Piezoelectric Voltage Constant and Sensitivity Enhancements Through Phase Boundary Structure Control of Lead-free (K,Na)NbO3-based ceramics

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Research Article

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Abstract

The piezoelectric voltage constant ($g_{33}$) is a material parameter critical to piezoelectric voltage-type sensors for detecting vibrations or strains. Here, we report a lead-free (K,Na)NbO$_3$ (KNN)-based piezoelectric accelerometer with voltage sensitivity enhanced by taking advantage of a high $g_{33}$. To achieve a high $g_{33}$, the magnitudes of piezoelectric charge constant $d_{33}$ and dielectric permittivity $\varepsilon_r$ of KNN were best coupled by manipulating the intrinsic polymorphic phase boundaries effectively with the help of Bi-based perovskite oxide additives. For the KNN composition that derives benefit from the combination of $\varepsilon_r$ and $d_{33}$, the value of $g_{33}$ was found to be 46.9 $\times$ 10$^{-3}$ V·m/N, which is significantly higher than those (20 - 30 $\times$ 10$^{-3}$ V·m/N) found in well-known polycrystalline lead-based ceramics including commercial Pb(Zr,Ti)O$_3$ (PZT). Finally, the accelerometer sensor prototype built using the modified KNN composition demonstrated higher voltage sensitivity (183 mV/g) when measuring vibrations, showing a 29% increase against the PZT-based sensor (142 mV/g).

1. Introduction

Piezoelectric sensors utilize the piezoelectric effect to measure force, strain, pressure, acceleration and acoustic emission by converting mechanical energy into electrical energy. These sensors are widely used for condition and safety monitoring of various industrial facilities owing to their outstanding characteristics, which include such as a fast response, excellent dynamic range and linearity, long term stability and minimal power consumption [1−3]. One of the major parameters related to such performance is the piezoelectric voltage constant ($g$, generated output voltage under applied stress). It is known that the parameter $g$ is always related to a piezoelectric charge constant $d$ through a dielectric permittivity $\varepsilon$ (i.e., $g = d/\varepsilon$) [4, 5]. Moreover, because the voltage sensitivity of a piezoelectric sensor is linearly associated with the $g$ instead of $d$ [6, 7], the constant $g$ can therefore be deemed the material figure of merit for piezoelectric sensing and energy harvesting applications.

Well-known perovskite-structured ferroelectrics, such as BaTiO$_3$ (BT), PbTiO$_3$ (PT), Pb(Zr,Ti)O$_3$ (PZT), Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$ (PMN-PT), could be candidate piezoelectric materials. Among them, soft PZT ceramics (e.g., PZT-5A) make the best transducer materials and are widely used for commercial piezoelectric sensors. The values of thickness-mode $g_{33}$ for commercial grades of soft PZT ceramics are normally between 21 and 26.5 $\times$ 10$^{-3}$ V·m/N (e.g., 24.8 $\times$ 10$^{-3}$ V·m/N for PZT-5A) [8]. The $g_{33}$ value of PMN-PT ceramics with ultra-high $d_{33}$ ($\geq$ 1600 pC/N) is only 21 $\times$ 10$^{-3}$ V·m/N, while that of BT ceramics is as low as 12.6 $\times$ 10$^{-3}$ V·m/N. Moreover, both ceramics suffer from low $T_c$ values that restrict applications over a wider temperature range. To the best of the authors’ knowledge, PMN-PZT ceramics exhibit the highest $g_{33}$ (28.4 $\times$ 10$^{-3}$ V·m/N) among lead-based polycrystalline ceramics [9].

Instead of conventional powder-processed polycrystalline ceramics, other material approaches have been used to increase $g_{33}$ further ($\geq$ 40 $\times$ 10$^{-3}$ V·m/N). These approaches include composite fabrication with
low-dielectric-constant materials (e.g., polymers) [10–14] and the <001> texturing process [9,15–18]. However, the use of low-dielectric-constant polymers leads to a narrow applicable temperature range owing to their low melting point. A texturing or single crystal process, such as the well-known templated grain growth (TGG) method, is not cost-effective. Moreover, it is unfortunate that most of the existing lead-based piezoceramic materials, including PZT, will not be available in the near future owing to the world-wide restriction on the use of toxic lead or lead oxide in electrical and electronic components [19–21]. Therefore, there is an obvious need to develop a lead-free counterpart with high $g$, and to validate its performance in a piezoelectric sensor relative to those of traditional PZT-based sensors. Considering that any increase in $d$ is usually accompanied by an increase in $\varepsilon$ [22], it is challenging to discover a high-$g$ polycrystalline lead-free piezoceramic by means of a conventional ceramic processing route (preferable for practical reasons).

