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Synthesis of (K, Na) (Nb, Ta)O_3 lead-free piezoelectric ceramic powders by high temperature mixing method under hydrothermal conditions

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Abstract

A facile hydrothermal route via high temperature mixing method was used to synthesize (K, Na) (Nb, Ta)O_3 lead-free piezoelectric ceramic powders. The influence of Ta doping and $K^+/(K^+ + Na^+)$ molar ratios in the starting solution on the resultant powders were investigated by X-ray diffraction, scanning electron microscope, transmission electron microscopy, and selected area electron diffraction. The Ta element was successfully doped into the alkaline niobate structure to form crystalline (K, Na) (Nb, Ta)O_3 lead-free piezoelectric ceramics powder. The microstructure, piezoelectric, ferroelectric, and dielectric properties of the sintered (K, Na) (Nb, Ta)O_3 ceramics from the obtained powders were investigated. The piezoelectric coefficient (d_{33}), electromechanical coupling coefficient (k_p), dielectric constant (ε_r), and remnant polarization (P_r) of the sample sintered at 1180 °C show optimal values of 210 pC/N, 34.0%, 2302, and 19.01 μC/cm^2, respectively.

Keywords: C. Piezoelectric properties; Lead-free piezoelectric ceramic; (K, Na) (Nb, Ta)O_3; Hydrothermal; HTMM

1. Introduction

To replace lead-containing piezoelectric materials, such as lead zirconate titanate (PZT), more environmental-friendly ceramics have been studied extensively, especially, the alkaline niobate-based piezoelectric ceramics due to its good piezoelectric properties and high Curie temperature. Among these ceramics, $K_xNa_{1-x}NbO_3$ (KNN) is considered as a candidate for lead-free piezoelectric ceramics [1–4]. KNN is a combination of ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$. This ceramic forms a morphotropic phase boundary (MPB) at approximately $x = 0.5$ [5,6]. Nevertheless, Wu et al. [7,8] concluded that the existence of MPB at $x = 0.5$ was quite controvertible in the KNN system, whereas, excellent piezoelectric properties were possibly obtained in the compositional range of $x = 0.4$–0.6. However, KNN ceramics are difficult to sinter, whereas, K_2O and Na_2O easily evaporate at high temperature sintering. One method of producing KNN ceramics is to use refined powder with enhanced sintering activity, prepared by molten-salt method, sol–gel routine or hydrothermal process [9,10]. Hydrothermal method has been proved as a facile route to prepare ceramic powders, such as $Na_{0.5}Bi_{0.5}TiO_3$, $KNbO_3$ and $NaNbO_3$ [11,12] piezoelectric ceramic powders. Powders synthesized through this method have better compositional homogeneity and fewer impurities that are beneficial to the performance of resultant ceramics. For example, the piezoelectric constant d_{33} of $BaTiO_3$ ceramics could reach as high as 350 pC/N using hydrothermally synthesized powders, compared with the samples (d_{33} is 190 pC/N) fabricated by the solid state reaction method [13].

Single perovskite phase of compositions near either of the end members in the $KNbO_3$–$NaNbO_3$ system may be obtained under hydrothermal conditions, whereas single-phase (K, Na)NbO_3 solid solution near the MPB composition is difficult to acquire [14,15]. These phenomena are due to the fact that Na reacts more readily with Nb to form $NaNbO_3$ than the reaction of K with Nb to form $KNbO_3$. The production of pure $KNbO_3$–$NaNbO_3$ solid solution powder with an accurate composition of $K_{0.5}Na_{0.5}NbO_3$ by hydrothermal method has the focus of various studies. Maeda et al. [16] reported the enhanced piezoelectric properties of KNN ceramics sintered from mixed $KNbO_3$ and $NaNbO_3$ hydrothermal powders. Su et al. [17] proved that Sb-doping promotes the formation of a single crystalline (K, Na) (Nb, Sb)O_3 phase due to the higher electronegativity of Sb compared with Nb. Ta ions have the

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same chemical valence (+5) and similar atomic radius [Ta (0.068 nm)] as that of Nb (0.069 nm). Matsubara et al. [18] and Lv et al. [19] have been proved that $(K_{0.5}Na_{0.5})$ $(Nb_{0.7}Ta_{0.3})O_3$ ceramics have highest value of piezoelectric coefficient and strain within different amount of Ta doping. Therefore, in the present work, the Ta element was introduced to the starting solution to prove that Ta-doping could inhabit the coexistence of $KNbO_3$ and $NaNbO_3$ phases in the products under hydrothermal conditions.

