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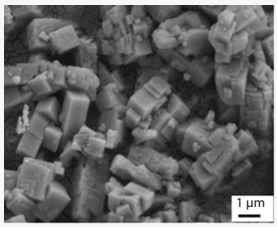
RESEARCH ARTICLE

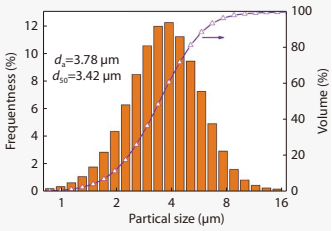
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Enhanced piezoelectric properties for potassium sodium niobate lead-free piezoelectric ceramics prepared by microwave technology

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Potassium-sodium niobate (Na, K)NbO_3 (NKN) powder was synthesized at low temperature via microwave-assisted hydrothermal solovthermal method (MHSM). The resultant powder was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). XRD results showed that pure (Na, K)NbO_3 powder with a single perovskite structure was successfully synthesized when the concentration of mineralization exceeded 1 M. In order to reduce the volatilization of alkaline elements, NKN ceramics derived from 5M-powder were prepared in a microwave furnace. Microstructure, stoichiometry, and electrical properties of the obtained ceramics were investigated. The piezoelectric coefficient (d_{33}), electromechanical coupling coefficient (k_p) and remnant polarization (P_r) of the sample sintered at 1050 °C show optimal values of 132 pC/N, 38% and 26.3 μC cm^{-2}, respectively. The results indicate that the microwave heating is a promising method for synthesizing and sintering NKN-based ceramics.





Although $PbZr_{1-x}Ti_xO_3$ (PZT)-based piezoelectric ceramics have dominated the market of piezoelectric devices for more than half a century because of their superior piezoelectric properties, they will be replaced in the near future due to the toxicity of lead. Therefore, it is urgent to find environment-friendly alternative materials to meet the growing environmental awareness. Among lead-free piezoelectric compositions, potassium-sodium niobate ((Na, K)NbO_3, NKN) is considered to be one of the promising candidate owing to its high curie temperature and good piezoelectricity[1-6]. However, the high-temperature sintering of traditional solid-state method makes alkali metal volatilize seriously, which causes the stoichiometric ratio deviation and affects the density of KNN ceramics, thereby damaging their piezoelectric properties[7-8]. Therefore, the piezoelectric coefficient of pure NKN ceramics fabricated by traditional solid-state method was no more than 80 pC/N[3, 9].

Special techniques like hot pressing and spark plasma sintering[10-11] are reported to be effective means for getting dense NKN ceramics, but the complex process and high fabricating cost make them unsuitable for industrial production. Therefore, sintering aids such as ZnO, CuO, and MgO have been applied to lower the sintering temperature and improve the density of NKN ceramics[5,12-15].

Another efficacious solution to obtain dense NKN ceramics is to manufacture them with ultrafine powders, based on the idea that the driving force of sintering is inversely proportional to the particle size of powders[16]. Several wet-chemical methods, such as sol-gel, hydrothermal method and pechini method, have been studied to synthesize ultrafine NKN powder[17-19]. Among them hydrothermal method is promising because it requires low temperature and delivers pure ultrafine powders without further heat treatment. Nevertheless, this method usually require dense mineralization and spend a long aging time[19]. Microwave-assisted hydrothermal solovthermal method (MHSM), as a modified hydrothermal method, has attracted more attention due to its thin mineralization concentration and short synthesis time. Bai et al. have successfully synthesized NKN powders through MHSM, reducing the concentration of mineralization from 10 M to 2 M[20]. In our previous study[21], ultrafine NKN powders have been fabricated using MHSM at 200 °C for only 30 min.

