Optimizing energy harvesting performance by tailoring ferroelectric/relaxor behavior in KNN-based piezocermics

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Received: December 29, 2021; Revised: March 11, 2022; Accepted: March 12, 2022
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Abstract: Piezoelectric energy harvesters (PEHs) fabricated using piezocermics could convert directly the mechanical vibration energy in the environment into electrical energy. The high piezoelectric charge coefficient ($d_{33}$) and large piezoelectric voltage coefficient ($g_{33}$) are key factors for the high-performance PEHs. However, high $d_{33}$ and large $g_{33}$ are difficult to simultaneously achieve with respect to $g_{33} = d_{33} / (\varepsilon_{0}\varepsilon_{r})$ and $d_{33} = 2Q_{0}\varepsilon_{r}P_{r}$. Herein, the energy harvesting performance is optimized by tailoring the CaZrO$_3$ content in $(0.964 - x)\text{(K}_{0.52}\text{Na}_{0.48})\text{(Nb}_{0.96}\text{Sb}_{0.04})\text{O}_{3} - x\text{CaZrO}_{3}$ ceramics. First, the doping CaZrO$_3$ could enhance the dielectric relaxation due to the compositional fluctuation and structural disordering, and thus reduce the domain size to $\sim 30$ nm for $x = 0.006$ sample. The nanodomains switch easily to external electric field, resulting in large polarization. Second, the rhombohedral–orthorhombic–tetragonal phases coexist in $x = 0.006$ sample, which reduces the polarization anisotropy and thus improves the piezoelectric properties. The multiphase coexistence structures and miniaturized domains contribute to the excellent piezoelectric properties of $d_{33}$ (354 pC/N). Furthermore, the dielectric relative permittivity ($\varepsilon_{r}$) reduces monotonously as the CaZrO$_3$ content increases due to the relatively low ion polarizability of Ca$^{2+}$ and Zr$^{4+}$. As a result, the optimized energy conversion coefficient ($d_{33} \times g_{33}$, 5508 $\times 10^{-15}$ m$^2$/N) is achieved for $x = 0.006$ sample. Most importantly, the assembled PEH with the optimal specimen shows the excellent output power ($\sim 48$ $\mu$W) and lights up 45 red commercial light-emitting diodes (LEDs). This work demonstrates that tailoring ferroelectric/relaxor behavior in (K,Na)NbO$_3$-based piezoelectric ceramics could effectively enhance the electrical output of PEHs.

Keywords: piezoelectric energy harvesters (PEHs); potassium sodium niobate (KNN); relaxor ferroelectric; miniaturized domains; multiphase coexistence
1 Introduction

With the development of the miniaturization and integration of electronic devices, the miniature power supply system has raised much attention [1–3]. On account of the human environment and energy crisis, more and more research is applied on the utilization of the abundant mechanical vibration energy in the environment [4–8]. Piezoelectric materials have received much attention due to their efficient and straight electromechanical coupling between vibrational energy and electrical energy, which is called piezoelectric energy harvesting technology [9]. Moreover, the piezoelectric energy harvesters (PEHs) have a simple structure and are easy to integrate with electronic devices compared with static electricity, triboelectricity, magnetoelectricity, and other mechanical energy conversion methods [10]. Therefore, PEHs are potential to replace conventional batteries to supply power to the small-scale electronic devices.

Recently, lead-based and lead-free (Ba,Ca)(Ti,Zr)O3-based piezoelectric ceramics are widely implemented in PEH devices due to their superior piezoelectric charge coefficient (d33) and piezoelectric voltage coefficient (g33). However, the lead-based materials are harmful to the environment and human being due to the toxicity of lead element [11]. The low operating temperature of (Ba,Ca)(Ti,Zr)O3-based ceramics due to the low Curie temperature (< 120 °C) restricts their practical application [12]. Potassium sodium niobate (KNN)-based ceramics are regarded as the attractive candidates for lead-free piezoelectric ceramics because of their high Curie temperature and excellent electromechanical properties [13,14]. Especially, Tao et al. [15] have obtained a high d33 of ~650 pC/N by doping strategy in KNN-based ceramics. Therefore, the KNN-based piezoelectric ceramics are regarded as attractive candidates for lead-free piezoelectric ceramics and expected to fabricate high-performance PEHs.