As a modified hydrothermal process, a high temperature mixing method (HTMM) under hydrothermal conditions was used in this study. The starting solutions and raw materials for HTMM were separately heated to a preset reaction temperature in a double-chambered autoclave before they were mixed to start the hydrothermal reactions. In the authors' previous work, Cd–Hap [20], Pb–Sr Hap [21], and (K, Na)NbO_3 [22,23] powders were successfully synthesized via HTMM.

In the present research, (K, Na) (Nb, Ta)O_3 powders were successfully prepared by HTMM under hydrothermal conditions, and (K, Na) (Nb, Ta)O_3 ceramics have been obtained by ordinary sintering method. Their phase structures, piezoelectric, dielectric, and ferroelectric properties, with emphasis on the influence of sintering temperature, were investigated.

2. Experimental procedure

(K, Na) (Nb, Ta)O_3 samples, denoted as KNNTx, where x indicates Ta/(Ta + Nb) molar ratio in the starting solution, were prepared via an isopropanol-assisted hydrothermal method. The starting materials included analytical-grade niobium pentoxide (Nb_2O_5), tantalum pentoxide (Ta_2O_5), potassium hydroxide (KOH), sodium hydroxide (NaOH), and isopropanol, all of which were obtained from Sinopharm Chemical Reagent Co. Ltd., China. First, a mixed solution of KOH and NaOH with different $K^+/(K^+ + Na^+)$ ratios was adjusted to 5.0 mol/L. Appropriate amounts of Nb_2O_5, Ta_2O_5 (with $x = 0.3$) and isopropanol were placed into one of the two chambers of a Teflon-lined multi-chamber autoclave, whereas the mixed alkaline solution was poured into the other chamber. These solutions were heated to the desired temperature and then mixed for hydrothermal treatment at 240 °C for 16 h. After the autoclave was gradually cooled down to room temperature, the precipitates formed were washed several times with deionized water and ethanol, and then dried at 80 °C for 24 h.

The as-prepared powders were mixed with 3 wt% polyvinylalcohol (PVA) solution, and then uniaxially pressed into pellets with a 1.5 cm diameter under 300 MPa pressure. After burning out PVA, the green disks were respectively sintered in air at selected temperatures between 1160 and 1200 °C for 2 h.

The density of the samples sintered at different temperatures was measured by the Archimedes method. The phase structure of the resultant powders was identified by powder X-ray diffraction (XRD; Bruker D8 Advance, Germany) using Cu Kα radiation ($\lambda = 0.15418$ nm). Elemental analysis for K, Na, Ta and Nb was performed using energy dispersive X-ray analysis (EDX; EDAX, America). The morphology of the products was observed by scanning electron microscope (SEM; FEI Quanta 200, the Netherlands) and transmission electron microscopy (TEM; JEOL JEM-2100, Japan). Selected area electron diffraction (SAED) was also used to characterize the phase structure.

Silver paste electrodes were formed at the two circular surfaces of the disk-shaped specimens after firing at 750 °C for 10 min to measure dielectric and piezoelectric properties. Poling was carried out in silicon oil under DC field of 2 kV/mm at 110 °C for 30 min. The piezoelectric constant d_{33} was measured using a quasistatic piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, Beijing, China). Dielectric properties as a function of temperature and frequency were measured by an impedance analyzer (HP4294A). Polarization versus electric field hysteresis loops were measured using a ferroelectric tester (TF Analyzer 2000). Piezoelectric and electromechanical properties were measured within 24 h after a poling process.