In this work, we report a lead-free (K,Na)NbO$_3$ (KNN)-based piezoelectric accelerometer with voltage sensitivity enhanced, in particular, by achieving high $g_{33}$ in a polycrystalline KNN ceramic. The properties of $\varepsilon$ and $d_{33}$ for KNN were modified to couple them in the best manner to achieve a high $g_{33}$ using two Bi-based perovskite oxide additives (Bi$_{0.5}$(Na$_{0.2}$K$_{0.1}$Li$_{0.7}$)$_{0.5}$ZrO$_3$: BNKLZ and BiScO$_3$: BS), the selection of which was based on our previous investigation [23]. When both $\varepsilon$ and $d_{33}$ were best coupled via control of the polymorphic phase boundary structure, the $g_{33}$ value of the KNN ceramic could be improved up to $46.9 \times 10^{-3}$ V·m/N, which is much higher than those found in well-known lead-based piezoceramics, including PZT. When applied to a piezoelectric accelerometer sensor, the optimized KNN composition exhibited higher voltage sensitivity (an increase of $\sim 29\%$) compared to PZT-5A.

2. Experimental

2.1. Preparation and characterization of ring-shaped piezoceramic samples

For integration into a prototype compression-mode accelerometer, ring-shaped polycrystalline piezoceramic samples with $(1-x-y)\text{KNN-}x\text{BNKLZ-}y\text{BS}$ compositions ($x \approx 0.03$, $y = 0 - 0.015$) were prepared using the conventional solid-state powder method. The BS was added at a smaller concentration (i.e., 0.125 mol% level) owing to its doping sensitivity to the structural and piezoelectric properties of KNN [23]. The details of preparation conditions are described in Fig. S1. The studied piezoceramic rings were 12.2–13.0 mm in outer diameter (O.D.), 7.2–7.9 mm in inner diameter (I.D.), and 2.55 mm in thickness. These rings had densities of 4.27–4.31 g/cm$^3$ ($\geq 95\%$ of the theoretical density) based on the Archimedes method (Fig. 1 (a)).

The phase and crystal structure of the ceramic samples were characterized by X-ray diffraction (XRD) $\theta$-2$\theta$ patterns and Rietveld refinements with an X-ray diffractometer (MiniFlex 600; Rigaku, Tokyo, Japan) using Cu Ka radiation (40 kV/15 mA, 4°/min). Rietveld refinement was performed using Rigaku’s PDXL software with the whole pattern powder fitting (WPPF) method. Three KNbO$_3$ crystal structure models
were used for fitting: orthorhombic (Amm2; JCPDS 01-071-0946; ICSD code 9533), rhombohedral (R3m; JCPDS 01-071-0947; ICSD code 9534), and tetragonal (P4mm; JCPDS 01-071-0948; ICSD code 9532) [23]. The fitting quality of the powder patterns was checked by means of the goodness-of-fit indicator S and the reliability factor $R_{wp}$. The microstructure and grain size were investigated using a field-emission scanning electron microscope (FE SEM; S-4800; Hitachi, Tokyo, Japan) with an operating voltage of 10 kV.

Dielectric permittivity $\varepsilon_r$ was measured for the unpoled and poled samples between −150 and 500 °C using an impedance analyzer (HP 4294A; Agilent; USA). The piezoelectric charge constant $d_{33}$ was measured at room temperature using a piezo-$d_{33}$ meter (ZJ-6B; IACAS; Beijing, China). The piezoelectric voltage constant $g_{33}$ was determined using the relation $g_{33} = d_{33}/(\varepsilon_0 \cdot \varepsilon_r)$ [18], where the $\varepsilon_0$ and $\varepsilon_r$ are the vacuum dielectric permittivity (= 8.854 pF·m$^{-1}$) and the relative dielectric permittivity calculated from the capacitance at 1 kHz of poled sample, respectively. Polarization-electric field (P-E) hysteresis loops were measured at room temperature using a standard Sawyer-Tower measurement circuit (TF Analyzer 2000E; aixACCT Systems GmbH; Aachen, Germany). Using the unipolar strain curves of the poled samples, large-signal piezoelectric constant $d_{33}^*$ was determined from the ratio of the maximum strain to the peak electric field ($d_{33}^* = S_{\text{max}}/E_{\text{max}}$). For a comparison, ring-shaped PZT ceramic samples were also prepared using commercially available PZT powders (PC51; IS Technologies; Incheon, South Korea) [24].