According to Islam and Priya [16], the energy conversion density of piezoelectric materials under the external excitation of alternating forces (u) can be expressed as follows:

\[ u = \frac{1}{2} (d \times g) \left( \frac{F}{A} \right)^2 \]  
(1)

where \( d \) is the piezoelectric constant, \( g \) is the piezoelectric voltage constant, \( F \) is the external force, and \( A \) is the force area. Therefore, the energy conversion coefficient \( d \times g \) is the key factor for high-performance PEHs. The piezoelectric voltage coefficient \( g_{33} \) in the poled piezoelectric ceramics can be calculated by Eq. (2) [17,18]:

\[ g_{33} = \frac{d_{33}}{\varepsilon_r} \]  
(2)

where \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m} \) is the permittivity of the vacuum. The high piezoelectric coefficient \( d_{33} \) and low dielectric relative permittivity \( \varepsilon_r \) should be simultaneously achieved in the piezoelectric ceramics to improve the output electrical energy of PEHs. Nevertheless, in ferroelectric materials, the \( d_{33} \) is proportional to the product of polarization and permittivity, which can be expressed as Eq. (3) [19]:

\[ d_{33} = 2Q \varepsilon_0 \varepsilon_r P_t \]  
(3)

where \( P_t \) is the remnant polarization along the polar axis, and \( Q \) is the electrostrictive coefficient of the paraelectric phase. The high \( d_{33} \) is correlated to the high \( \varepsilon_r \), which runs counter to the principle in Eq. (2). Thus, \( d_{33} \) should be enhanced by the improvement of polarization instead of \( \varepsilon_r \). In a word, the \( d_{33} \) or \( P_t \) should be as large as possible; meantime, the \( \varepsilon_r \) should be as low as possible.

From a thermodynamic perspective, the energy barrier of polarization anisotropy could be reduced by constructing multiphase coexistence structures and miniaturized domains [20–22]. In the relaxor ferroelectric, the domain size could be sharply reduced to nanoscale because of the local structural heterogeneity induced by compositional fluctuations. The nanodomains have a fast response to the external electric fields, which facilitates the polarization switching and improves the polarization intensity [23]. Hence, the excellent piezoelectric property \( d_{33} \) would be achieved in the piezoelectric ceramics with nanodomain configurations. Generally speaking, the relaxor KNN-based ceramics can be designed by the A-/B-sites compositional fluctuation [15,23]. If the doping components have the low polarizability, it is expected to reduce the \( \varepsilon_r \) of the piezoelectric ceramics at the same time.

In this work, the Ca2+ and Zr4+ with low ion polarizability are doped in KNN-based ceramics to tailor the diffused phase transition and achieve the easy-switching nanoscale domain structure. An expected large \( d_{33} \) of 354 pC/N and relatively low \( \varepsilon_r \) of 2441 are obtained by optimizing the composition. Thus, the high energy conversion coefficient \( (d_{33} \times g_{33}) \) of 5508 × 10⁻¹⁵ m²/N was achieved. Furthermore, the cantilever-type PEHs were also fabricated using the as-prepared
piezoelectric ceramic disk, which exhibited the excellent output power of ~48 μW.