3. Results and discussion

The effects of the $K^+/(K^+ + Na^+)$ molar ratio in the starting solution on the phase evolution were investigated in Fig. 1. Both K-rich and Na-rich (K, Na)NbO_3 phases were observed in the patterns of KNN [Fig. 1(a)], indicating that an $NaNbO_3$ phase coexists with the $KNbO_3$ phase in the sample. Similar results were observed in our preparation of (K, Na)NbO_3 solid solution before [22]. These phenomena may be caused by the fact that Na reacts more readily with Nb to form $NaNbO_3$ than the reaction of K with Nb to form $KNbO_3$. However, with an increased Ta concentration in the starting solution, a single-phase was observed in the patterns of KNNT sample [Fig. 1(e)], showing that Ta doping is beneficial for the preparation of single phase powders. The monoclinic Na(Nb, Ta)O_3 [Fig. 1(b), JCPDS card No. 74-2437], orthorhombic K(Nb, Ta)O_3 [Fig. 1(h), JCPDS card No. 71-2171], and KNNT [Fig. 1(c–g)] were successfully synthesized from the starting solution

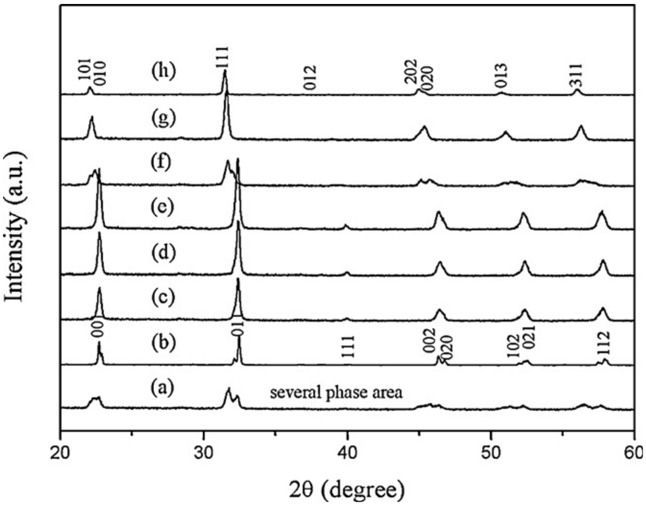
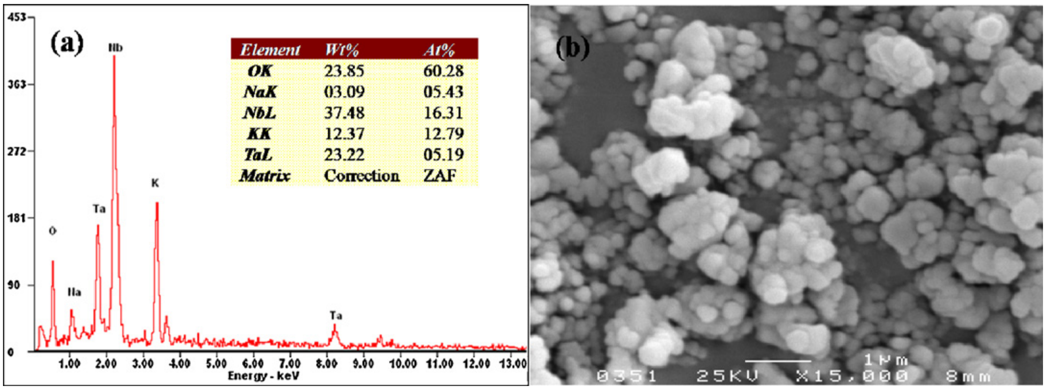


Fig. 1. XRD patterns of KNN particles synthesized by HTMM from the starting solution with $K^+/(K^+ + Na^+)$ molar ratio of 0.7 (a), and KNNT0.3 samples with different $K^+/(K^+ + Na^+)$ molar ratios: (b) 0, (c) 0.5, (d) 0.6, (e) 0.7, (f) 0.8, (g) 0.9, and (h) 1.0.



Element	*Wt%*	*At%*
OK	23.85	60.28
NaK	03.09	05.43
NbL	37.48	16.31
KK	12.37	12.79
TaL	23.22	05.19
Matrix	Correction	ZAF

Fig. 2. Energy spectrum (a) and SEM image (b) of KNNT synthesized by HTMM from the starting solution with $K^+/(K^+ + Na^+)$ molar ratio of 0.8.