2.2. Fabrication and vibration experiments of a piezoelectric accelerometer prototype

To investigate the performance of the modified KNN ceramics in practical device applications, a piezoelectric accelerometer sensor prototype was fabricated based on a compression-mode design, in which the piezoelectric element was designed to work under compression [25]. The basic structure of the accelerometer sensor prototype is shown in Fig. 1 (b). The piezoelectric element (1) consisted of two piezoceramic rings cut for the longitudinal effect and oriented with their polarities opposite from the central electrode. They were preloaded by a screw (2) that acts as a very rigid spring between the seismic mass (3) and the tail (4) and the base plate (5). The insulating layer (6) was located at the gap between the tail and the base plates. The electrode (7) captured the output signal and fed it to the connector. When the base plate is accelerated, the seismic mass exerts a proportional force on the piezoceramic element. The materials used for the mass, electrode, tail, base, and insulating layer were tungsten, copper, 316 stainless steel and epoxy, respectively. The accelerometer sensor prototype was prepared using the sensor components according to the fabrication procedure illustrated in Fig. S2. A reference sensor was also prepared using the identical procedure with ring-shaped PZT ceramics.

The vibration test was conducted using a calibrated accelerometer tester (28959FV; Endevco, San Juan Capistrano, California, USA) that included a built-in vibration exciter, signal generator, and computer-controlled amplifier/servo mechanism (Fig. 1 (c)). The applied acceleration range was between 1 and 10 g (g, gravitational acceleration = 9.8 m/s$^2$). The sensor calibration was made using an internal high-
frequency reference accelerometer with a sensitivity of 50 mV/g at 100 Hz. The output voltage characteristics were measured at a constant frequency of 159 Hz using a digital oscilloscope (DSO-X 2024A; Keysight Technologies, Santa Rosa, California, USA). Finally, the voltage sensitivity $S_v$ was determined from the acceleration-to-output voltage characteristics.

3. Results And Discussion

3.1. Properties of the ring-shaped KNN-BNKLZ-BS ceramic samples

The room-temperature XRD patterns revealed that KNN-0.03BNKLZ-yBS ceramic samples ($y = 0 - 0.015$) were of a pure perovskite structure without second phases, indicating homogeneous solid solutions in the investigated dopant concentrations (Fig. 2 (a)). However, there was a significant change of phase structure as a function of the BS concentration, as shown in the amplified XRD patterns ($2\theta = 44^\circ$ to $47^\circ$) (Fig. 2 (a)). The detailed structural properties such as constituent phases and crystal symmetry, cell parameters and actual phase fractions are shown in the Rietveld refinement results (Figs. 2 (b) and S3). Both the low $R_{wp}$ of less than 10% and the $S$ value close to 1 prove high reliability of the resulting data (Table 1) [23]. It can be seen that three polar phases of rhombohedral (R), orthorhombic (O), and tetragonal (T) were present in different ratios as a function of BS concentration. In the absence of BS doping, the KNN-0.03BNKLZ ceramic exhibited a coexistence of R, O and T phases with a fair proportion of O phase(63 %). From the fact that a virgin KNN displays an O symmetry at room temperature, the coexistence of R, O, and T phases suggests that the addition of 0.03 mol% BNKLZ induced the shift of two polymorphic phase transition temperatures of R-O ($T_{\text{R-O}}$) and O-T ($T_{\text{O-T}}$) toward the room temperature. As the BS was added, the volume fraction of the O phase decreased and at the same time the R or T phases increased. Finally, the O phase disappeared at $y = 0.01$, leaving the R and T phases. Upon further increasing $y$, the R phase became enriched ($y = 0.015$). As a result, the addition of BS is also found to be effective to move the $T_{\text{R-O}}$ and $T_{\text{O-T}}$ into the room temperature region and thus to form the R-T structure.
According to the $\varepsilon_r$–$T$ curve of KNN-0.03BNKLZ ceramic ring sample (Fig. 3 (a)), there was a sharp dielectric peak representing a typical ferroelectric-paraelectric transition (i.e., $T_c$) and the $T_c$ determined from the corresponding dielectric peak position was about 369 °C. The chemical modification with BS induced a gradual decline of $T_c$ with a peak broadening associated with the transition from normal phase to diffuse ferroelectric phase. The loss of $T_c$ was minor ($\Delta T_c \approx 46$ °C) in the studied BS concentrations: the lowest $T_c$ was measured to be 323 °C at $y = 0.015$. Indeed, the decline of $T_c$ induced by doping with the BNKLZ and BS perovskite compounds was not significant, as compared to the case of the well-known Sb$^{5+}$ ion doping [26].