For NKN based ceramics, sintering temperature and holding time are two important factors that affect the volatilization of alkali metals. Due to the large particle size and uneven distribution of the powder synthesized by traditional solid-state method, ceramics often requires higher temperatures and longer holding times to density, which inevitably exacerbates the volatilization of alkali metals. On the contrary, the

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Received 8 April 2023; Accepted 28 May 2023; Published online

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DOI: 10.54227/mlab.20230019

powder synthesized by wet chemical method can achieve densification by sintering at lower temperatures due to its fine particle size and uniform distribution. Wu et al. synthesized NKN ceramic powder using traditional solid-state method and sintered it at a temperature of 1120 °C for 2 h, with a relative density of 92.5% and a d_{33} of 125 pC/N[9]. Zhou et al. sintered NKN powder synthesized by microwave hydrothermal method at 1000 °C for 2 h, with a d_{33} of 126 pC/N[22]. Microwave sintering is known to be adequate for shorting sintering time due to its fast heating rate. According to the report of Mahdi[23], KNN ceramics prepared by microwave sintering (total heating time of 36 min without soaking time) showed nearly the same density, dielectric, piezoelectric and ferroelectric behavior as those obtained in conventionally sintered ceramics (with a heating rate of 5 °C min^{-1} and soaking time of 2 h).

In the present study, microwave-assisted hydrothermal solovthermal method (MHSM) was utilized to synthesize NKN powder, and the influence of the mineralization concentration on the synthesized powder was characterized. Also, the electrical properties of NKN ceramics (from as-MHSMed powder) sintered in microwave furnace were investigated with special emphasis on sintering temperature. The d_{33} of 132 pC/N and P_r of 26.3 μC cm^{-2} can be achieved by microwave sintering at 1050 °C for only 30 min, which better than that of the ceramics prepared by traditional sintering at 1120 °C for 2 h[9]. The results show that the microwave solvothermal synthesis and microwave sintering have great potential for preparing KNN-based ceramics.

Experimental

Preparation process

Analytical-grade potassium hydroxide (KOH), sodium hydroxide (NaOH), niobiumpentoxide (Nb_2O_5) and isopropanol were used as starting materials. All of these chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd, China. First, a mixed solution of KOH and NaOH with a KOH/NaOH ratio of 3:1 was adjusted to 1.0-8.0 mol L^{-1}. Then appropriate amounts of Nb_2O_5 and isopropanol were dispersed in the mixed hydroxide solution, and stirred for 30 min. The slurry was poured into a 100 ml teflon lined reactor with 60% filling ratio. The reactor was placed in a microwave synthesizer (XH-800G, BJXH, China) and the reaction was operated at 2.45 GHz. According to our previous study, MHSM temperature was set at 200 °C and hold time to 90 min. After the reaction was completed, the precipitates were filtered and washed several times with deionized water and dried at 100 °C for 6 h.

The as-MHSMed powder was mixed with 5 wt.% polyvinyl alcohol(PVA) solution, and then uniaxially pressed into pellets of 10 mm in diameter and 1.0 mm in thickness under a pressure of 80 MPa. After burning out PVA, the green disks were sintered in microwave furnace at selected temperatures between 1000 °C and 1080 °C for 30 min in air to get dense ceramics. For electrical characterization, synthetic ceramics were polished and coated with Ag paste on both parallel surfaces, and then fired at 550 °C for 30 min. Subsequently, the ceramics were polarized along the thickness direction by applying a direct current electric field of 3 kV mm^{-1} at 120 °C for 30 min.

Performance testing

Density of ceramics was determined by the Archimedes method. Phase structure was determined using x-ray powder diffraction with a Cu *K* radiation (λ=1.5416 Å) filtered through a Ni foil (Rigaku; RAD-B system, Tokyo, Japan). The morphology of as-MHSMed powders and ceramics was observed using a scanning electron microscope (SEM, S-450, HITACHI, Tokyo, Japan). After ultrasonic distribution for 10 min, the mean particle size and particle size distribution of as-MHSMed powders were measured by a laser particle size analyzer (Horiba LA-960, Japan). The concentrations of K and Na were determined by energy dispersive X-ray (EDS) analysis on SEM. Dielectric properties were examined using a precision impedance analyzer (Agilent, 4294A). The piezoelectric constant d_{33} was measured using a quasi-static piezoelectric coefficient testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). A precision impedance analyzer (Agilent, 4294A) was used to calculate the planar electromechanical coupling coefficient k_p on the basis of IEEE standards by resonance–antiresonance method. Ferroelectric hysteresis loops were measured at 100 Hz using a ferroelectric tester (RT6000HVA, Radiant Technologies, Inc., Albuquerque, NM).

