Fabrication of potassium sodium niobate nano-particle/polymer composites with piezoelectric stability and their application to unsteady wind energy harvesters

Zhenjin Wang (iD), and Fumio Narita (iD)

View Online   Export Citation   CrossMark

Lock-in Amplifiers
... and more, from DC to 600 MHz   Watch

Fabrication of potassium sodium niobate nano-particle/polymer composites with piezoelectric stability and their application to unsteady wind energy harvesters

Zhenjin Wang [iD] and Fumio Narita[a)] [iD]

AFFILIATIONS

Department of Materials Processing, Graduate School of Engineering, Tohoku University, Aoba-yama 6-6-02,
Sendai 980-8579, Japan

[a)]Author to whom correspondence should be addressed: narita@material.tohoku.ac.jp

ABSTRACT

We investigated the effects of poling conditions on the piezoelectric performance of potassium sodium niobate [(K,Na)NbO$_3$, KNN]/polymer composites, to obtain their unsteady energy harvesting potential. KNN nanoparticle/polymer composites were designed and fabricated and the poling condition test was performed. The composites were polarized using the corona poling method for various poling conditions and then the piezoelectric coefficient d_{33} was measured. It was found that piezoelectricity does not decrease over days. Scanning electron microscopic observations were conducted to study the distribution of the nanoparticles in the matrix. Meanwhile, the microstructure of the composites was studied by X-ray diffraction. Unsteady wind energy harvesting tests were accomplished to investigate the output voltage characteristics in the KNN nanoparticle/polymer composites in unsteady winds. The study represents an important step in developing flexible energy harvesters with stable performance.

Published under license by AIP Publishing. https://doi.org/10.1063/1.5127937

I. INTRODUCTION

Lead-free piezoelectric materials have received a lot of attention due to their high electrical properties[1] and (K,Na)NbO$_3$ (KNN) material has extensively been studied in particular.[2] To induce piezoelectricity in ferroelectric ceramics, an electrical field has to be applied to align the poling axes of the crystallites to the symmetry nearest to that of the applied electric field. This process is called polarization and the degree of which can be characterized by the longitudinal piezoelectric coefficient d_{33}. It is well-known that poling conditions affect the performance of lead-based or lead-free piezoelectric materials.[3–5] Recently, attention has been paid to study the influence of poling conditions on the piezoelectric coefficient of KNN or (KNN)-based materials.[4,6,7]

A particular class of piezoelectric composites consists of a polymer matrix in which ceramic particles are randomly distributed without being connected to each other.[6] Recently, research in composite piezoelectric nanogenerators has gained traction in recent years owing to their advantages, such as reduced leakage current, increased flexibility, ecofriendly nature, cost-effectiveness, biodegradability, and the ease of fabrication of piezoelectric nanogenerators.[8] Although there has been some research into the poling condition of the KNN or KNN-based ceramics, the effects of poling condition on the KNN/epoxy composites have been little studied. To improve the piezoelectric performance of KNN/epoxy composites, suitable poling conditions are very important and the piezoelectric characteristic of KNN/epoxy composites polarized under different conditions needs to be understood.

Banerjee *et al.*[3] found that the piezoelectric constant of the corona polarized composites is larger than that of the common contact polarized composites. In the contact poling method, the samples are discharged by a high direct current in a controlled oil bath. Before the polarization, the electrode is needed so the size of the samples is limited to the small size. Besides, short will happen in the weak spot of the samples and damage the sample. However, in the corona poling method, the samples were heated by the hot plate and the electrical charge from a

corona needle was then sprayed onto the sample's surface. Because the bottom surface of the sample is connected to the ground, the electric field between the sample surfaces is created. In the corona poling method, the electrodes are not needed before poling, so there is no shorting and it can be used for large samples.

With an increasing interest in the Internet of Things (IoT), energy harvesting has gained attention, and the research direction has moved away from just looking at sensors and actuators to an interest in collecting energy from the environment (e.g., vibration, wind, water drop) by using piezoelectric materials.[9] In recent years, piezoelectric carbon fiber reinforced polymer (CFRP) laminated composites have been fabricated by embedding KNN nanoparticles with epoxy interlayers and successfully polarizing the CFRP composites.[10] Also, the output voltage and power were measured for a unimorph cantilever made of stainless steel with a commercial macrofiber composite (MFC) sheet under uniform wind speed.[11] In addition, the barium titanate/epoxy composites were developed by corona poling to discuss the wind energy harvesting characteristics.[12] It was found that the piezoelectric performance decreases within seven days after poling.

In this paper, the KNN nanoparticle/epoxy composites were fabricated and the relationship among poling conditions, piezoelectric performance, piezoelectric stability after poling, and phase structures were investigated. Meanwhile, the output voltage of KNN nanoparticle/epoxy composites due to unsteady winds was measured. This research presented an opportunity for the application of KNN nanoparticle/epoxy composites in natural wind energy harvesters.

