to 1200°C. In the case of 0.4BNZ-0.6PT, as shown in Figure 6(a), as the sintering temperature was increased up to 1100°C, the piezoelectric charge coefficients increased up to 438 pC/N, and then decreased as the sintering temperature was increased further. It seems that the sintering temperature-dependent piezoelectric charge coefficient exhibits a behaviour similar to that of the sintering temperature-dependent bulk density and dielectric constant. In particular, the 0.4BNZ-0.6PT ceramics sintered at 1200°C showed a steeply decreased piezoelectric coefficient of 128 pC/N.

The piezoelectric properties of 0.4BMZ-0.6PT are shown in Figure 6(b). Similar to 0.4BNZ-0.6PT ceramics, the piezoelectric charge coefficient increased with increasing sintering temperature up to 1100°C. The piezoelectric charge coefficient showed its highest value of 351 pC/N, when sintered at 1100°C. However, as the sintering temperature was increased above 1100°C, the piezoelectric charge coefficient decreased monotonically. The reduction rate increased in the range 1175–1200°C. The specimen sintered at 1200°C showed a piezoelectric charge coefficient of 315 pC/N. It seems that this increased piezoelectric charge coefficient has a close relationship with the density and grains. Therefore, it can be argued that dipoles in the well-grown piezoelectric materials influence the piezoelectric properties of the sintered ceramics. By comparing Figure 2, a higher bulk density means a closed packed structure and improved piezoelectric properties. In addition, by considering Figure 1, the sintering temperature of 1175°C for 0.4Bi(Ni0.5 Zr0.3)O3–0.6(Pb,Ti)O3 and 0.4Bi(Mg0.5 Zr0.3)O3–0.6(Pb,Ti)O3

Figure 5. Field emission scanning electron microscopy (FE-SEM) images of (a) 0.4Bi(Ni0.5 Zr0.3)O3–0.6(Pb,Ti)O3 and (b) 0.4Bi(Mg0.5 Zr0.3)O3–0.6(Pb,Ti)O3 ceramics sintered at different temperatures from 1050 to 1200°C.

Figure 6. Piezoelectric charge coefficient ($d_{33}$) of (a) 0.4Bi(Ni0.5 Zr0.3)O3–0.6(Pb,Ti)O3 and (b) 0.4Bi(Mg0.5 Zr0.3)O3–0.6(Pb,Ti)O3 piezoelectric ceramics for different sintering temperatures from 1050 to 1200°C.
piezoelectric ceramics is the optimized sintering temperature for density and piezoelectric properties, with a well crystallized structure.

Figure 7 displays the electromechanical coupling factor ($k_p$) of the $0.4\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ and $0.4\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ ceramics sintered at temperatures from 1050 to 1200°C. As shown in the figure, the electromechanical coupling factors of the $0.4\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ and $0.4\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ ceramics increased up to 1100°C, and then decreased. The shape of the electromechanical coupling factor of the $0.4\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ and $0.4\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ ceramics is similar to that of the piezoelectric charge coefficient shown in Figure 6. The highest values of the electromechanical coupling factor of the $0.4\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ and $0.4\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ ceramics were 57.3% and 50.8%, respectively.

Figure 8 shows the poling temperature and electric field dependence of the piezoelectric coefficient of the $0.4\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ and $0.4\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ ceramics sintered at 1100°C. As shown in Figure 8(a), the piezoelectric coefficient was increased with temperature up to 80°C, and then decreased. In addition, in Figure 8(b), the piezoelectric coefficient was increased and saturated as the electric field increased to 5 kV. The piezoelectric coefficient of the $0.4\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ and $0.4\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ ceramics reached the maximum value of 440 and 355 pC/N, respectively, at a poling temperature of 80°C and electric field of 4 kV/mm.

### 3.5. Energy harvesting application

Figure 9(a) displays the schematic of the output power and energy measuring system with applied mechanical force. By employing this system, a uniform force can be applied to a piezoelectric specimen and the generated output power and energy can be measured. This system was designed and tested to obtain the actual output power and energy of the $0.4\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ and $0.4\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$$-0.6\text{PbTiO}_3$ piezoelectric ceramics. The force was applied to the piezoelectric ceramics using a mechanical system, which applied a force of 350 N to the sample at a cycle rate of approximately 0.18 Hz [20, 21]. Figure 9(b) shows equivalent circuit to obtain the generated output power. By applying this circuit, power can be calculated by multiplying open circuit voltage and short circuit current. Figure 9(c) shows energy harvesting circuit to obtaining energy. Stored voltage in the capacitor (1 µF) using full bridge rectifier is measured and calculated into energy density. By applying the energy harvesting circuit, output power and energy can be generated depending on the input forces.