Table 1

| BS (mol%) | Phase structure | Cell parameters | Phase fraction (%) | $R_{wp}$ (%) | S |
|-----------|----------------|----------------|-------------------|--------------|---|
|           |                | $a$ (Å)        | $b$ (Å)           | $c$ (Å)      | $\alpha = \beta = \gamma$ (°) |
| 0         | R-O-T          | 3.9792         | 3.9792            | 3.9792       | 89.7972       | 21.1 (R3m:$R$) | 9.30 | 1.02 |
|           |                | 3.9574         | 5.6537            | 5.6586       | 90            | 63.0 (Amm2)    |
|           |                | 3.9599         | 3.9599            | 4.0103       | 90            | 15.9 (P4mm)    |
| 0.25      | R-O-T          | 3.9805         | 3.9805            | 3.9805       | 89.7495       | 31.5 (R3m:$R$) | 9.75 | 1.08 |
|           |                | 3.9551         | 5.6170            | 5.7252       | 90            | 44.1 (Amm2)    |
|           |                | 3.9615         | 3.9615            | 4.0049       | 90            | 24.4 (P4mm)    |
| 0.5       | R-O-T          | 4.0070         | 4.0070            | 4.0070       | 89.7434       | 14.9 (R3m:$R$) | 9.37 | 1.03 |
|           |                | 3.9577         | 5.6278            | 5.6359       | 90            | 19.1 (Amm2)    |
|           |                | 3.9670         | 3.9670            | 4.0099       | 90            | 66.0 (P4mm)    |
| 0.75      | R-O-T          | 3.9926         | 3.9926            | 3.9926       | 89.8112       | 16.0 (R3m:$R$) | 5.64 | 1.39 |
|           |                | 3.9531         | 5.6533            | 5.6847       | 90            | 16.9 (Amm2)    |
|           |                | 3.9694         | 3.9694            | 4.0117       | 90            | 67.1 (P4mm)    |
| 1.0       | R-T            | 3.9984         | 3.9984            | 3.9984       | 89.5362       | 16.3 (R3m:$R$) | 9.48 | 1.03 |
|           |                | 3.9687         | 3.9687            | 4.0114       | 90            | 83.7 (P4mm)    |
| 1.25      | R-T            | 3.9883         | 3.9883            | 3.9883       | 89.7915       | 25.9 (R3m:$R$) | 9.94 | 1.09 |
|           |                | 3.9740         | 3.9740            | 4.0126       | 90            | 74.1 (P4mm)    |
| 1.5       | R-T            | 3.9824         | 3.9824            | 3.9824       | 89.9918       | 53.3 (R3m:$R$) | 9.20 | 1.01 |
|           |                | 3.9706         | 3.9706            | 4.0092       | 90            | 46.7 (P4mm)    |
For a pure KNN ceramic, there are two intrinsic polymorphic phase transitions, R-O transition at \(-123 \, ^\circ\text{C} (T_{\text{R-O}})\) and the O-T transition at \(200 \, ^\circ\text{C} (T_{\text{O-T}})\). The presence of a phase boundary at each phase transition temperature is typically characterized by slight dielectric anomalies (Fig. 3 (b)). In the absence of BS doping, the KNN-0.03BNKLZ ceramic had the shift of \(T_{\text{R-O}}\) and \(T_{\text{O-T}}\) values to about \(-83 \, ^\circ\text{C}\) and \(147 \, ^\circ\text{C}\), respectively, owing to the effect of \(\text{Bi}^{3+}\) and \(\text{Zr}^{4+}\) ions that are known to play the roles in decreasing \(T_{\text{O-T}}\) and increasing \(T_{\text{R-O}}\), respectively [27, 28]. When the BS was added, both the dielectric peaks gradually approach the room-temperature region. Finally, the peaks converge to create a broad bulge peak centered at/near room temperature \((y = 0.01)\). Then, the bulge peak becomes weaker, as the BS was added further. The appearance of a dielectric bulge peak is associated with the R-T structure caused by the extinction of O phase. The weakened bulge peak relates to the enrichment of R phase relative to T phase. As a result, the BS doing induces the transition from a triphasic R-O-T to a diphasic R-T structure, varying the fraction of each polar phase. The room-temperature phase structure predicted from such \(\varepsilon_r - T\) behaviors is well supported by the above XRD and Rietveld refinement results.