II. EXPERIMENT PROCEDURE

A. Material preparation

The lead-free piezoelectric composites were fabricated using KNN nanoparticles and epoxy resin. The raw materials $KO_{0.5}$, $NaO_{0.5}$, $NbO_{2.5}$ were mixed with a final molar ratio of 0.25 K:0.25 Na:0.5 Nb, and a solid-state reaction method was used to obtain the $K_{0.5}Na_{0.5}NbO_3$ particle. The diameter of the KNN nanoparticle

was about 880 nm, the volume fraction of the KNN nanoparticles was held steady at 32 vol. %. Although the increase of the volume fraction in the KNN nanoparticles will cause an increase of piezo-electricity, the higher volume fraction makes the piezoelectric composite brittle and high porosity. We found that if the volume fraction of the particle becomes higher than 32 vol. %, the quality of samples will decline rapidly.

Figure 1(a) displays the fabrication method. First, the KNN nanoparticles were mixed with epoxy, the volume fraction of the particles being 32 vol. %. Then, a Thinky conditioning mixer AR-100 (Thinky Co., Japan) was used to mix the particles with the epoxy. The mixture was stirred for 30 min and defoamed for 10 min. The mixture was then poured into a mold and put into a vacuum oven DP200 (Yamato Scientific Co. Ltd., Japan) at 60 °C for 20 min. This process helped to reduce air bubbles inside the composite. The mold consists of three parts, the upper and bottom parts are aluminum plane, and the center part is a Teflon sheet with a thickness of 0.2 mm. There is a hole of size 40×50 mm in the center of the sheet. The mixture was poured into the hole, and during the solidification, high pressure was applied on the mold to ensure the thickness of the samples. Finally, the composite solidified at a temperature of 135 °C for 45 min and was cut to the required size. The size of the samples is shown in Figs. 1(b) and 1(c). The geometric size of the samples for the poling condition tests was $12.0 \times 3.0 \times 0.2$ mm^3, while that of unsteady wind energy harvesting testing was $25.0 \times 10.0 \times 0.2$ mm^3.

B. Poling treatment

The samples were polarized using a corona poling machine (ELC—01 N, ELEMENT Co. Ltd., Japan) along the thickness direction. Besides, only output voltage from the corona needle is used and it is assumed that the voltage on the sample's upper surface equals the voltage of the corona needle.

Below conditions were employed to discuss the effect of poling condition on the piezoelectric coefficient d_{33} of the KNN/epoxy composites.
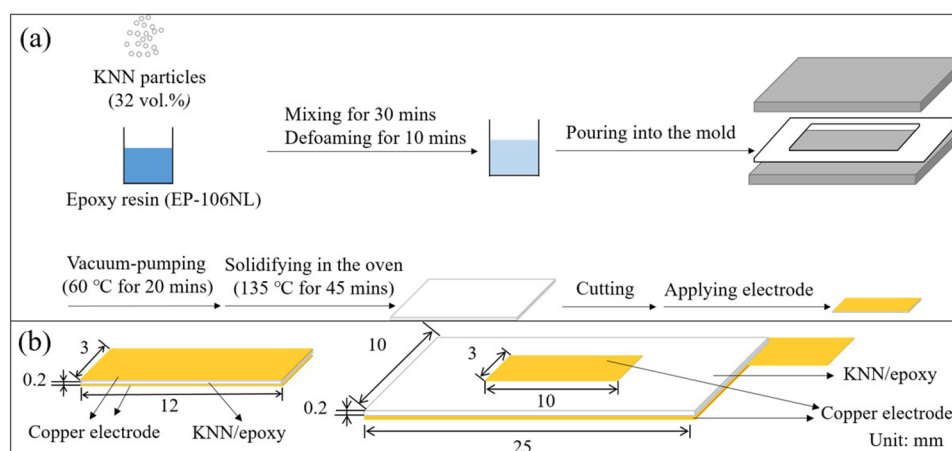

FIG. 1. Schematic of (a) KNN/epoxy composite manufacturing procedure, (b) poling condition test sample (left) and energy harvesting test sample (right).

1. 25–100 °C, 30 kV/mm, 10 min, 15 mm away from the corona needle,
2. 100 °C, 0–45 kV/mm, 10 min, 15 mm away from the corona needle,
3. 75 °C, 30 kV/mm, 0–40 min, 15 mm away from the corona needle, and
4. 75 °C, 15 kV/mm, 10 min, 6–15 mm away from the corona needle.

For each condition, three samples were used.

After poling treatment, the electrodes were attached to the upper and bottom surface of the samples. The electrical properties of the composites were evaluated on 24 h after poling.

Moreover, in order to investigate the changes in the piezoelectric performance of the KNN/epoxy composites after poling over time, three samples were polarized by the condition: 75 °C, 35 kV/mm, 30 min, and 15 mm away from the corona needle. d_{33} of the samples was then measured by a piezo-d_{33} meter within one week after poling.

Before the unsteady wind energy harvesting test, three samples were polarized at 75 °C, 30 kV/mm, for 30 min and 15 mm away from the corona needle.