with different $K^+/(K^+ + Na^+)$ molar ratios. When the $K^+/(K^+ + Na^+)$ molar ratios in the starting solution are 0.5, 0.6, and 0.7 [Fig. 1(c–e)], the XRD patterns of the products were the same as that of Na(Nb, Ta)O_3, except that the 2θ values shift toward the low angle, indicating that the K^+ ions were doped into the Na(Nb, Ta)O_3 crystal lattice and formed the Na-rich KNNT solid solutions. When the $K^+/(K^+ + Na^+)$ molar ratio in the starting solution was 0.9 [Fig. 1(g)], the XRD patterns of the products were the same as that of K(Nb, Ta)O_3, except that the 2θ values shift toward the high angle, indicating that the Na^+ ions were doped into the K(Nb, Ta)O_3 crystal lattice and formed the K-rich KNNT solid solutions. However, when the $K^+/(K^+ + Na^+)$ molar ratio was 0.8, neither Na-rich KNNT nor K-rich KNNT solid solutions were obtained. The powders exhibit a single-phase structure with an orthorhombic symmetry (space group Pm) that can be indexed according to JCPDS Card No.77-0038 ($Na_{0.35}K_{0.65}NbO_3$). Furthermore, the energy spectrum indicates the presence of K, Na, Nb, and Ta elements in the resultant products, validating successful doping of Ta into the KNN lattice [Fig. 2(a)].

SEM image of the sample (K, Na) (Nb, Ta)O_3 synthesized from the starting solution with the $K^+/(K^+ + Na^+)$ molar ratio of 0.8 is shown in Fig. 2(b). The as-prepared sample is well crystallized with a grain size of approximately 200 nm.

The TEM image [Fig. 3(a)] of the orthogonal-shaped morphology of the KNNT single crystal synthesized from the starting solution with $K^+/(K^+ + Na^+)$ molar ratio of 0.8, and the corresponding SAED pattern [Fig. 3(b)] of the single crystalline KNNT indexed as orthorhombic in structure, are consistent well with the present XRD analysis.

Fig. 4(a) shows the XRD patterns of the KNNT ceramics sintered at 1160–1200 °C. The enlarged XRD pattern of the ceramics in the range of 2θ from 45° to 47° is shown in Fig. 4(b). All samples show a pure perovskite structure without any secondary phase. Similar to pure KNN ceramics, the KNNT ceramics at room temperature have an orthorhombic symmetry when the sintering temperature under 1170 °C. With further increasing temperature, the phase structure changes to a single tetragonal symmetry. Therefore, a phase transformation between the orthorhombic and the tetragonal phase can be identified in the sintering temperature between 1170 °C and 1190 °C, during which two kinds of ferroelectric phases with different symmetries may coexist. In the previous studies [24], this kind of phase structure transition behavior was attributed to the extent of volatilization of alkali metal ions under high temperature sintering. The weight changes of the samples were recorded before and after sintering. It is found that the increase in weight loss percentage with increasing sintering temperature, which also demonstrates that the volatilization of alkali metal ions should be related to the phase structure transition behavior. Many studies have confirmed that sodium and potassium volatilize easily during high temperature sintering [25–27].

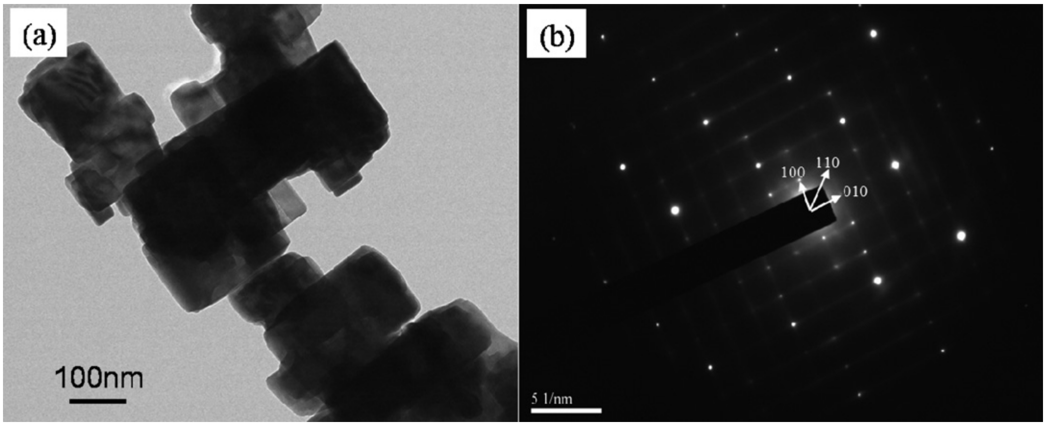


Fig. 3. TEM image (a) and the corresponding SAED pattern (b) of KNNT synthesized by HTMM from the starting solution with $K^+/(K^+ + Na^+)$ molar ratio of 0.8.