2 Experimental

The \((0.964−x)(K_{0.52}Na_{0.48})(Nb_{0.96}Sb_{0.04})O_3−0.036(Bi_{0.5}Na_{0.5})ZrO_3−xCaZrO_3\) (KNNS–BNZ–xCZ, \(x = 0.001–0.02\)) ceramics were prepared by a conventional solid-state reaction method. The preparation procedure and characterization including phase structure, microstructure, and electrical properties are described in the Electronic Supplementary Material (ESM). Subsequently, the piezoelectric ceramics were fabricated to cantilever-type energy harvesters to evaluate the energy harvesting capability [24]. Epoxy glue (353ND, Epoxy Technology, Billerica, USA) was used to attach the ceramic pieces (10 mm × 10 mm × 0.6 mm) to the stainless steel substrate cantilever beam (120 mm × 12 mm × 0.9 mm). The piezoelectric cantilever with a unimorph structure was mounted on a smart shaker (HEV-20, Foneng Technology Industry Inc., Nanjing, China) with an integrated power amplifier (HEAS-20, Foneng Technology Industry Inc., Nanjing, China). The vibration acceleration of the cantilever beam was measured by a piezoelectric accelerometer system (CT1050LC, Chengke Electronic Technology Inc., Shanghai, China) and a data acquisition card (CT1050LC, Chengke Electronic Technology Inc., Shanghai, China). The output voltage and current of the harvester were measured using a digital oscilloscope (InfiniiVision DSOX3014T, Keysight, Santa Clara, USA) and a digital source meter (2450, Keysight, Santa Clara, USA).

3 Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns at room temperature of the KNNS–BNZ–xCZ ceramics in the 2θ range of 20°–80°. A typical perovskite structure was formed with tiny secondary phase of CaNb2O6. Further observation of the enlarged XRD patterns in the 2θ range of 44.5°–46° revealed the obvious changed shape of (002)/(200) diffraction peaks, suggesting the composition-driven structural transition. A distinct split of the (002)/(200) peak near 45° was observed for 0.01 ≤ x ≤ 0.09 ceramics, indicating the multiphase coexistence state containing tetragonal (T), orthorhombic (O), and rhombohedral (R). Similar phase boundary has been verified in many Sb and BNZ co-doped KNN-based systems with respect to the previous reports [20,25,26]. As the CaZrO3 content exceeded x = 0.01, the (002)/(200) peaks merged into a single (200) peak, which meant that the phase structure transformed to the pseudo-cubic phase [27,28]. The composition-driven phase transition could be explained by the different sizes of ion radii between dopant (Ca2+ and Zr4+) and the elements in A-/B-sites in the KNN lattices. To further elucidate the phase transition, the XRD patterns of three typical compositions were Rietveld refined with the assistance of GSAS software as displayed in Fig. 2. The Rietveld refinements of \(x = 0.001\) and \(x = 0.006\) ceramics were obtained using the mixed-phase models containing \(R_3m\) (R), \(Amm2\) (O), and \(P4mm\) (T) space groups, while the \(x = 0.015\) ceramic was fitted using \(P4mm\) (T) space group (Table 1). It could be observed that the fitting lines corresponded well with the measured curves, accounting for the reliability of
Fig. 2 Rietveld-refined XRD patterns of (a) \( x = 0.001 \), (b) \( x = 0.006 \), and (c) \( x = 0.015 \) samples.

Table 1 Lattice parameters and refinement parameters of the KNNS–BNZ–\( \chi \)CZ ceramics obtained from the XRD Rietveld refinement