C. Characterization

SEM observation (JSM-7800F, JEOL Ltd., Japan) was implemented to assess the cross-sectional morphology of the KNN/epoxy composites. The piezoelectric coefficient d_{33} was evaluated by a piezo-d_{33} meter (YE2730A, Sinocera Piezotronics Inc., China). Besides, Rigaku SmartLab (Rigaku Co., Japan) was used to obtain the crystalline structure and phase of the KNN/epoxy composite which was operated at 45 kV and 200 mA, using a CuKα wavelength of 0.154 nm. The recorded 2θ range of the peaks was 20°–60°. The XRD patterns were obtained in the surface of the composite film samples with the scanning area of 10×10 mm.

D. Unsteady wind energy harvesting test

The equipment for the unsteady wind energy harvesting test is given in Fig. 2. The wind speed was measured by a thermos-anemometer (FUSO 8908, FUSO Co. Ltd., Japan). As we all know, the natural wind is a chaotic fluctuation, rather than a continuous, steady fluctuation.[13] The 3 and 5-leaf fans [Figs. 2(a) and 2(b)] were designed to convert continuous wind into discontinuous wind, which is more similar to wind in nature. The fans were made by the polyethylene terephthalate (PET) film and a 3D printed plastic core.
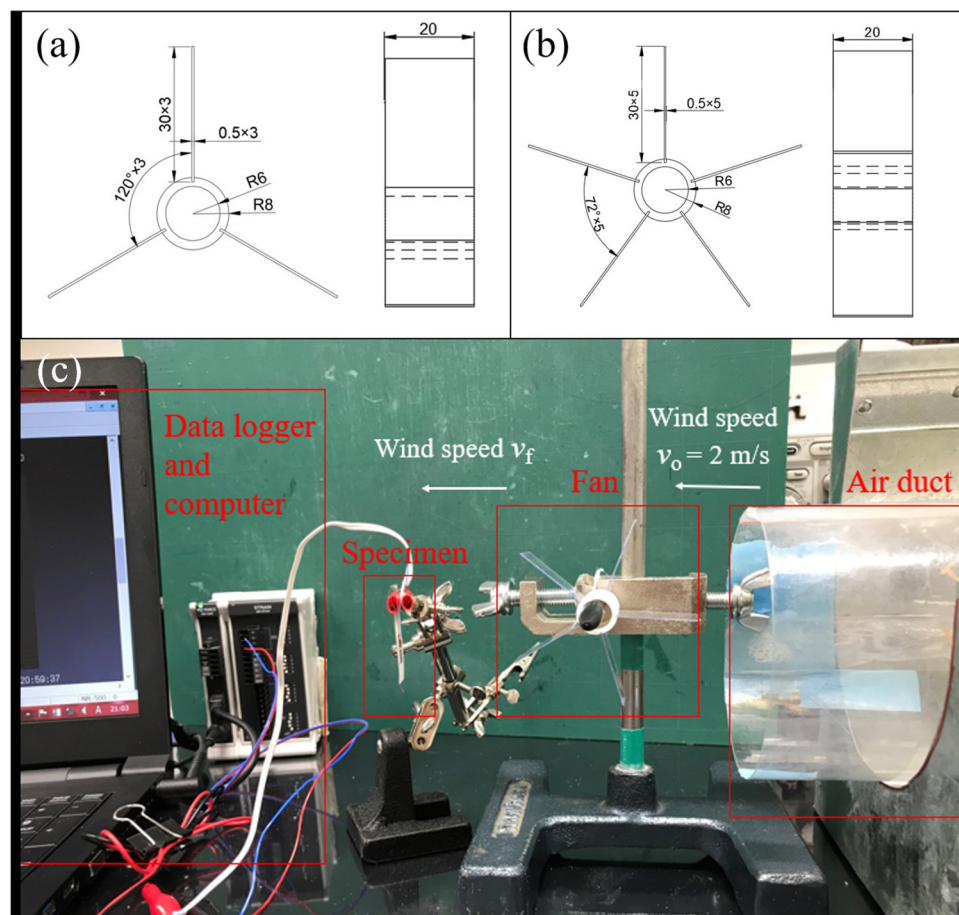

FIG. 2. Wind energy harvesting test setup: (a) 3-leaf fan, (b) 5-leaf fan, and (c) instrument of the test.

Figure 2(c) illustrates the wind energy harvesting test. The sample was fixed 10 mm away from the fan and connected to the computer and data logger (Keyence NR-500, Keyence Co., Japan). Continuous wind with a speed of $v_o = 2\,\mathrm{m/s}$ from the duct was then changed using the fan fixed in front of the duct. After that, the discontinuous wind v_f acted on the samples and the data logger and computer recorded the real-time output voltage of the samples. 3 different samples were tested on 3 occasions in each group to ensure authenticity and universality.

III. RESULTS AND DISCUSSION

A. Scanning electron microscopy

The microstructure of the composite and the dispersion of KNN particles within the epoxy matrix was observed by SEM. The cross-sectional SEM image of the KNN/epoxy composite is shown in Fig. 3.

The SEM image shows that the dispersion of KNN particles on the upper, central, and bottom parts of the sample's cross sections is similar. From Fig. 3(d), we can see that there is no particle precipitation on the bottom of the sample, which indicates that the KNN particles are uniformly distributed within the matrix. It proves that the piezoelectric particles and the epoxy have been well mixed. However, bubbles were not avoided completely and some voids still exist in the composite. The voids are approximately 1–$10\,\mu m^2$ in diameter.

