



# Energy-Harvesting Device Based on Lead-Free Perovskite

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#### Abstract

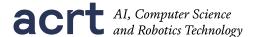
This research investigates the solid-state synthesis of lead-free (K, Na) $_{0.5}$ NbO $_3$  ceramics to improve the performance of triboelectric nanogenerators (TENGs) for energy-harvesting applications. The TENGs have developed as potential devices for converting mechanical energy into electrical energy. However, traditional TENG materials frequently include lead, which raises environmental and health problems. To overcome this issue, lead-free ceramics were examined as alternative materials with superior properties. In this work, a TENG was fabricated using potassium sodium niobate (KNN) ceramics as one triboelectric layer, Kapton as the other triboelectric layer, and a flexible substrate. The aim was to create TENGs with improved performance and environmental sustainability. The output performance of the TENG was estimated to be 70 V and 1100 nA. The TENG was further used to charge capacitors, light up an LED, and harvest energy from various body motions.

Keywords: lead-free, triboelectric, biomechanical, LED

#### 1. Introduction

A triboelectric nanogenerator (TENG) converts mechanical energy into electrical energy using the triboelectric effect and electrostatic induction [1–3]. This unique device uses friction between two material combinations to generate an electric





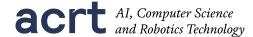
charge. TENGs may generate power from mechanical actions as simple as tapping, rubbing, or pushing, making them ideal for harvesting energy from ordinary activities or environmental sources such as wind or water [4–7]. TENGs have promising applications in wearable electronics, self-powered sensors, and renewable energy harvesting, providing a sustainable and efficient method of producing electricity without relying on existing power sources [8–12].

A lead-free piezoelectric material such as potassium sodium niobate (KNN) is gaining importance in energy harvesting and electronics due to its unique properties and environmental friendliness [13–16]. KNN exhibits a perovskite structure (ABO<sub>3</sub>), where larger A-site cations (potassium and sodium) occupy the corners, smaller B-site cations (niobium and titanium) reside in the center, and oxygen anions position at the face centers, facilitating ferroelectric properties [17]. This configuration generates a highly ordered lattice that gives the KNN its piezoelectric potential. In addition, the crystal structure can be modified by doping or alloying to improve piezoelectric performance and stability, making it suitable for several applications [18, 19].

Unlike typical piezoelectric materials, which often contain harmful substances such as lead, KNN provides safer alternatives without compromising its effectiveness [20, 21]. This makes it an ideal solution for applications that require the extraction of energy from mechanical vibrations, movements, or deformations. KNN-based materials have been effectively incorporated into TENGs. When paired with triboelectric materials, KNN can greatly improve the energy conversion efficiency of TENGs. Previously, KNN-based materials have been explored commonly in the piezo-tribo electric hybrid energy device or single piezoelectric nanogenerator (PENG) by some authors to design various self-powered applications. Abdulla et al. have demonstrated a KNN/PVDF/MWCNT hybrid device based on composite films that can produce an output of 54.1 V and 29.4 µA [22]. Nair et al. have produced 2.1 V and 42 nA by simply tapping their fingers on a PENG device based on PVDF-KNN composites [23]. Verma et al. have used a PENG device based on KNN/PVDF composites for harvesting energy using body motions and generated a voltage of 11.2 V [24]. Composites based on PDMS–KNN–xBTO were prepared by Vivekananthan *et al.* to showcase a battery-free security system [19].

In the present work, a lead-free material KNN is synthesized, and various types of material characterization are performed. Furthermore, a TENG device was fabricated and operated in the vertical contact separation mode. The long-term stability output and glowing of LED were performed using TENG. It was used to harvest energy from various body motions. This innovative technology harnesses human motion to potentially power wearable devices or consumer electronics, offering a sustainable energy source.