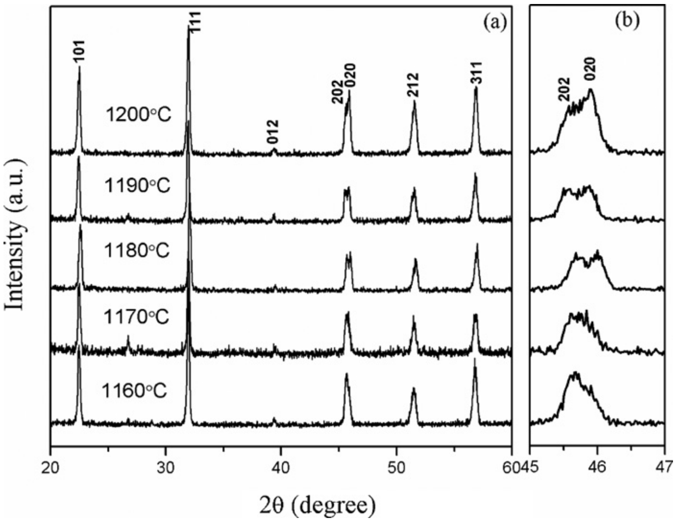


Fig. 4. X-ray diffraction patterns of the KNNT ceramics sintered at different temperature in the ranges of 2θ: (a) from 20° to 60° and (b) from 45° to 47°.

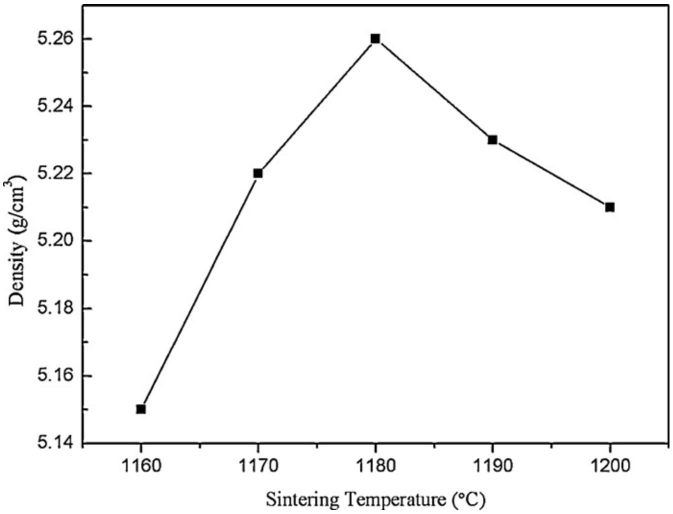


Fig. 5. Density change of KNNT samples as a function of sintering temperature.