In general, the interface between ceramics and epoxy resin is weak. In order to improve the interface properties, silane, titanate, aluminate and zirconate coupling agents are effective for the surface treatment on our KNN nanoparticles. Moreover, surface treatment agents such as fatty acids, fatty acid esters, higher alcohols, and hardened oils can be used. Further study is needed to clarify the interface strengthening mechanism.
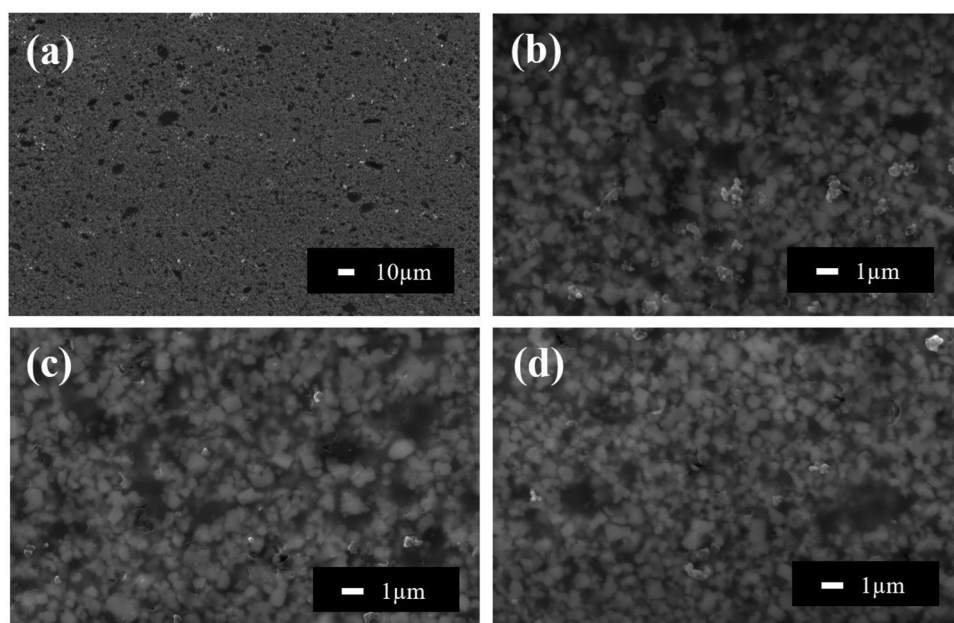
B. The effect of poling condition

The effects of poling condition and time after poling on the piezoelectric coefficient d_{33} of the KNN/epoxy composite are depicted in Fig. 4. d_{33} of the polarized KNN/epoxy changes in the range of 0.5–7.9 pC/N.

During poling, the electric domain of the piezoelectric material is easier to rotate or move under a suitable poling temperature, so a suitable poling temperature is helpful for increasing the polarization of materials. Figure 4(a) shows d_{33} vs temperature for the KNN/epoxy composites. As the poling temperature increases, d_{33} of KNN/epoxy composites increases and then decreases after reaching the critical temperature (75 °C). The average value of d_{33} at 75 °C is 6.6 pC/N, which is 11 times that at 25 °C (average value 0.6 pC/N). The optimized poling temperature is very important in improving the polarization of the KNN/epoxy composite. d_{33} of the KNN/epoxy composites can be greatly improved by poling temperature changes. The KNN/epoxy composite has high piezoelectric property when the poling temperature is 75 °C.

The poling voltage dependence of the piezoelectric coefficient d_{33} in KNN/epoxy composites is shown in Fig. 4(b). After the electric field (referred to as voltage in this paper) reaches 20 kV/mm, d_{33} of the composite increases as the poling voltage increases, then d_{33} becomes saturated and keeps close to the value of approximately 6.0 pC/N. The saturation poling voltage of the KNN/epoxy composite is approximately 30 kV/mm.