| Sample          | Space group | \( a \) (nm) | \( b \) (nm) | \( c \) (nm) | Phase fraction (%) | \( \alpha, \beta ({}^\circ) \) | \( \gamma ({}^\circ) \) | \( R_{wp} (%) \) | \( R_p (%) \) |
|-----------------|-------------|---------------|---------------|-------------|-------------------|-----------------|----------------|----------------|--------------|
| \( x = 0.001 \) | \( P4mm \)  | 0.39408       | 0.39408       | 0.39544     | 36.56             | 90              | 90              | 8.96           | 6.31         |
|                 | \( Amm2 \)  | 0.39827       | 0.56670       | 0.56830     | 33.57             | 90              | 90              | 7.50           | 5.86         |
|                 | \( R3m \)   | 0.56217       | 0.56217       | 0.69179     | 29.87             | 90              | 120             |               |              |
| \( x = 0.006 \) | \( P4mm \)  | 0.39478       | 0.39478       | 0.39637     | 19.66             | 90              | 90              |               |              |
|                 | \( Amm2 \)  | 0.39672       | 0.55890       | 0.55998     | 38.48             | 90              | 90              | 7.50           | 5.86         |
|                 | \( R3m \)   | 0.56785       | 0.56785       | 0.69083     | 41.86             | 90              | 120             |               |              |
| \( x = 0.015 \) | \( P4mm \)  | 0.39764       | 0.39764       | 0.39782     | 100               | 90              | 90              | 8.32           | 6.42         |

The crystal structure of KNNS–BNZ–\( \chi \)CZ ceramics was further characterized by the temperature-dependent \( \varepsilon_r \) and dielectric loss (\( \tan \delta \)) curves measured at 1 kHz as displayed in Fig. 3(a). Two abnormal dielectric peaks have been observed, which correspond to ferroelectric–ferroelectric at low temperature (\( T_f \)) and the tetragonal to cubic phase transition at Curie temperature (\( T_C \)). As the doping CaZrO\(_3\) content increased, the \( T_C \) decreased rapidly and \( T_f \) shifted towards room temperature [29]. By further increasing the CaZrO\(_3\) content, the two dielectric peaks would merge into a unimodal peak. The \( T_f \) of \( x < 0.01 \) samples located near room temperature, which was well matched with the R–O–T multiphase coexistence structure obtained by the XRD analysis. \( T_f \) vanished when \( x > 0.01 \), in coincidence with the pseudo-cubic phase of \( x = 0.015 \) ceramic. In addition, the frequency-dependent \( \varepsilon_r-T \) and \( \tan \delta-T \) curves of the three typical compositions are depicted in Figs. 3(b)–3(d). To precisely evaluate their diffused phase transition, the empirical law of the modified Curie–Weiss model is employed in Fig. S1 in the ESM to calculate the diffuseness coefficient (\( \gamma \)), which was also enwritten in Figs. 3(b)–3(d). \( \gamma = 1 \) represented a normal ferroelectric, which fully complied with the Curie–Weiss law, while \( \gamma = 2 \) described an ideal relaxor ferroelectric with complete diffuse phase transition [30]. The dielectric dispersion became stronger and stronger as the CaZrO\(_3\) content increased since the \( \gamma \) values of \( x = 0.001, 0.006, \) and 0.02 are 1.65, 1.71, and 1.95, respectively. The \( x = 0.02 \) sample exhibited a strong frequency-dependent dielectric behavior with a broad phase transition as a function of the applied frequency. The prominent dielectric diffusiveness behavior occurred mainly due to the random local elastic fields and local charge imbalance induced by the compositional fluctuation and structural disordering in the \( A-/B \)-sites of ABO\(_3\) lattice [31,32]. Therefore, when the doped elements were introduced into the KNN lattice, the long-range ferroelectric ordering would be broken up, resulting in the domain refinement and the formation of polar nano-regions (PNRs).