The open-circuit voltage and short-circuit current measured using this mechanical force system is shown in Figure 10(a-d). The open-circuit voltage and short-circuit current were measured using the samples sintered at 1100°C, which showed the best...
Among the 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics sintered at temperatures between 1050 and 1200°C. Figure 10(a,c) shows the open-circuit voltage of the 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics poled at 80°C and 4 kV for 30 min, respectively. The samples were subjected to a pressure energy of 350 N (0.18 Hz), during which the voltage peak values of the 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics were 15.5 V and 10.3 V, respectively. Figure 10(b,d) shows the short-circuit current of the 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics. In the same condition as the voltage measurement, a pressure energy of 350 N was applied at a frequency of 0.18 Hz, during which the current peak value of the 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics were 1.35 μA and 1.16 μA, respectively. The generated power densities were calculated considering the sample size. The specimen diameter was approximately 10.5 mm and thickness was 1 mm. Therefore, power densities of 0.23 and 0.14 mW/cm³ were obtained from the 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics, respectively. Both 0.23 and 0.14 mW/cm³ were enough energy sources for the sensor applications.

Figure 11 shows the measured voltage across the 1 μF capacitor. The full bridge rectifier was employed to collect the positive and negative output voltages from the 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics. The output voltages of 5.38 and 4.18 V were obtained for 0.4BNZ-0.6PT and 0.4BMZ-0.6PT, respectively. Additionally, the actual stored energy was calculated by measuring the stored voltage applied across the 1 μF capacitor. The stored energy was calculated using the following equation [20]:

$$E = \frac{1}{2} CV^2$$  

where C is the capacitance of capacitor that stored the applied voltage and V is the measured voltage across the capacitor. The stored energy density was

![Figure 9](image1.png)  
**Figure 9.** Schematics of mechanical force system (a) [14,15], (b) equivalent circuit for open circuit voltage and short circuit current system to obtain power (b) [Watt] and equivalent circuit for energy measuring system based on the full bridge rectifier with capacitors (c) [Joule].

![Figure 10](image2.png)  
**Figure 10.** (a) and (b) represent for open-circuit voltage and short-circuit current of 0.4Bi(Ni₀.₅Zr₀.₅)O₃-0.6(Pb,Ti)O₃ ceramics, while (c) and (d) represent for open-circuit voltage and short-circuit current of 0.4Bi(Mg₀.₅Zr₀.₅)O₃-0.6(Pb,Ti)O₃ ceramics, respectively.
calculated considering the sample size. In this experiment, a load capacitor of 1 \( \mu F \) was employed. If the load capacitors are changed, then the applied voltage can be changed. Therefore, the generated output energy may also be changed; however, this is not true. The stored energy can be changed but the generated output energy cannot be changed. The main reason for choosing a capacitance of 1 \( \mu F \) was that we considered impedance matching methods. By considering impedance matching methods, optimized capacitors can be collected, and the stored energy can be optimized. Therefore, energy densities of 1.67 and 1.01 mJ/cm\(^3\) were obtained from the 0.48BNZ-0.6PT and 0.4BMZ-0.6PT ceramics, respectively. Meanwhile, the energy density of (33)-mode can be derived from the following (2) ~ (5) equations:

\[
g_{33} = \frac{d_{33}}{\varepsilon_{33}} \tag{2}
\]

\[
d_{33} = k_{33} \sqrt{\varepsilon_{33} s_{33}} \tag{3}
\]

\[
V = g_{33} \times \frac{t}{s} F \tag{4}
\]

\[
E_{\text{max}} = \frac{1}{2} CV^2 \tag{5}
\]

Substituting (2) to (4) into (5) gives the following equation:

\[
E_{\text{max}} = \frac{1}{2} (d_{33} \times g_{33}) \frac{t}{s} F^2 \tag{6}
\]

where \( t \) is thickness (m), \( s \) is area (m\(^2\)) and \( F \) is force (N).