On the one hand, when poling voltage is equal to 15 kV/mm, d_{33} of the KNN/epoxy composite remains at zero. It has been shown that 15 kV/mm is not high enough to enable poling of the KNN/epoxy composite. We evaluated the samples which were polarized under different distances (6 mm–15 mm) between the corona needle and the samples. Table I lists the results and which
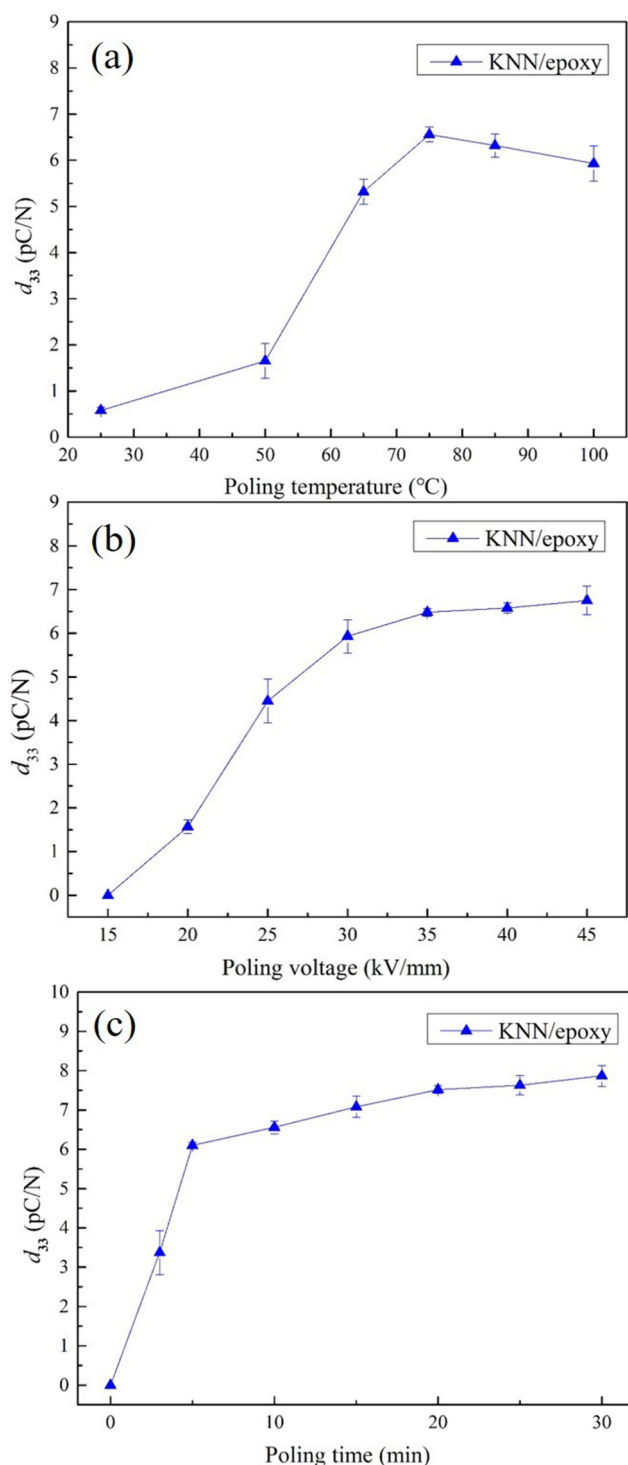

FIG. 3. The cross-sectional SEM image of the KNN/epoxy composite: (a) overall, (b) upper, (c) center, and (d) bottom view.

TABLE I. Effect of the interval to corona needle on the piezoelectric coefficient.

Interval to corona needle (mm)	Voltage (kV/mm)	Temperature (°C)	Time (min)	d_{33} (pC/N)
6	15	75	10	0
10	15	75	10	0
15	15	75	10	0

indicates that d_{33} stays at zero, although the distance between the corona needle and sample was shortened. We have assumed that this is because 15 kV/mm is not high enough to make the electric domain of the KNN/epoxy composite rotate or move.

Figure 4(c) shows the influence of poling time on d_{33} of KNN/epoxy composite. It is shown that d_{33} reaches an average value of 7.9 pC/N within the poling duration of 30 min, which is 2.3 times d_{33} obtained after poling for 3 min (average value 3.4 pC/N). Besides this, d_{33} of KNN/epoxy composite increases sharply with an increase in the poling time, and d_{33} reaches a relatively high value (6.1 pC/N, average value) after 5 min. However, the rate of increase in d_{33} between the poling times of 5 to 30 min is much smaller than that between 0 and 5 min. This is important and clearly differentiates KNN from lead zirconate titanate (PZT). The domain switching of PZT needs more than an hour to take place.[8] The small distortion from the cubic perovskite phase inside the KNN makes the potential barrier substantially lower and non-180° domain switching is easier than that in PZT. Hence, the KNN/epoxy composite is easier to polarize, compared with PZT and it can reach saturation in a shorter time period.[14]

Figure 5 displays the variation of d_{33} with time after poling. This indicates that d_{33} of KNN/epoxy composite shows great stability after poling. There is almost no change in d_{33} for 7 days after poling.
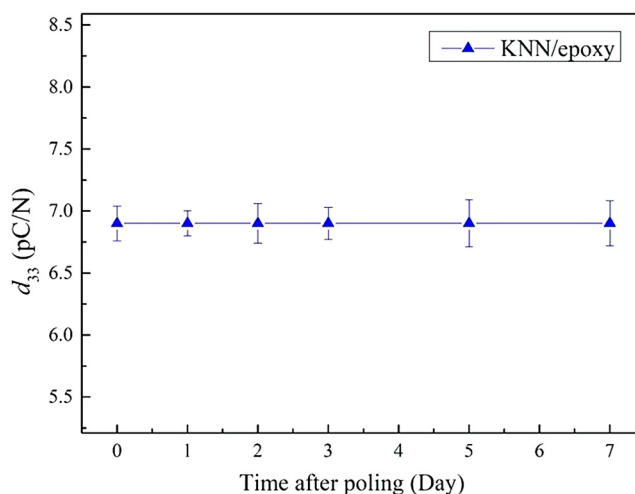

FIG. 4. d_{33} of the KNN/epoxy composite polarized using the corona poling method: d_{33} vs poling (a) temperature (30 kV/mm, 10 min), (b) voltage (100 °C, 10 min), and (c) time (75 °C, 30 kV/mm).