It is well known that the evolution of the microstructural features has a great influence on the electrical properties. Hence, the surface morphologies of the KNNS–BNZ–\( \chi \)CZ ceramics were observed by the scanning electron microscopy (SEM) in Fig. S2 in the ESM. All of the ceramics exhibit a dense microstructure with cuboid-like grains, which was in coincidence with the high relative density in Table S1 in the ESM. The average grain size was highly sensitive to the CaZrO\(_3\), which decreased extremely from 1.5 to 0.3 \( \mu \)m as the CaZrO\(_3\) content increased from \( x = 0.001 \) to \( x = 0.02 \). It declared
that the addition of CaZrO$_3$ inhibited the grain growth. It may be due to the fact that the donor (Ca$^{2+}$) and acceptor (Zr$^{4+}$) hindered the grain boundary motion and reduced the interface energy during the sintering process, where the similar phenomena were reported in the recent literatures such as KNN-based [33], (B$_{0.5}$N$_{0.5}$)TiO$_3$-based [34], and BaTiO$_3$-based [35] systems. Figure S3 in the ESM displays the element mappings of the $x = 0.006$ ceramic by the energy-dispersive X-ray spectroscopy (EDS) analysis. It was observed that there was no element enrichment between grains and grain boundaries, resulting in the good chemical homogeneity. The chemical compositions of $x = 0.006$ sample are semi-quantitatively analyzed by the EDS spectrum in Fig. S4 in the ESM, and the atomic proportions are listed in Table S2 in the ESM. It could be found that a small amount of K element volatilized, and Na element hardly volatilized during the sintering process.

The refinement of the grain size and the prominent diffused phase transition could reduce the domain size [36]. Hence, the bright-field TEM images of the three typical compositions were employed to explore the domain configuration in Fig. 4. It can be obviously found that the domain structures evolved gradually from the lamellar shape with a width of about 200 nm for $x = 0.001$ ceramic, to a hierarchical domain topography with a lamellar shape and smaller width of about 30 nm for $x = 0.006$ sample, and ultimately formed unfeatured and homogeneous PNRs for $x = 0.015$ ceramic. The occurrence of nanodomains contributed to the increasing piezoelectricity on account of the easy polarization switching to the external electric field.

Fig. 3  (a) Temperature-dependent dielectric relative permittivity curves ($\varepsilon_r$–T) of the KNNS–BNZ–xCZ ceramics measured at 1 kHz. $\varepsilon_r$–T and tanδ–T of the ceramics with (b) $x = 0.001$, (c) $x = 0.006$, and (d) $x = 0.02$ samples measured at different frequencies.

Fig. 4  Bright-field TEM images of (a) $x = 0.001$, (b) $x = 0.006$, and (c) $x = 0.015$ samples. (d) HRTEM image and the corresponding SAED pattern of $x = 0.006$ sample.
[22,37]. To exclude the possible inducement of chemical inhomogeneity to the formation of diverse domain topography, the local element distributions across the grains were confirmed by EDS analysis. The results are shown in Fig. S5 in the ESM. As can be seen, all elements were homogeneously distributed in this sample. The homogeneous element distributions illustrated by TEM–EDS and SEM–EDS analysis evidence again that the doped CaZrO3 was well merged into the matrix of KNN-based lattice. A long-range ordered structure was found for $x = 0.006$ ceramic by the high-resolution transmission electron microscopy (HRTEM). The interplanar spacings were identical to the (100) and (011) lattice planes, which was also confirmed by the selected area electron diffraction (SAED) pattern in the inset of Fig. 4(d). The good crystallinity was in coincidence with the XRD results.