It should be noted that the observed phase evolution significantly affects the magnitude of room-temperature \(\varepsilon_r\) (Fig. 3 (c)). The relatively low \(\varepsilon_r\) values between \(467 - 473\) were obtained in the R-O-T region containing a considerable amount of O phase (at less than \(y = 0.0025\)). Then, the \(\varepsilon_r\) value increased with the reduction of O phase. The peak value of about 1630 was obtained at \(y = 0.01125\) that corresponded to the T-rich R-T structure. However, the \(\varepsilon_r\) continuously decreased, as the \(y\) increased further with the enrichment of R phase in the R-T structure.

The results indicate that the R-O-T phase boundary, if it has a fair proportion of O phase, can result in the decreased \(\varepsilon_r\) at room temperature. This is believed to be due to the formation of a relatively flat \(\varepsilon_r - T\) region near room temperature between two dielectric anomalies. On the contrary, the formation of R-T phase boundary, characterized by the bulged dielectric peak formed by merging of two dielectric anomalies \((T_{\text{R-O}}\) and \(T_{\text{O-T}})\), increases the room-temperature \(\varepsilon_r\) value. The suppression of the bulge peak, associated with the enrichment of R phase in the R-T structure, can also lead to the reduction of the room-temperature \(\varepsilon_r\). Therefore, it is found that the magnitude of room-temperature \(\varepsilon_r\) can be greatly changed with the type of phase boundary structure, which originates from an intrinsic characteristic of a KNN material system that possesses two temperature-dependent polymorphic phase transitions, i.e., R-O and O-T.

Figure 4 (a) shows the dependence of room-temperature piezoelectric properties on the BS concentration \((y)\). The trend of \(d_{33}\) as a function of BS concentration is found to be roughly similar to but different in detail from that of \(\varepsilon_r\). That is, the \(d_{33}\) shows a continuous increase up to \(y = 0.01\), above which a dramatic decrease follows. It should be noted that this behavior was different from that observed in \(\varepsilon_r\) (Fig. 3 (c)). Namely, the \(\varepsilon_r\) slightly increases until \(y = 0.00625\), after maintaining nearly constant levels up to \(y = 0.0025\). Then, it shows a large increase up to \(y = 0.01125\), after which it decreases.
Notably, this difference in increasing and decreasing rates of $\epsilon_r$ and $d_{33}$ leads to substantial changes in the magnitude of their ratio, eventually giving a wide range of $g_{33}$ values from 8.0 to $46.9 \times 10^{-3}$ V·m/N. The maximum $g_{33}$ ($46.9 \times 10^{-3}$ V·m/N) was observed for the sample with $y = 0.0025$ thanks to the best combination of $d_{33}$ ($208\pm1.2$ pC/N) and $\epsilon_r$ ($502\pm3.7$). In fact, this $g_{33}$ value was significantly higher than those found in well-known polycrystalline ferroelectrics including commercial PZT, PMN-PT, and BaTiO$_3$ ceramics ($12.6 - 28 \times 10^{-3}$ V·m/N) (Fig. 4 (b)). It was also comparable to those of textured PMN-PT and PMN-PZT [9, 17] or porous PZT ceramics [14]. We also ascribe a much lower $g_{33}$ value ($23.8\pm0.2 \times 10^{-3}$ V·m/N) obtained from the sample with $y = 0.01$ to the high-\(\epsilon_r\) effect ($1571\pm2.5$), in spite of the best $d_{33}$ property ($330.7\pm2.3$ pC/N).