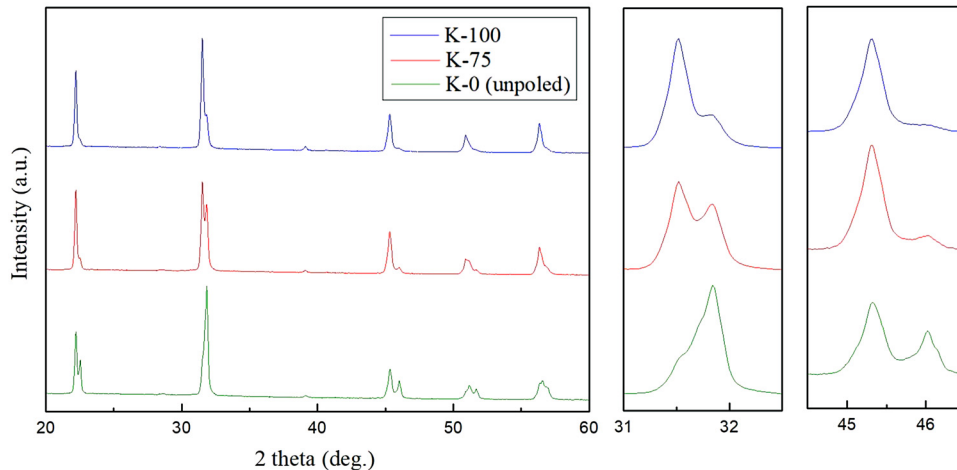**FIG. 5.** d_{33} as a function of time (75 °C, 35 kV/mm, 30 min).

FIG. 6. XRD pattern of the KNN/epoxy composite with different poling temperatures.

C. X-ray diffraction

The KNN/epoxy composites were polarized under different temperatures and the conditions are as below:

(1) K-0: unpolarized,
(2) K-75: 75 °C, 35 kV/mm, 30 min,
(3) K-100: 100 °C, 35 kV/mm, 30 min.

The corona needle is 15 mm away from the samples.

Figure 6 shows the XRD patterns. From Fig. 6, the unpoled KNN/epoxy is characterized by (110)/(001) peak splitting about $2\theta = 22°$ and (220)/(020) peak splitting about $2\theta = 45°$, which shows that it is in the orthorhombic phase.[15] When poling temperature increases to 75 °C, the X-ray pattern shows (220)/(020) peak splitting about $2\theta = 45°$ and peak splitting at about $2\theta = 32°$. Hence, according to these peaks, we concluded that the phase structure of the composite transforms from an orthorhombic phase to a mixed phase of orthorhombic and tetragonal phases. On the other hand, the sample polarized at 100 °C only has a (200) peak at about $2\theta = 45°$ and slight peak splitting at about $2\theta = 32°$ which should be a characteristic of a cubic phase, slightly mixed with a tetragonal phase.

Although the (200) and (002) peaks of K-75 are not clear enough to prove the tetragonal structure of the material, we assume that the structure of K-75 is a mixed phase of orthorhombic and tetragonal by the following reasons: First, as mentioned above, evident splitting is found from Fig. 6 when $2\theta = 32°$ in K-75, which matches to the feature of tetragonal.[15] Second, when $2\theta = 45°$, the peak shows similar features with the orthorhombic phase. Third, the phase transition of KNN is orthorhombic-tetragonal-cubic. The K-0 and K-100 show the obvious feature of orthorhombic and cubic, so the tetragonal phase should appear between them. In summary, we assume that K-75 consists of the orthorhombic phase and the tetragonal phase. On the other hand, even though the tetragonal phase is not necessary for the KNN to show the piezoelectric response, the material with a mixed phase of orthorhombic and tetragonal phases always shows better piezoelectricity. The domain volume fractions were easier to switch during poling for the coexistence of orthorhombic and tetragonal domains.[2,16]

Overall, the appearance of the tetragonal phase makes the composite has improved piezoelectricity after 75 °C poling. We believe that this orthorhombic and tetragonal mixed phase structure has better piezoelectricity than a purely orthorhombic structure, after poling. It is well-known that the cubic structure does not exhibit piezoelectric effects. The tetragonal phase transforms into the cubic phase with an increase in the poling temperature, so the piezoelectricity of the composite decreases with increasing poling temperature.

Even though the orthorhombic-tetragonal phase transition temperature is about 200 °C for the pure KNN, there are some research studies proving that the electric field can also induce phase transition in the ferroelectric material.[17] So we assume that the combined action of electric field and temperature leads to the phase transition of the composites. Based on Fig. 6, the phase transition happened indeed. The electric field and temperature combined induced phase transition of the piezoelectric composites should be a complex subject and warrants further study.

D. Unsteady wind energy harvesting

First, the samples were polarized and the average d_{33} of the samples was 12.1 pC/N. Table II gives the details of the condition of poling and d_{33}.