The ferroelectric–relaxor transition had a great influence on the dielectric, ferroelectric, and piezoelectric properties. The polarization ($P–E$) and bipolar strain ($S–E$) curves of the KNNS–BNZ–$x$CZ ceramics were measured under an external electric of 4 kV/mm in Figs. 5(a) and 5(b), respectively. To further discuss the variation of the electrical properties, the key parameters including the maximum polarization ($P_{\text{max}}$, the polarization under the maximum electric field), remnant polarization ($P_r$, the polarization when the external electric field was removed), converse piezoelectric coefficient ($d_{33}^*$, calculated by $S_{\text{max}}/E_{\text{max}}$, where $S_{\text{max}}$ and $E_{\text{max}}$ are the maximum strain and electric field, respectively), and coercive field ($E_c$, the electric field when the polarization was zero) were compared as a function of composition ($x$) as summarized in Fig. 5(c). It can be seen that $E_c$ increased with the increase of $x$, because the donor ($\text{Ca}^{2+}$) and acceptor ($\text{Zr}^{4+}$) increased. For the composition with $x < 0.01$, a typical ferroelectric feature with square-shaped $P–E$ loops was observed. When the $x$ further increased especially for $x > 0.01$, the long-range ferroelectric ordering domains disappear and only PNRs remain, leading to slim $P–E$ curves and the deterioration of ferroelectric polarization. Therefore, three regions marked with Region I (ferroelectric), Region II (ferroelectric and relaxor mixture), and Region III (relaxor) were divided. In addition, $P_{\text{max}}$, $P_r$, and $d_{33}^*$ exhibit a similar tendency. The initial slightly decrease in Region I might be ascribed to the reducing grain size (Fig. S6 in the ESM) because of the increasing proportion of non-ferroelectric grain boundary and clamping effects of the domain walls [38–40]. The subsequent boost in Region II should attribute to the R–O–T multiphase coexistence near room temperature and the miniaturized domain size. On one hand, the R–O–T multiphase coexistence phase boundary reduced the polarization anisotropy and weakened the energy barriers, and thus enhanced their ferroelectric and piezoelectric properties. On the other hand, these nanoscale domains could switch easily to the external electric field and contribute to the high piezoelectric response [41,42]. The $P_{\text{max}}$, $P_r$, and $d_{33}^*$ values dramatically decreased as the CaZrO3 content further

![Fig. 5](https://www.springer.com/journal/40145)

Fig. 5 (a) $P–E$ loops and (b) unipolar $S–E$ curves of the KNNS–BNZ–$x$CZ ceramics at 4 kV/mm. (c) $P_{\text{max}}$, $P_r$, $E_c$, and $d_{33}^*$ as a function of $x$. (d) $d_{33}$, $\tan\delta$, electromechanical coupling coefficient ($k_p$), $\varepsilon_r$, $g_{33}$, and $d_{33} \times g_{33}$ as a function of $x$.
increased in Region III due to the degraded ferroelectric polarization. In addition, the $x = 0.006$ ceramic exhibited an excellent temperature stability as verified by the temperature-dependent $P$–$E$ loops in Fig. S7 in the ESM.

The other dielectric and piezoelectric properties were also determined as displayed in Fig. 5(d). All the ceramics exhibit low $\tan \delta$, which should be correlated with the dense microstructure. The $\varepsilon_r$ reduced monotonously as the CaZrO$_3$ content increased in all the regions because of the relative low ion polarizability of Ca$^{2+}$ (0.472 Å$^3$) and Zr$^{4+}$ (0.376 Å$^3$) [43]. The $d_{33}$ first increased and then decreased, achieving the peak value (354 pC/N) with $x = 0.006$, because of its large polarization intensity with respect to $d_{33} = 2Q_{0}\varepsilon_rP_t$ [19]. The $k_p$ had a similar tendency to $d_{33}$ variation, increasing first and then decreasing with the increased CaZrO$_3$ content, and could be maintained over 38% for $x = 0.005$–0.007. In addition, $g_{33}$ and $d_{33} \times g_{33}$ were calculated since they were two important parameters for evaluating the energy harvest capability of piezoelectric materials [16]. The $g_{33}$ increased first and then decreased, reaching the maximum ($15.56 \times 10^{-3}$ Vm/N with $x = 0.006$) in Region II, because of the relative low dielectric permittivity and the boosted $d_{33}$ in this region with respect to $g_{33} = d_{33} / (\varepsilon_0\varepsilon_r)$. The excellent $d_{33}$ and $g_{33}$ result in the optimized $d_{33} \times g_{33}$ ($5508 \times 10^{-15}$ m$^2$/N) for $x = 0.006$ sample. These high parameters with high $d_{33}$ and $g_{33}$ values were excellent comprehensive performance for the practical applications of PEHs.