As shown in Fig. 4 (c), the behavior of $\epsilon_r$ and $d_{33}$ as a function of BS concentration can be characterized by two regions, i.e., Regions A and B, based on their change rates with respect to the value at $y = 0$. Region A corresponds to the samples with $y = 0 - 0.00625$, characterized by a lower increase rate of $\epsilon_r$ compared to that of $d_{33}$. For the samples with $y = 0.0075 - 0.015$, however, the trend is reversed and the change (increase or decrease) rate of $\epsilon_r$ is higher than that of $d_{33}$, as indicated by Region B. Hence, the $d_{33}$-to-$\epsilon_r$ ratios in Region A should be higher than those in Region B, which yields high magnitudes of $g_{33}$. The peak $g_{33}$ value was obtained at the highest $d_{33}$-to-$\epsilon_r$ ratio ($y = 0.0025$), while the lowest $d_{33}$-to-$\epsilon_r$ ratio ($y = 0.015$) led to the lowest $g_{33}$ (indicated by red arrows in Fig. 4 (c)). From this observation, some valuable information can be drawn that the $d_{33}$-to-$\epsilon_r$ ratio needs to be increased in such a way that a larger increase in $d_{33}$ goes with an increase in $\epsilon_r$ as small as possible in order to increase $g_{33}$. Generally, it is well known that the variation in magnitude of $d_{33}$ and $\epsilon_r$ is similar and they increase or decrease simultaneously upon modification with dopants or processing technique, leading to minor changes in the magnitude of their ratio [16, 22]. Contrary to one's expectation, our results demonstrate that the independent control of $d_{33}$ and $\epsilon_r$ for a polycrystalline KNN ceramic system is possible by means of manipulation of the phase boundary structure to finally yield a greater level of the $d_{33}$-to-$\epsilon_r$ ratio.

The transduction coefficient ($d \times g$) was also determined (Fig. S4) because it is an important parameter required to generate higher power in energy harvesting or generator applications [29]. In this work, high levels of transduction coefficient ($9,601 - 10,163 \times 10^{-15}$ m$^2$/N) comparable to that of PZT-5A ($9,699 \times 10^{-15}$ m$^2$/N) were obtained in the R-O-T region ($y = 0.0025 - 0.00625$). For the sample with the highest $g_{33}$ ($y = 0.0025$), the transduction coefficient was $9,765 \times 10^{-15}$ m$^2$/N and, on the other hand, the sample ($y = 0.01$) with the highest $d_{33}$ and R-T structure had its much lower value (only $7,871 \times 10^{-15}$ m$^2$/N).

The microstructure was characterized for the corresponding sintered ceramic rings (Fig. 5). The bimodal grain structure, characterized by large grains (defined as more than 20 µm) imbedded into the smaller matrix grains (defined as less than 2 µm) [30], was typically observed until $y = 0.0125$ (Fig. S5). Upon the evolution of microstructure, the large grains became dominant with the increase in $y$ up to $y = 0.01$, accompanied by the reduction of the small-grained area. With the further increase in $y$, the size of the
large grains dramatically decreased owing to the effect of the solubility limits of low-melting-point Bi$^{3+}$ ion or its oxides in KNN lattice. The observed structural evolution was typical of many KNN-based ceramics doped with Bi-containing perovskite oxides [30–33]. Regarding the $d_{33}$ behavior shown in Fig. 4 (a), the well-established grain size effect should have a strong contribution. Namely, as the increased grain boundaries generally constrain the domain wall motion, the decreased grain sizes induced the decline of $d_{33}$. This is possibly combined with the involved phase boundary structure. It has been reported that a T-rich phase boundary structure in a KNN system is favored for piezoelectricity owing to the more positive role of the irreversible tetragonal-electric induced phase transition compared to the rhombohedral- or orthorhombic-electric induced phase transition [34–36]. Hence, the T-rich R-T phase boundary structure as well as the large-grained structure is considered to be responsible for the enhanced $d_{33}$ observed at near $y = 0.01$.

Finally, to investigate the performance of the modified-KNN ceramics in practical device applications, two KNN compositions were introduced to fabricate the prototype accelerometer sensors: they were $y = 0.0025$ and $y = 0.01$ with the highest $g_{33}$ and $d_{33}$ values, respectively. Most of the dielectric and electromechanical properties measured for three types of ring-shaped samples including PZT-5A are presented in Table S1. Their sensing performances were investigated and compared through the vibration test. Figs. 6 (a) and (b) shows the constituent components and piezoceramic rings fabricated according to the proposed design [25] and the compression-mode prototype accelerometer sensor assembled using them, respectively. The vibration test results obtained from the prepared sensors are shown in Fig. 7. The continuous vibration was applied under cyclic loading with sine-wave modes and the output voltage signals were observed. It can be seen that the peak-to-peak amplitudes of time-dependent output voltages as a function of gravitational acceleration $g$ (= 9.8 m/s$^2$) were different for three sensors (Fig. 7 (a)), indicating different sensing capabilities. The generated output voltage determined at a constant frequency of 159 Hz increased linearly with the applied acceleration (Fig. 7 (b)). In the acceleration range of 1 – 10 g, the values of Pearson's correlation coefficient $R$ as a measure of the linear association between two variables, were almost “unity”, demonstrating a perfect linear response to the applied acceleration and thereby excellent reliability of the fabricated sensor prototypes. For the sensor using the modified-KNN ($y = 0.0025$) with the highest $g_{33}$, the slope, representing a voltage sensitivity $S_v$, was determined to be 183 mV/g. Notably, it was significantly higher than that using commercial PZT (142 mV/g) with a 29% increase, showing a clear potential to replace the PZT-based sensors. On the contrary, the $S_v$ for the sensor using the KNN ceramic with $y = 0.01$ was much lower (119 mV/g), even if this composition had the highest $d_{33}$.