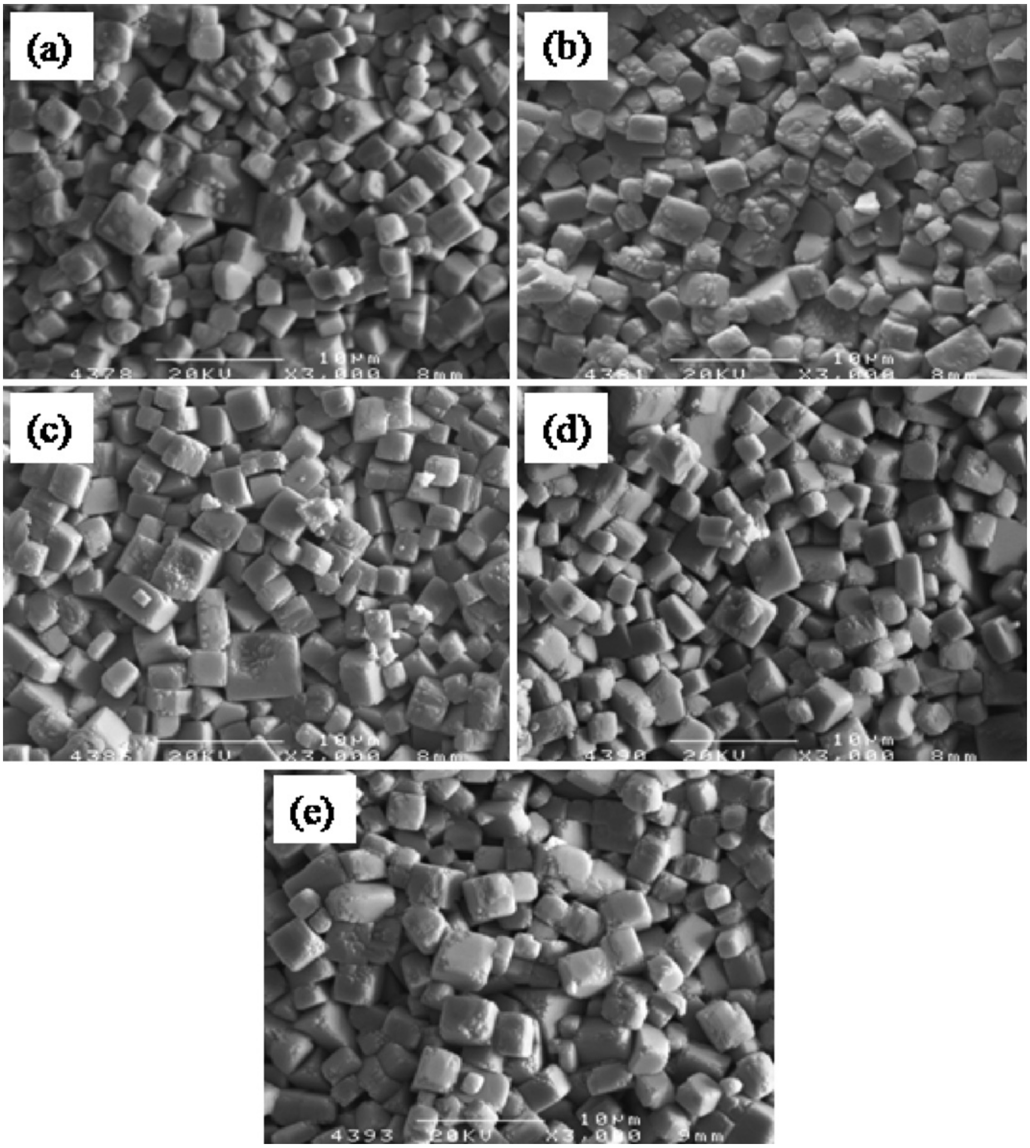


Fig. 6. SEM micrographs of KNNT ceramic samples sintered at (a) 1160 °C, (b) 1170 °C, (c) 1180 °C, (d) 1190 °C, and (e) 1200 °C.

The variation in the sintered densities of the KNNT ceramics as a function of sintering temperature is illustrated in Fig. 5. The sintering temperature varied within a narrow range, but the density changes markedly. The density of the samples increases from 5.15 to 5.26 g/cm^3 when the sintering temperature is increased from 1160 to 1180 °C. The highest density value obtained for the KNNT ceramics is equivalent to about 99.4% of their theoretical density (5.29 g/cm^3), implying that high densification is realized by normal sintering for the present KNN-based ceramics. However, the density tends to decrease when the temperature is further increased. Compared with the previous reports [18,19], excellent sintering activity of the hydrothermal powders and the introduction of Ta element are possible reasons for the relatively high density in the KNN-based system.

SEM micrographs of the microstructures of KNNT ceramics sintered at 1160–1200 °C are presented in Fig. 6. The microstructure becomes denser when the sintering temperature is increased from 1160 °C to 1180 °C. However, the large grains are easy to distinguish until the sintering temperature is increased to 1180 °C. Then, square grains grow and result in a bimodal distribution containing coarse and faceted grains 5 μm in length. Numerous small grains are distributed at the boundaries of coarse grains. It has been observed that the sintering temperature is relatively high in the KNN based ceramics. This should be attributed to the high melting temperature of $KTaO_3$ as compared to $KNbO_3$ (1370 °C vs. 1039 °C) [18].