Results and discussion

The influence of the concentration of mineralizer

Fig. 1 shows the XRD patterns of NKN powders synthesized by MHSM at 200 °C for 90 min with different concentration of mineralizer. It can be seen that the samples show a single phase perovskite structure without any detectable secondary phases when the concentration of mineralizer is greater than 1 M. For the sample with 1 M, a minute amount of second phase Nb_2O_5 (PDF32-0710) is formed due to too thin alkaline concentration. As the alkaline concentration increases from 3 M to 8 M, a splitting peak of (202)/(020) occurs at 2θ = 45-47°, which indicates the formation of a single phase orthorhombic perovskite structure. It is interesting that as the alkaline concentration increases from 1 M to 5 M, the 2θ of diffraction peak in (110) space shifts to a lower angle, and almost no changes as it further increases to 8 M. This may be attributed to the fact that NaOH is more reactive than KOH, and thus there are more Na^+ ions react with Nb_2O_5 at low alkaline concentration, even though the K^+/Na^+ molar ratio is constant in the detected alkaline solution[24]. With increasing alkaline concentration, there are more K^+ ions will enter into the lattice of NKN, which leads to the diffraction peak of (110) shift to a low angle owing to that K^+ (1.64 Å) radius is larger than Na^+ (1.39 Å) radius. However, when the alkaline concentration exceeds 5 M, the angle of diffraction peak in (110) remains nearly unchanged, indicating that the solid solubility of K^+ in NKN lattice will no longer increase.

The SEM images of as-MHSMed powders with different concentration of mineralizer are shown in Fig. 2. It is observed that as-MHSMed powders exhibit a typical quadrate-like morphology, except that a few smaller crystals adhere to the larger ones for the sample with 3 M concentration, which leads to slight agglomeration, as shown in Fig. 2a. When the

DOI: 10.54227/mlab.20230019

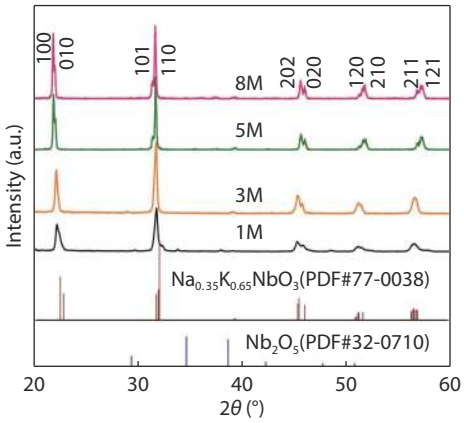


Fig. 1 XRD patterns of NKN powders synthesized by MHSM with different mineralizer concentrations.

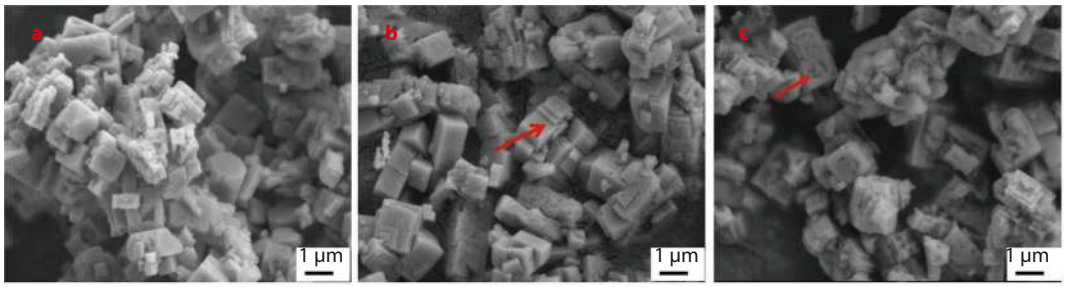


Fig. 2 SEM images of NKN powders with different mineralizer concentrations: **a** 3 M; **b** 5 M; **c** 8 M.

concentration of mineralizer exceeds 3 M, the crystal presents a stepwise growth mode, as shown by the arrows in Fig. 2b and Fig. 2c, in addition, obvious small holes appear on the crystal surface of the sample with 8 M concentration.