#### 2. Synthesis and experimental techniques

The typical solid-state reaction approach can produce KNN powder. Initially, high-purity oxides and carbonates such as potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>), procured from Loba Chemie, India, were taken in appropriate equimolar amounts. The ingredients were uniformly mixed in an agate mortar by adding alcohol as a medium for the following two hours to achieve a homogeneous mixture and then dried to collect the powder mixture. This homogeneous mixture was then transferred into an alumina crucible and put into a muffle furnace at 900 °C for 5 h to obtain the crystalline phase. After calcination, the powder was collected for various types of characterization. The TENG device is fabricated by taking PET as a substrate, and copper tape is used as an electrode. The calcinated KNN powder is spread on the copper electrode and fixed by cold press, which was used as a positive triboelectric layer and Kapton is taken as another triboelectric layer. The device is neither packed nor polled; hence the contribution of piezoelectric behavior of KNN is negligible. Therefore, this design setup can only act as a triboelectric nanogenerator. The dielectric properties were measured by using a pellet. For this purpose, a pelletizer was used to cold-press the KNN powder in disc shape (dimension 10 mm and thickness 1.5 mm) with the help of an organic binder, namely polyvinyl alcohol 2 wt%.

The X-ray diffractometer (XRD; Rigaku, Japan), with Cu–K $\alpha$  radiation operating at ambient temperature and the X-ray source wavelength  $\lambda$  = 1.5406 Å, was utilized to measure the X-ray spectra. Using a 514 nm excitation source, a Raman spectrometer (LabRAM, Japan) was used to record the Raman spectrum analysis of KNN particles. Using a scanning electron microscope (SEM; Zeiss Sigma 300, USA), the surface morphology of KNN particles was investigated. The dielectric properties were measured using an impedance analyzer (Hioki IM3470, Japan) at room temperature. The TENG output was measured and traced using a Keithley 6514 electrometer and a linear motor was used to apply periodic contact separation of TENG.

#### 3. Results and discussion

The KNN ceramics are synthesized by solid-state reaction. Figure 1a shows the Rietveld analysis of XRD spectra of KNN at room temperature. The KNN ceramics are seen to have an orthorhombic symmetry [25–27]. Using the MAUD (Materials Analysis Using Diffraction) tool, a Rietveld refinement of the XRD patterns is conducted to establish the crystal lattice parameters [28]. The crystal lattice parameters are as follows: a = 3.9459 Å, b = 5.6447 Å, and c = 5.6764 Å. The Raman spectra of KNN powders at room temperature are displayed in Figure 1b. There are three characteristic Raman peaks (870 cm<sup>-1</sup>, 620 cm<sup>-1</sup>, and 250 cm<sup>-1</sup>) in the spectra



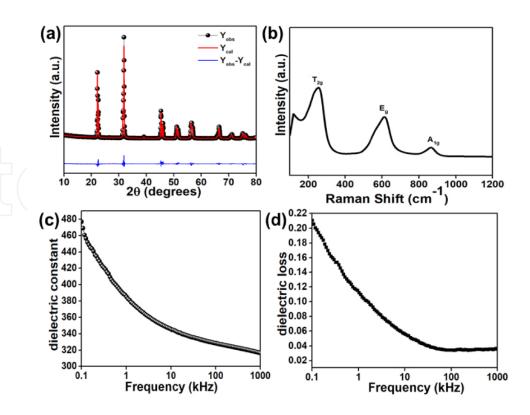


Figure 1. (a) Rietveld refinement of XRD pattern of KNN ceramics, (b) Raman spectra of KNN ceramics, and (c, d) dielectric constant and loss of KNN ceramics at room temperature, respectively.

of KNN, which are related to the internal vibrations of the NbO<sub>6</sub> octahedron. Other groups also reported similar Raman spectra of KNN ceramics [17, 29, 30]. The dielectric constant and loss of KNN ceramics at room temperature are measured and presented in Figures 1(c,d), respectively. It shows that both dielectric constant and loss are higher at low frequencies and reduced at higher frequency zones. The dielectric constant is higher at low frequencies due to the reason that all polarizations are activated in this zone, and as one moves to a higher frequency, the dipoles cannot follow the fast-changing electric field leading to a decrease in the dielectric constant value [31, 32]. Compared to the grain borders, the grains are far more conducting. Only at low frequencies does the movement of charge carriers to the grain border, which causes a greater energy loss, predominates. Because of this, the loss factor in this low-frequency region is higher than that in the high-frequency region [33].