The voltage sensitivity $S_v$ of a piezoelectric sensor is linearly associated with $g_{33}$, while its charge sensitivity $S_q$ is related to $d_{33}$ [6, 7]. By considering only the piezoceramic and seismic mass, those relations are simplified by the following equations:
\[
S_q = n \cdot d_{33} \cdot m_s \cdot g \tag{1}
\]
\[
S_v = S_q / (C_s + C_c) \cong (n \cdot g_{33} \cdot m_s \cdot g) (t/A) \tag{2}
\]

Here, \( C_s, C_c, n, m_s, g, t \) and \( A \) are the capacitances of sensor and cable, number of piezoceramic layer, weight of seismic mass, acceleration, thickness and area of piezoceramic, respectively, as listed in Table 2. Following this theoretical relation, the test results revealed a strong correlation between the \( S_v \) and \( g_{33} \), as shown in Fig. 7 (c): a larger magnitude of \( g_{33} \) leads to a higher level of \( S_v \). Meanwhile, it can be seen that there is a deviation from the direct proportional relationship between the \( S_v \) and \( g_{33} \). The observed deviation may relate to the effect of another material factor besides \( g_{33} \), that is, the energy conversion efficiency \( \eta \). Since the \( \eta \) is only dependent on the electromechanical coupling factor \( k_p \) and mechanical quality factor \( Q_m \), high efficiency for piezoelectric conversion devices usually requires large \( k_p \) and \( Q_m \) values [37]. When the \( \eta \) was determined based on the impedance analysis, we obtained different values of \( \eta \) for three samples, as presented in Table 2. The higher \( \eta \) of about 85.9% for PZT-5A compared to those for modified-KNN ceramics (64.1% and 75.8% for \( y = 0.0025 \) and \( y = 0.01 \), respectively) is considered to be responsible for the \( S_v \) higher than predicted by a linear correlation in Eq. (2). The slight deviation from a linear relationship between the \( S_v \) and \( g_{33} \) for two KNN compositions might also be explained by such a different-\( \eta \) effect.

### Table 2

Properties of modified (m)-KNN and PZT piezoceramic rings and accelerometer sensor prototypes built using them (seismic mass \( m_s = 21.5 \) g, cable capacitance \( C_c = 15 \) pF)

| Material         | Piezoceramic ring | \( C_s \) (pF) | \( S_v \) (mV/g) |
|------------------|-------------------|----------------|------------------|
|                  | \( A \) (mm\(^2\)) | \( t \) (mm) | \( d_{33} \) (pC/N) | \( \varepsilon_r \) (-) | \( g_{33} \) (10\(^{-3}\)V·mN\(^{-1}\)) | \( \eta \)       |
| m-KNN \( y = 0.0025 \) | 334.86 | 2.55 | 208.2 | 502 | 46.9 | 64.1±0.8 | 311 | 183 |
| m-KNN \( y = 0.01 \) | 306.90 | 2.55 | 330.7 | 1571 | 23.8 | 75.8±1.1 | 838 | 119 |
| PZT-5A           | 303.26 | 2.55 | 371.6 | 1607 | 26.1 | 85.9±0.3 | 804 | 142 |