The corresponding particle size distribution of as-MHSMed powders are shown in Fig. 3. It can be observed that as the concentration of mineralizer increases from 3 M to 8 M, the average particle size (d_a) and cutting particle size (d_{50}) increase from 2.56 μm and 2.12 μm to 5.92 μm and 3.62 μm, respectively. In addition, compared to the samples with 3M and 8M concentration, the powder with 5 M concentration has a fine morphology and a narrow distribution.

Microstructure and EDS spectra

To evaluate the microwave sintering of NKN ceramics, the as-MHSMed powder with 5 M concentration was pelletized and sintered at 1000-1080 °C in microwave furnace (with a heating rate of 25 °C min^{-1} and soaking time of 0.5 h). Fig. 4 shows the SEM images of the fracture surface of NKN ceramics sintered at different temperatures. As shown in Fig. 4, the sample sintered at 1000 °C has a blurry microstructure with small grains, indicating insufficient grain growth. The samples sintered at higher temperature exhibit rectangular grains, and the grain size increases with the increase of sintering temperature. The average grain sizes of the samples sintered at 1000 °C, 1020 °C, 1050 °C and 1080 °C are 0.60, 0.96, 1.31 and 1.76 μm, respectively, and the corresponding densities are 4.21, 4.28, 4.30 and 4.25 g cm^{-3}, respectively. The reason for the decrease in density of the sample sintered at 1080 °C may be due to the severe volatilization of alkali metals at high temperature.

The EDS spectra of NKN ceramics sintered at different temperatures are shown in Fig. 5. It is observed that as the sintering temperature increases from 1000 °C to 1080 °C, the $K^+/(Na^+ + K^+)$ molar ratio increases from 0.454 to 0.502 , all of which are less than that of the precursor solution 0.75. On the one hand, it is because Na^+ reacts more readily with Nb_2O_5 than K^+ to form NKN. On the other hand, the volatilization of sodium is more severe than that of potassium, resulting an increase in $K^+/(Na^+ + K^+)$ molar ratios with increasing sintering temperature, which is also reported by Wang [25].

Density and electrical properties

P-E hysteresis loops of NKN ceramics sintered at different temperatures are depicted in Fig. 6. The samples sintered at 1000 °C, 1020 °C, 1050 °C and 1080 °C present remnant polarization (P_r) values of 16.2, 18.9, 26.3 and 20.8 μC cm^{-2} as well as coercive field (E_c) values of 12.8, 11.1, 9.6 and 9.3 KV cm^{-1}, respectively. P_r first increases and then decreases and E_c decreases monotonically with increasing sintering temperature. As reported by Jin[26], the value of P_r is manly affected by grain size and density. On the one hand, as domain size is proportional to the square root of grain size, a larger grain is conducive to its polarization, thus increasing its P_r. On the other hand, a higher density is beneficial for increasing the polarization voltage, thereby enhancing its P_r. As mentioned above, the optimal value of 26.3 μC cm^{-2} may be the result of the synergistic effect of grain size and density. Compared to P_r, the influencing factors of E_c are more complicated, mainly including composition, grain size, defect concentration, crys-