Figure 2a displays the SEM micrograph of the KNN sample. The surface morphology displays the densely packed and cube-shaped grains. Figure 2b shows the color mapping of the elements present in KNN ceramics such as K, Na, Nb, and O, which spread uniformly over the surface. Figure 2c shows the EDS spectra of





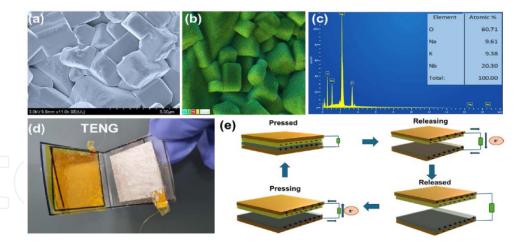


Figure 2. (a) SEM micrograph of KNN ceramics, (b) color mapping of elements K, Na, and Nb in KNN ceramics, (c) EDS spectra with atomic percentage present in KNN ceramics, (d) digital picture of TENG KNN powder and Kapton as triboelectric layers, and (e) working mechanism of TENG operation in vertical contact separation mode.

KNN ceramics and atomic percentage in the insert. Figure 2d shows a digital image of the fabricated TENG using KNN powder, with Kapton serving as the triboelectric layer. The device is tested by vertical contact and separation mode. Due to contact, electrification charges are generated on the surfaces of triboelectric layers. As a result, negative charges are developed on Kapton whereas positive charges are formed on another triboelectric layer (KNN powders). Here, Kapton acts as a negative triboelectric layer. The detailed working mechanism of the TENG is shown in Figure 2e.

Figure 3a shows the voltage and Figure 3b the current of the TENG, which has an active area of 2. 5 cm × 2. 5 cm. Figure 3c shows the long-term stability of the TENG device, confirming the device is useful for many applications. The stability was measured at a constant force of 5 N and 2 Hz. Figure 3d shows the charging of capacitors using TENG. The output of TENG is AC, which is converted to DC using a bridge rectifier. Figure 3e shows the powering of an LED using TENG. Here the digital image of the LED in off and on conditions is shown. Hence it can be confirmed that the TENG can act as a sustainable power source. Figures 4a–f show the voltage of the TENG attached to various body parts. The TENG can be activated by performing actions like walking, tapping, and stretching, which transforms mechanical energy into electrical power. Thus, TENG provides a sustainable energy source by using human motion to power wearables, sensors, and small electronics.



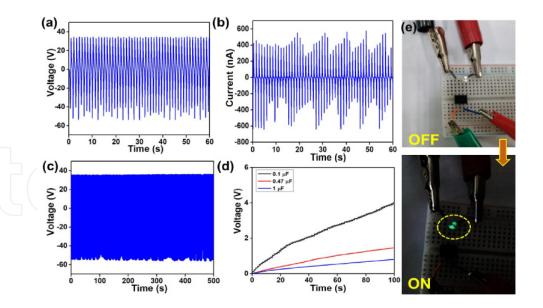


Figure 3. (a) Voltage, (b) current, (c) stability of TENG voltage, (d) charging of capacitor using TENG, and (e) digital image of LED glowing using TENG.

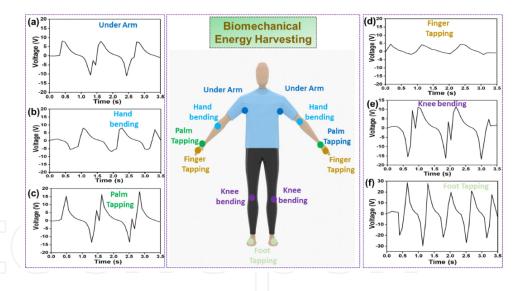


Figure 4. (a–f) Biomechanical energy harvesting using various human activities and corresponding voltage of TENG output.

#### 4. Conclusions

This study explores the synthesis of lead-free  $(K, Na)_{0.5}NbO_3$  ceramics via the solid-state method. Various types of material characterization such as structural, morphology, and electrical properties of KNN are provided in detail. TENGs follow the principle of contact electrification and electrostatic induction. Lead-free



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ceramics have been investigated as viable alternatives to lead-based ceramics. In this research, a TENG operating in vertical contact separation mode was constructed utilizing one triboelectric layer composed of KNN ceramics, another layer consisting of Kapton, and a PET flexible substrate. Experimental results showcased the output performance of TENG reaching 70 V and 1100 nA. Furthermore, the TENG was employed to charge capacitors, illuminate LEDs, and harness energy from diverse bodies. This work focuses on efficient and environmentally friendly, energy-harvesting devices for a wide range of applications such as wearable electronics and self-powered sensors.

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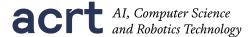
### Conflict of interest

The authors declare no conflict of interest.

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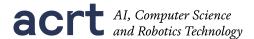
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