Figure 7 displays the unsteady wind energy harvesting results of the KNN/epoxy composite. It is found in Fig. 7(a) that the average output voltage changes ΔV for the 3-leaf fan group is 3.41 mV, while

TABLE II. Poling conditions of wind energy harvesting samples.

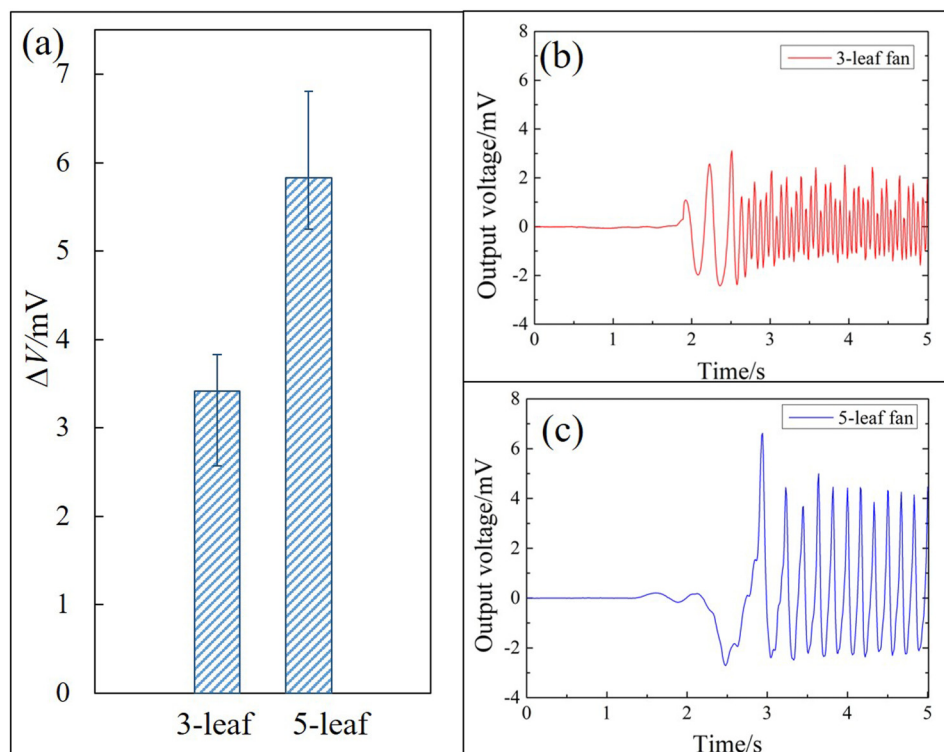| Name	Temperature (°C)	Voltage (kV/mm)	Time (min)	d_{33} (pC/N)
K-W-1	75	30	30	11.4
K-W-2	75	30	30	12.7
K-W-3	75	30	30	12.3

FIG. 7. Wind energy harvesting test results: (a) the output voltage of different fans, (b) the real-time output voltage with the 3-leaf fan, and (c) the real-time output voltage with the 5-leaf fan.

for the 5-leaf fan group, it is 5.83 mV (average value). The 5-leaf fan group has 71% higher ΔV than the 3-leaf fan group.

Figures 7(b) and 7(c) indicate the real-time output voltage of the 3 and 5-leaf fan groups. Evidently, the variation frequency of the 3-leaf fan group is higher than that of the 5-leaf fan group. The number of leaves and the weight of the fan cause the renewed wind frequency different. The speed of the renewed wind changed by the 3-leaf fan is much quicker, approximately 1.5 m/s, while the wind changed by the 5-leaf fan is approximately 0.8 m/s. Besides, the wind frequency of the 3-leaf fan is 15 Hz, while for the 5-leaf fan, the wind frequency is 5.5 Hz.

This proves that the smaller wind speed produces larger electrical energy gain. This seems to be due to the frequency. The 3-leaf fan is easier to move, so the frequency of the 5-leaf fan is much smaller than the 3-leaf fan under the same original wind.

For piezoelectric materials, the variability of the stress causes the change in charge, which is the principle for energy harvesting. When the wind frequency becomes large, the stress changes within the composites will also become rapid. When a new air pulse arrived at the composites, the stress within the composite has not yet been released totally, so the variability of the stress became smaller. Finally, the output voltage also becomes lower. In general, the KNN/epoxy composite can induce more electrical energy at lower frequency wind.

IV. CONCLUSIONS

The KNN/epoxy composites with piezoelectric stability were successfully fabricated and the corona poling method was utilized to enhance the piezoelectric coefficient of the composite. The influences of phase transition and poling condition on piezoelectric performance were discussed.

A large d_{33} (approximately 7.9 pC/N) of a KNN/epoxy composite can be achieved by the corona poling method at a poling temperature of 75 °C, a poling voltage of 30 kV/mm, and a poling time of 30 min.

The phase transitions were found under different poling temperatures. The orthorhombic and tetragonal mixed-phase KNN/epoxy was seen under a poling temperature of 75 °C. The d_{33} of a KNN/epoxy composite shows great stability after poling.