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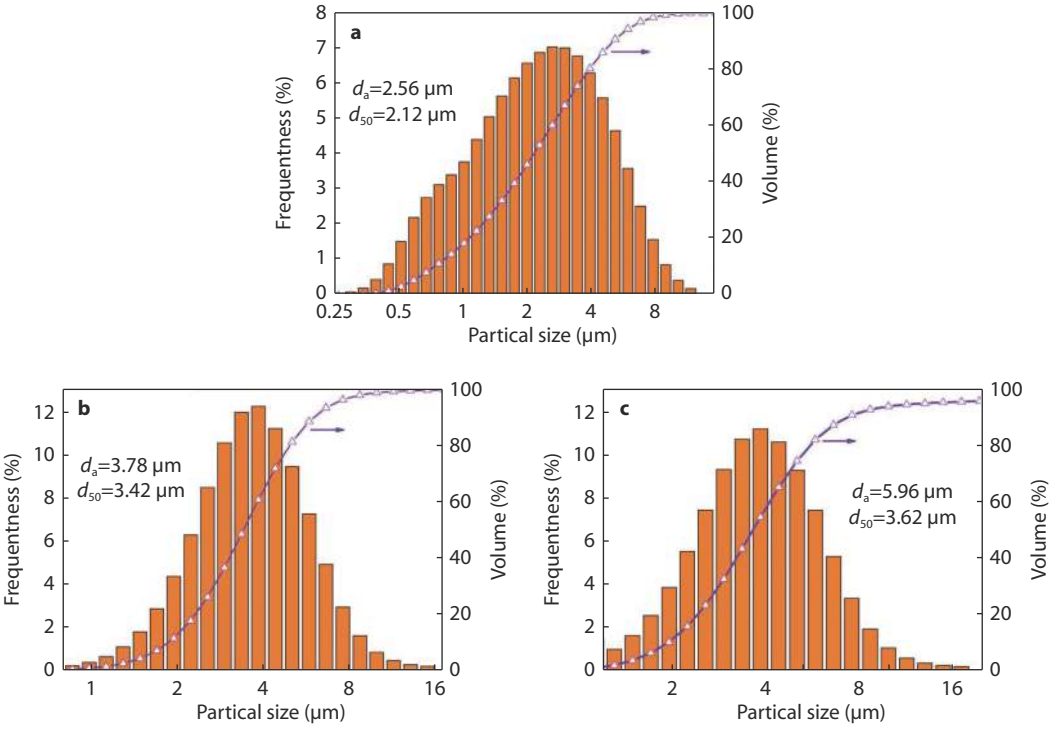


Fig. 3 Particle size distribution of NKN powders with different mineralizer concentrations: **a** 3 M; **b** 5 M; **c** 8 M.

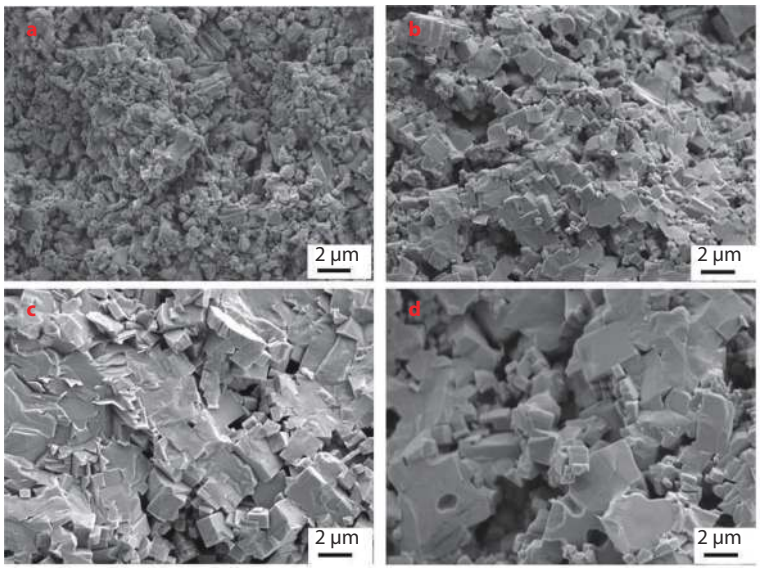


Fig. 4 SEM images of the fracture surface of NKN ceramics sintered at different temperatures: **a** 1000 °C; **b** 1020 °C; **c** 1050 °C; **d** 1080 °C.

tallinity, and phase structure. The variation of E_c may be the result of the synergistic effect of these factors, and its detailed mechanism still needs further research.