Subsequently, the $x = 0.001$, 0.006, and 0.015 ceramic samples were chosen to assemble a cantilever beam type PEH to verify the power generation capability of KNNS–BNZ–$x$CZ ceramics with different domain configurations [44]. The cantilever beam was first fixed to the shaker by a custom-designed fixture, the square ceramic samples were plated by epoxy glue to the cantilever beam, and the lead lines at the bottom and top of ceramics were used to connect the instruments or load resistances. By applying a continuous mechanical vibration with sine wave modes to the shaker, the samples were subjected to alternating stress, and the generated voltage could be recorded by an oscilloscope. Related parameters and the simulation of cantilever structure from finite element analysis had been repeatedly reported by Yan et al. [45,46]. Figures 6(a) and 6(b) feature continuous voltage and current waveform signals generated by the PEH under the external mechanical resonance with a vibration excitation with 1g (gravitational acceleration) at 80.3 Hz. The highest output voltage (open-circuit) of 12.1 V (peak to peak) and output current (short-circuit) of 19.3 μA (peak to peak) were achieved in the PEH fabricated by $x = 0.006$ sample. Figures 6(c)–6(e) illustrate the output voltage, current, and power values across load resistances, respectively. With the load resistance increased, the output current decreased and the output voltage increased. The optimal power value (~48 μW) was obtained at a load resistance of 700 kΩ, which matched the internal impedance of energy harvester [47]. The output power
of the KNNS–BNZ–xCZ-based energy harvester in this study was much higher than the values of the previously reported KNN-based PEHs as summarized in Table 2 [48–53]. In addition, the power density of the $x = 0.06$ energy harvester was calculated, and the obtained value was 0.96 $\mu$W/mm$^3$. Although this value was smaller than that of the membrane-structured energy harvester, it was significantly superior to that of the bulk-structured energy harvester. In order to verify the practical application of KNNS–BNZ–xCZ-based PEH, the circuit shown in Fig. 6(f) was used to assemble 45 red commercial light-emitting diodes (LEDs) and full bridge rectifier. When the PEH started working, the LEDs were lit up immediately without energy storage (Fig. 6(f)). The excellent performance of KNNS–BNZ–xCZ-based PEH in energy harvesting indicated its great potential in wireless sensors or self-powered micro devices.

### 4 Conclusions

In summary, the ferroelectric, ferroelectric–relaxor mixture, and relaxor materials were obtained by tailoring the CaZrO$_3$ content in KNNS–BNZ–xCZ in this work. The dielectric, ferroelectric, and piezoelectric properties as well as the power generation characteristics were evaluated systematically. On one hand, the multiphase coexistence structures and miniaturized domains in the ferroelectric–relaxor ceramics generate the excellent piezoelectric properties. On the other hand, the relative low ion polarizability of Ca$^{2+}$ and Zr$^{4+}$ partly reduces $\varepsilon_r$. As a result, the expected large $d_{33}$ of 354 pC/N and relatively low $\varepsilon_r$ of 2441 are simultaneously achieved in the $x = 0.06$ sample, which optimizes the $d_{33} \times g_{33}$. Furthermore, the cantilever-type PEHs fabricated using the $x = 0.06$ ceramic exhibit an excellent output power of ~48 $\mu$W and light up 45 red commercial LEDs. Our results demonstrate that the energy harvesting performance of PEHs could be boosted by optimizing the phase structure, relaxor behavior, and doping strategy in the (K,Na)NbO$_3$-based piezoelectric ceramics.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 52072150 and 51972146), the China Association for Science and Technology (Young Elite Scientists Sponsorship Program), and the State Key Laboratory of New Ceramics and Fine Processing Tsinghua University (No. KF202002).

### Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

### Electronic Supplementary Material

Supplementary material is available in the online version of this article at https://doi.org/10.1007/s40145-022-0587-1.

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