Voltage can be induced in the polarized KNN/epoxy composite due to very small unsteady winds, and the amount of the collected voltage is related to the frequency and speed of the wind. The KNN/epoxy composite can induce a voltage of 5.83 mV in low frequency, low speed winds (0.8 m/s).

Compared to the barium titanate/epoxy composites,[12] the KNN/epoxy composites show higher and more stable piezoelectricity and better unsteady wind energy harvesting performance. We believe that the KNN/epoxy composite is more suitable for energy harvesting devices.

REFERENCES

[1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, "Lead-free piezoceramics," Nature 432, 84–87 (2004).

[2] Y. Guo, K. Kakimoto, and H. Ohsato, "Phase transitional behavior and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3–LiNbO_3$ ceramics," Appl. Phys. Lett. 85, 4121–4123 (2004).

[3] S. Banerjee, K. A. Cook-Chennault, W. Du, U. Sundar, H. Halim, and A. Tang, "Piezoelectric and dielectric characterization of corona and contact poled PZT-epoxy-MWCNT bulk composites," Smart Mater. Struct. 25, 115018 (2016).

[4] J. Wu, Y. Wang, and H. Wang, "Phase boundary, poling conditions, and piezoelectric activity and their relationships in $(K_{0.42}Na_{0.58})(Nb_{0.96}Sb_{0.04})O_3–(Bi_{0.5}K_{0.5})_{0.90}Zn_{0.10}ZrO_3$ lead-free ceramics," RSC Adv. 4, 64835–64842 (2014).

[5] T. Zheng and J. Wu, "Relationship between poling characteristics and phase boundaries of potassium–sodium niobate ceramics," ACS Appl. Mater. Interfaces 8, 9242–9246 (2016).

[6] I. Y. Abdullah, M. Yahaya, M. H. H. Jumali, and H. M. Shanshool, "Enhancement piezoelectricity in poly(vinylidene fluoride) by filler piezoceramics lead-free potassium sodium niobate (KNN)," Opt. Quantum Electron. 48, 149 (2016).

[7] J. Wu, D. Xiao, Y. Wang, W. Wu, B. Zhang, and J. Zhu, "Improved temperature stability of $CaTiO_3$-modified $[(K_{0.5}Na_{0.5})_{0.96}Li_{0.04}](Nb_{0.91}Sb_{0.05}Ta_{0.04})O_3$ lead-free piezoelectric ceramics," J. Appl. Phys. 104, 024102 (2008).

[8] V. Vivekananthan, N. R. Alluri, Y. Purusothaman, A. Chandrasekhar, and S.-J. Kim, "A flexible, planar energy harvesting device for scavenging road side waste mechanical energy via the synergistic piezoelectric response of $K_{0.5}Na_{0.5}NbO_3$-$BaTiO_3$/PVDF composite films," Nanoscale 9, 15122–15130 (2017).

[9] F. Narita and M. Fox, "A review on piezoelectric, magnetostrictive, and magnetoelectric materials and device technologies for energy harvesting applications," Adv. Eng. Mater. 20, 1700743 (2018).

[10] F. Narita, H. Nagaoka, and Z. Wang, "Fabrication and impact output voltage characteristics of carbon fiber reinforced polymer composites with lead-free piezoelectric nano-particles," Mater. Lett. 236, 487–490 (2019).

[11] M. Usman, A. Hanif, I.-H. Kim, and H.-J. Jung, "Experimental validation of a novel piezoelectric energy harvesting system employing wake galloping phenomenon for a broad wind spectrum," Energy 153, 882–889 (2018).

[12] Z. Wang and F. Narita, "Corona poling conditions for barium titanate/epoxy composites and their unsteady wind energy harvesting potential," Adv. Eng. Mater. 21, 1900169 (2019).

[13] T. Hara, M. Shimizu, K. Iguchi, and G. Odagiri, "Chaotic fluctuation in natural wind and its application to thermal amenity," Nonlinear Anal. Theory Methods Appl. 30(5), 2803–2813 (1997).

[14] S. Huang, J. Chang, F. Liu, L. Lu, Z. Ye, and X. Cheng, "Poling process and piezoelectric properties of lead zirconate titanate/sulphoaluminate cement composites," J. Mater. Sci. 39, 6975–6979 (2004).

[15] H. Du, W. Zhou, F. Luo, D. Zhu, S. Qu, and Z. Pei, "An approach to further improve piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$-based lead-free ceramics," Appl. Phys. Lett. 91(20), 202907 (2007).

[16] J. Wu, D. Xiao, and J. Zhu, "Potassium-sodium niobate lead-free piezoelectric materials: Past, present, and future of phase boundaries," Chem. Rev. 115, 2559–2595 (2015).

[17] J. E. Daniels, W. Jo, J. Rödel, V. Honkimäki, and J. L. Jones. "Electric-field-induced phase-change behavior in $(Bi_{0.5}Na_{0.5})TiO_3–BaTiO_3–(K_{0.5}Na_{0.5})NbO_3$: A combinatorial investigation," Acta Mater. 58, 2103–2111 (2010).