For NKN-based piezoelectric ceramics, samples with good piezoelectric and ferroelectric properties should have high P_r and low E_c. Zuo et al. have reported a remnant polarization of 15 μC cm^{-2} in NKN[27]. Mahdi et al. obtained a P_r = 18 μC cm^{-2} in NKN prepared by microwave technology[23], and Gu et al. measured a P_r = 22.9 μC cm^{-2} in Ta doped NKN[19]. All these reported values are less than 26.3 μC cm^{-2} determined in this work, indicating that the sample sintered at 1050 °C exhibits an excellent ferroelectricity.

Density and electrical properties of NKN ceramics sintered at different temperatures are summarized in Table 1. It can be seen that as the sintering temperature increases from 1000 °C to 1080 °C, the piezoelectric coefficient (d_{33}), electromechanical (k_p), density (ρ), and remnant polarization (P_r) first increase and then reduce, and reach their maximum values of 132 pC/N, 38%, 4.30 g cm^{-3} and 26.3μC cm^{-2}, respectively, at the densification sintering temperature of 1050 °C. It is repor-

DOI: 10.54227/mlab.20230019

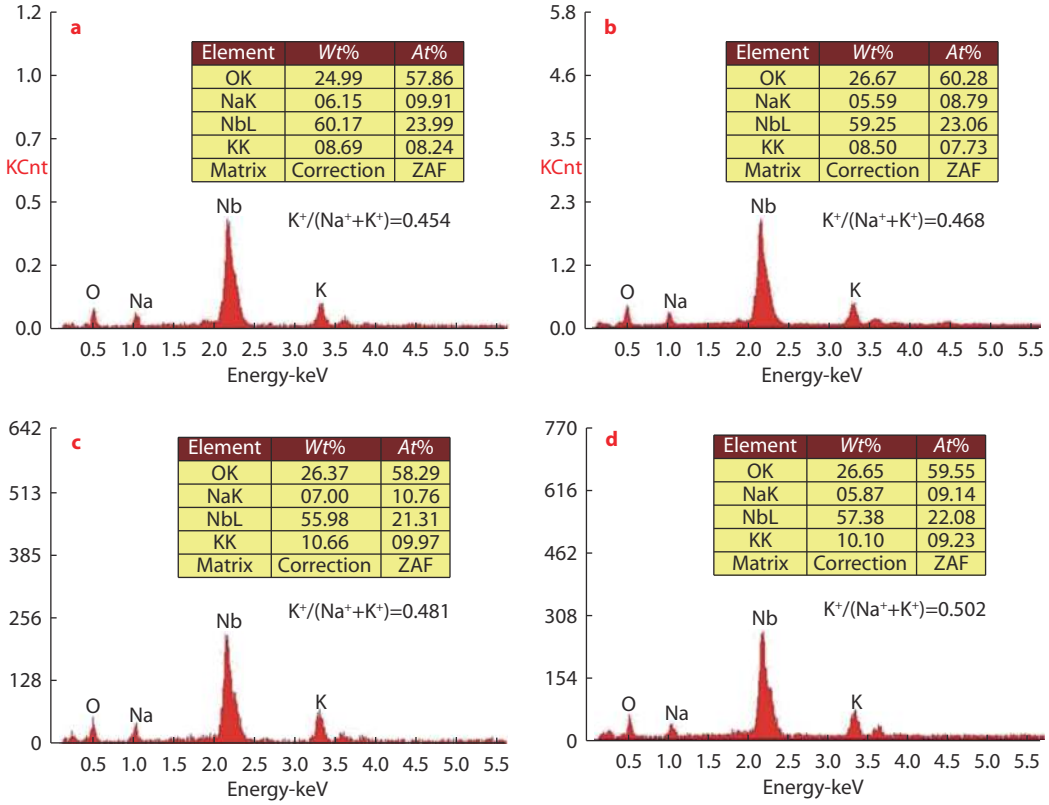


Fig. 5 EDS spectra of NKN ceramics sintered at different temperatures: **a** 1000 °C; **b** 1020 °C; **c** 1050 °C; **d** 1080 °C.