The sintering temperature dependence of piezoelectric coefficient (d_{33}) and electromechanical coefficient (k_p) are illustrated in Fig. 7(a), whereas Fig. 7(b) depicts the dielectric constant (ε_r) and mechanical quality factor (Q_m) for the KNNT ceramics at 1160–1200 °C. The peak values of d_{33} and k_p at 210 pC/N and 0.34, respectively, were obtained at 1180 °C. Q_m exhibits a converse varying trend, typically in the range of 1160–1200 °C. The KNNT system shows a more obvious "valley" region around 1180 °C within the sintering temperature range from 1170 to 1190 °C, indicating a sharp increase to 65 as the sintering temperature descends to 1200 °C. Interestingly, the increase in ε_r (1400–2900) can be observed by increasing sintering temperature from 1160 to 1200 °C indicating that the present dielectric properties are apparently better than those obtained in previous reports (<1000) [19]. The enhanced dielectric properties may be due to the dense structure and high density of the sample (Fig. 6).

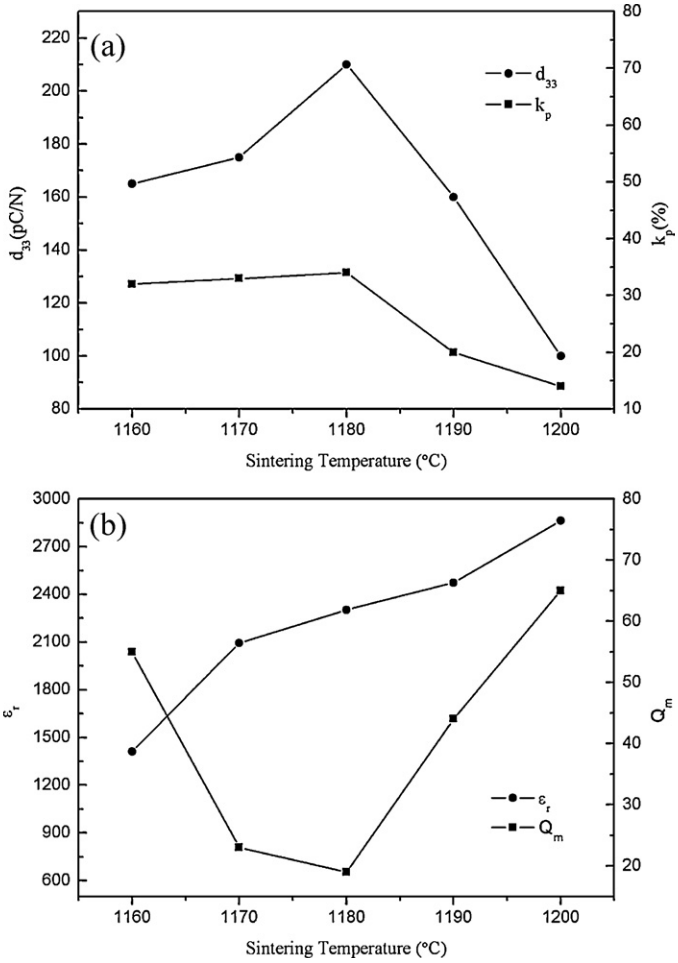


Fig. 7. Sintering temperature dependence of (a) piezoelectric coefficient (d_{33}) and planar mode electromechanical coupling coefficient (k_p) as well as (b) dielectric constant (ε) and mechanical quality factor (Q_m) for the KNNT ceramics.

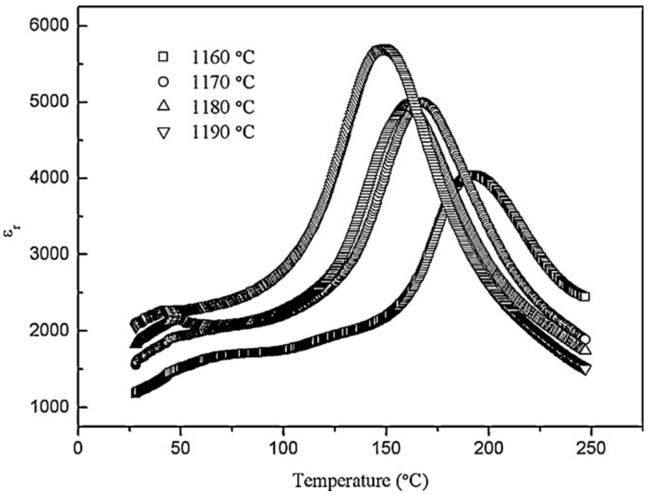


Fig. 8. Temperature dependence of the dielectric constant for the KNNT ceramics.