The energy density is produced by piezoelectric element is proportional to the transduction coefficient \((d_{33} \times g_{33})\), where \( d_{33} \) is the piezoelectric charge coefficient and \( g_{33} \) is the piezoelectric voltage coefficient, given by \( g_{33} = d_{33}/(\varepsilon_{33} F) \) [22]. The optimized piezoelectric materials for energy harvesting should have both a high piezoelectric charge coefficient and a low dielectric constant. The piezoelectric voltage coefficients of 0.48BNZ-0.6PT and 0.4BMZ-0.6PT ceramics were \( 25.02 \times 10^{-3} \) V/m/N and \( 28.37 \times 10^{-3} \) V/m/N, respectively. In addition, the transduction coefficient of \( 10960 \times 10^{-15} \) m\(^2\)/N and \( 9960 \times 10^{-15} \) m\(^2\)/N were obtained from the 0.48BNZ-0.6PT and 0.4BMZ-0.6PT ceramics, respectively. We believe that the energy density of 0.48BNZ-0.6PT higher than 0.4BMZ-0.6PT is result from improving the transduction coefficient. Table 1 lists the comparison of piezoelectric properties for the lead-based energy harvesters [23–31]. Since energy harvesters converting environmental energy to electrical energy, in the case of low input energy, the generated output energy also relatively small [27,28]. And for the hybrid type energy harvester case, some energy can be converted to heat energy, the generated electrical energy can be small [27]. As shown in the Table 1, 0.48BNZ-0.6PT and 0.4BMZ-0.6PT piezoelectric ceramics have relatively high output voltage and energy density.
compared to that of the different piezoelectric ceramics.

4. Conclusions

For the first time, piezoelectric Bi(Nb0.5Zr0.5)O3–PbTiO3 (BNZ-PT) and Bi(Mg0.5Zr0.5)O3–PbTiO3 (BMZ-PT) ceramics were selected and compared for energy harvester applications. Although BNZ-PT and BMZ-PT ceramics have lower lead contents, they showed relatively higher piezoelectric charge coefficient $d_{33}$ with lower dielectric constant, which can replace PZT ceramics. XRD analysis results suggested that 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics were well-crystallized to form a rhombohedral and tetragonal mixture. The uniformity of grain growth and presence of porosity were also confirmed by FE-SEM images. As a result, it was confirmed that the sintering temperature had a significant effect on the grain size and density of BNZ-PT and BMZ-PT ceramics. The piezoelectric constants for 0.4BNZ-0.6PT and 0.4BMZ-0.6PT ceramics were 438 and 351 pC/N, respectively. Generated output energy densities of 1.67 and 1.01 mJ/cm$^3$ were obtained from 0.4BNZ-0.6PT and 0.4BMZ-0.6PT, respectively. These results demonstrate that the proposed the 0.4BNZ-0.6PT is an outstanding candidate for utilize in the piezoelectric energy harvester with a lower lead content.

Disclosure statement

No potential conflict of interest was reported by the authors.

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| Materials | $d_{33}$ (pC/N) | $k_p$ (%) | Structure | Pressure or acceleration | Output voltage | Energy density | Reference |
|-----------|----------------|-----------|-----------|------------------------|----------------|----------------|-----------|
| PZT       | 390            | -         | Cantilever| 1.96 m/s$^2$           | -              | 0.2 mW/cm$^2$ | [23]      |
| PZT       | -              | -         | Cantilever| 2.5 m/s$^2$           | -              | 0.7 mW/cm$^2$ | [24]      |
| Mn-PZT    | -              | 36        | Bulk ceramic | 9 MPa         | -              | 3.0 mW/cm$^2$ | [25]      |
| PMN–PZT   | 665            | 78        | Bulk ceramic |               | -              | 0.14 mW/cm$^2$ | [26]      |
| PMN–PT    | 240            | 47        | Bulk ceramic |               | -              | 0.33 mJ/cm$^2$ | [27]      |
| BMZ–PT    | 440            | 50.8      | Bulk ceramic | 5.33 kPa       | 9.34 V       | 0.85 mJ/cm$^2$ | [28]      |
| BNZ–PT    | 438            | 57.3      | Bulk ceramic | 4 MPa         | 17.91 V      | 0.23 mJ/cm$^2$ | This work |

Table 1. Comparison of piezoelectric properties for the lead-based energy harvesters.
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