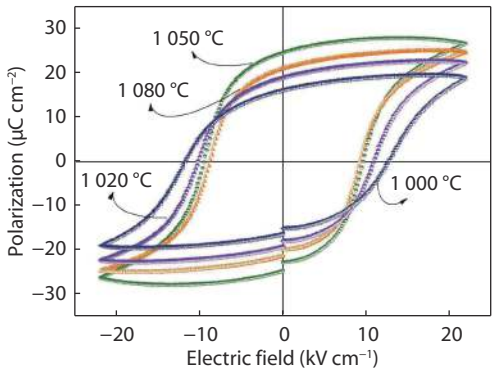


Fig. 6 *P-E* hysteresis loops of NKN ceramics sintered at different temperatures.

ted that, for NKN-based piezoceramics, piezoelectric properties are closely related to the morphtropic phase boundary (MPB) between two orthorhombic phases, as well as densification[27]. Although some researchers carried out MPB on pure NKN or NKN-based piezoceramics with the Na/K ratio of 0.5/0.5[28-30], while others believe that the composition of MPB should be approximated to 0.525/0.475 Na/K ratio[31-32], which can be determined by the phase diagram of $NaNbO_3$-$KNbO_3$, as reported by Tennery and Hang[33]. On the other hand, it has been reported that d_{33} is due in part to the combined effect of ε_r and P_r in NKN-based ceramics, which could be illuminated by the equation of $d_{33} \sim \alpha\varepsilon_r P_r$[34]. It can be seen from Fig. 5 and Table 1, the sample sintered at 1050 °C has a $K^+/(Na^+{+}K^+)$ molar ratio of 0.481, indicating that whose composition is relatively close to MPB, and posses large $\varepsilon_r P_r$ value of 13729 μC cm^{-2}. All these suggest that the sample sintered at 1050 °C exhibits excellent piezoelectricl properties.

In addition, it can also be observed from Table 1 that the relative dielectric constant (ε_r) monotonically increase, while the dielectric loss (*tanδ*) monotonically decreases with the the increase of sintering temperature. The *tanδ* drops from 0.042 to 0.018, while ε_r raises from 410 to 531, as the sintering temperature increases from 1000 °C to 1080 °C. The variations of *tanδ* and ε_r may be due to the increases of density and/or grain size. It has been reported that the *tanδ* and the ε_r are highly dependent on the density (ρ) and grain size for NKN-based ceramics[35-36].

Conclusion

A single phase orthorhombic perovskite NKN powder has been successfully synthesized using MHSM with a thin concentration of alkali liquor above 1 M. In order to avoid severe volatilization of alkali metals during high-temperature sintering process, as-MHSMed powder with 5 M concentration was pelleted and sintered in a microwave furnace. Enhanced electrical properties of d_{33} ~132 pC/N, k_p ~38%, P_r ~ 26.3μC cm^{-2}, and ε_r ~522 are obtained in the ceramic sintered at an optimal temperature of 1050 °C. Compared with the sample prepared by traditional synthesis method, the d_{33} has increased by 65%, indicating that the microwave heating is a promising method for synthesizing and sintering NKN-based ceramics.

ACKNOWLEDGEMENTS

DOI: 10.54227/mlab.20230019

Table 1. Summary of physical and electrical properties of NKN ceramics sintered at different temperatures.

ST (°C)	d_{33} (pC/N)	k_p (%)	ρ (g. cm^{-3})	p_r (μC. cm^{-2})	tanδ (@10 KHz)	ε_r (@10 KHz)	$\varepsilon_r p_r$ (μC. cm^{-2})
1000	86	25	4.21	16.2	0.042	410	6642
1200	125	35	4.28	18.9	0.031	458	8656
1500	132	38	4.30	26.3	0.028	522	13729
1800	120	32	4.25	20.8	0.018	531	11045

This work was supported by the Higher Education Key Project of Henan Province (Grant No. 15A430005), the PhD Start-up Fund of Henan University of Science and Technology (Grant No. 09001542).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR'S CONTRIBUTION

Haitao Li conducted the research; Mingyang Li wrote the results and discussion; Xiaoxue Jiang wrote the introduction; Changda Zhu organized the data; Hongguang Wang wrote the experimental; Aowei Deng wrote the conclusion; Guozhong Zang reviewed & edited; Yongjun Gu draw charts.

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