Fig. 8 shows the temperature dependence of dielectric constant of KNNT ceramics sintered at 1160, 1170, 1180, and 1200 °C, which are measured at 100 kHz. As we know, pure KNN ceramics would undergo two phase transitions nearly at 200 and 420 °C, corresponding to the orthorhombic–tetragonal ($T_{o\text{–}t}$) and tetragonal–cubic (or Curie temperature T_C) phase transition temperatures, respectively [1]. Similar to pure KNN ceramics, the two phase transitions are observed in the KNNT ceramics. In the previous studies [28], the substitution of Ta for Nb shifts both T_C and $T_{o\text{–}t}$ to lower temperatures. As shown in Fig. 8, the T_C for all samples synthesized at 1160, 1170, 1180, and 1200 °C are 190, 172, 165, and 148 °C, respectively. With increasing sintering temperature, the T_C shifts to lower temperature, which may be due to the change of the phase structure [29]. In addition, according to Fig. 4, although the coexistence of orthorhombic and tetragonal phases is observed both in the KNNT ceramics sintered at 1180 and 1190 °C, the

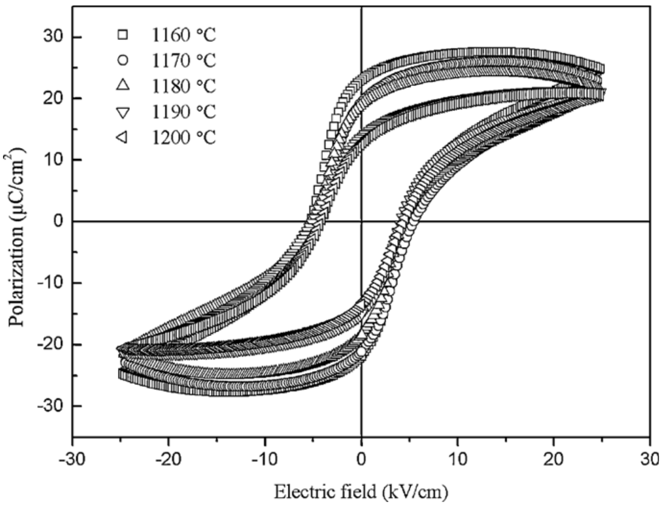


Fig. 9. Polarization hysteresis loops of the KNNT ceramics synthesized at 1160–1200 °C.

d_{33} value of the ceramics sintered at 1190 °C is much lower than that sintered at 1180 °C as can be clearly seen from Fig. 7. This is mainly because the T_{o-t} of the ceramics sintered at 1180 °C is more close to room temperature as shown from Fig. 8, because many studies confirmed that the *T*o-t near room temperature is favorable for enhancing piezoelectric properties [30].

P–E hysteresis loops of KNNT ceramics sintered at 1160–1200 °C are depicted in Fig. 9. The samples with increasing sintering temperature present remnant polarization (P_r) values of 22.91, 19.33, 19.01, 13.64, and 13.00 μC/cm^2 as well as E_c values of 3.7, 4.3, 3.3, 3.4, and 3.5 kV/cm, respectively. E_c is one-third of those obtained from KNNT ceramics sintered by solid state reaction [28], so poling is facile due to the low E_c. The sample sintered at 1180 °C exhibits good ferroelectricity.

4. Conclusions

Single-phase lead-free KNNT ceramics have been prepared using hydrothermal precursors synthesized by HTMM and solid state sintering. Ta-doping promotes the formation of a single crystalline (K, Na) (Nb, Ta)O$_3$ phase rather than the K and Na-rich perovskite phases coexisting in the pure KNN powders without Ta-doping. After poling treatment, the KNNT ceramics show typical ferroelectric and piezoelectric characteristics. Compared with traditional sintering method, enhanced piezoelectric and electromechanical properties are obtained from the sample synthesized at the optimal temperature of 1180 °C, in which d_{33}, k_p, ε and P_r are 210 pC/N, 34.0%, 2302, and 19.01 μC/cm^2, respectively. Furthermore, the electrical properties would be enhanced considerably when the K/Na molar ratio is close to 1.0. The present HTMM method provides a new potential route for preparing other KNN-based materials.

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