### 4. Conclusions

In this work, we report a lead-free KNN-based piezoelectric accelerometer with enhanced voltage sensitivity, especially by using a high-g polycrystalline KNN ceramic produced by traditional solid-state powder technique. To achieve a high \( g_{33} \) in a KNN system, the magnitude of room-temperature \( \varepsilon_r \) was tuned by controlling two temperature-dependent polymorphic phase boundaries (R-O and O-T) with the
help of Bi-based perovskite oxide additives (BNKLZ and BS), followed by coupling to that of $d_{33}$. For the KNN composition with 3 mol% of BNKLZ and 0.25 mol% of BS, the highest value of $g_{33}$ was obtained owing to the best coupling effect of $\varepsilon_r$ and $d_{33}$. The obtained $g_{33}$ was $46.9 \times 10^{-3}$ V·m/N, which was indeed greater than those $(20 - 30 \times 10^{-3}$ V·m/N) found in well-known polycrystalline lead-based ceramics including commercial PZT. The enhancement in $g_{33}$ allowed a high level of transduction coefficient ($d_{33} \times g_{33}$) comparable to that of PZT-5A. Concerning the control of the phase boundary structure of a KNN system, the R-O-T structure was found to be beneficial to improving the $g_{33}$, compared to the R-T structure. Finally, in the application of a piezoelectric accelerometer, the sensor prototype fabricated using the modified KNN composition demonstrated higher voltage sensitivity (183 mV/g) in detecting vibrations, showing a 29% increase against the PZT-based sensor (142 mV/g). This work demonstrates that a high-g polycrystalline lead-free KNN piezoceramic can be obtained through the phase boundary structure control, ultimately showing great potential for replacing PZT in piezoelectric sensing and energy harvesting applications.

**Declarations**

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**Electronic Supplementary Material**

Supplementary material (Preparation details on piezoceramic sample and sensor prototype, Rietveld refinement results for q-2q XRD patterns, Transduction coefficient data, Grain size distributions) is available in the online version of this article at https://doi.org/

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Figures
Figure 1

(a) A ring-shaped KNN-BNKLZ-BS piezoceramic prepared using conventional solid-state powder process (Fig. S1). (b) Cross-sectional view of a compression-mode accelerometer sensor prototype (1: piezoceramic ring; 2: screw; 3: seismic mass; 4: tail; 5: base plate; 6: insulating layer; 7: electrode). Poling directions are indicated by arrows. (c) Block diagram of experimental setup for voltage sensitivity measurements.

Figure 2

(a) XRD q-2q patterns and magnified view (2q = 44° to 47°) of unpoled KNN-0.03BNKLZ-yBS ceramic rings (y = 0 – 0.015). The crystallographic indexing adopted for a tetragonal perovskite phase. (b)
Quantitative phase fractions analyzed by Rietveld refinement method.

Figure 3

Temperature-dependent dielectric permittivity $\varepsilon_r$ of KNN-0.03BNKLZ-yBS ceramic rings ($y = 0 - 0.015$): (a) 25 - 500 °C, (b) -150 - 200 °C. (c) Variation of room-temperature $\varepsilon_r$ with BS concentration for poled and unpoled samples.

Figure 4

(a) Properties of $d_{33}$ and $g_{33}$ of ring-shaped KNN-0.03BNKLZ-yBS ceramics ($y = 0 - 0.015$). Properties of commercial PZT-5A are indicated by dashed line for comparison. (b) Comparison of piezoelectric voltage constant $g_{33}$ of modified-KNN ceramic (this work; $y = 0.0025$) with well-known polycrystalline piezoelectric ceramics (PMN-PZT, PMN-PT, PZT-5H, PZT-5A, PZT-4, BaTiO$_3$) [4,5,16]. (c) Magnitudes of $\varepsilon_r$, $d_{33}$, and $g_{33}$.

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$d_{33}$, and $g_{33}$ normalized to each value at $y = 0$. Red arrows indicate material compositions with highest and lowest $g_{33}$ values.

**Figure 5**

SEM images for ring-shaped KNN-0.03BNKLZ-$y$BS ceramics ($y = 0 – 0.015$). Area fraction of large grains ($\geq 20$ mm) are also presented determined from Fig. S5.
Figure 6

(a) Images of constituent sensor components (base, tail, electrode, mass, screw) and modified-KNN piezoceramic rings fabricated according to proposed design [25]. (b) A compression-mode accelerometer sensor prototype assembled using sensor components and piezoceramic rings according to fabrication procedures (Fig. S2).
Figure 7

(a) Variation of output voltage with time under cyclic loading of sine-wave modes at different accelerations (0 - 10 g) obtained from accelerometer sensor prototypes built with modified (m)-KNN (y = 0.0025 and 0.01) and PZT-5A ceramics. (b) Plots of output voltage versus acceleration obtained at 159 Hz. (c) Voltage sensitivity determined from a slope between voltage and acceleration.

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