

# Two-Step Sintering: An Approach to Broaden the Sintering Temperature Range of Alkaline Niobate-Based Lead-Free Piezoceramics

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**In this paper, a typical Li- and Ta/Sb-modified alkaline niobate-based ceramics prepared by conventional sintering and two-step sintering were investigated in terms of their phase transition behaviors and various properties. The phase structures of the ceramics sintered by conventional sintering shifted remarkably from a polymorphic phase transition (PPT) to a tetragonal symmetry with the increase of sintering temperature. However, the ceramics sintered by two-step sintering maintained PPT over a wide sintering temperature range. Similar to that, the various properties of the ceramics sintered by conventional sintering are strongly dependent on sintering temperature and the ceramics with good properties can only be obtained in a narrow sintering temperature range, while the ceramics with excellent properties were obtained by two-step sintering over a wide sintering temperature range. The results indicate that two-step sintering is an effective way to broaden the sintering temperature range of (K, Na)NbO<sub>3</sub>-based ceramics.**

## I. Introduction

In recent years, various attempts have been made to search for alternative lead-free piezoelectric ceramics and considerable progresses have been achieved.<sup>1–4</sup> Among them, Li- and Ta/Sb-modified (K, Na)NbO<sub>3</sub> (KNN) ceramics have been considered as promising candidates for lead-free piezoelectric ceramics because of their excellent electrical properties.<sup>4</sup> However, limited by poor sintering ability and performance repeatability, such materials have not been widely used in piezoelectric devices. So far, KNN-based ceramics are mostly prepared within a narrow processing window in terms of sintering temperature.<sup>5,6</sup> Slight fluctuation of sintering temperature may result in deteriorated performance.<sup>7–9</sup> Several studies have tried various methods to overcome the problem, such as hot pressing,<sup>10</sup> spark plasma sintering,<sup>11</sup> and so on. However, the problem of the narrow processing window in terms of the sintering temperature for KNN-based ceramics has not been solved yet even the above methods can achieve highly dense ceramics at a low temperature.

Two-step sintering has been reported for preparing nanograin ceramics.<sup>12</sup> In the process, the sample is first heated to a higher temperature to achieve an intermediate relative density (above 75%), then rapidly cooled down and held at a lower temperature

until it is fully dense. Recently, it is found that two-step sintering could also effectively broaden the sintering temperature ranges of KNN-based materials.

In the paper, a typical Li- and Ta/Sb-modified KNN ceramics were prepared by conventional sintering and two-step sintering, respectively. The effects of the different sintering methods on the phase-structures, microstructures, and electrical properties of the ceramics were systematically studied.

## II. Experimental Procedure

A typical Li- and Ta/Sb-modified KNN composition, 0.9625 (Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub>)–0.0375 Li(Ta<sub>0.4</sub>Sb<sub>0.6</sub>)O<sub>3</sub> (KNN–LTS), was prepared by a conventional method from high-purity alkali carbonates and oxides of Nb, Sb, and Ta (>99.9%). After mixed according to the nominal composition, the powder mixtures were calcined twice at 850°C for 5 h. The calcined powders were then milled again for 24 h with a PVB binder (0.5 wt%). After compaction, disk specimens were sintered by conventional sintering and two-step sintering, respectively, in air without any protection. Figure 1 shows the sketch of conventional sintering and two-step sintering. For the two-step sintering process, after burning off PVB at 550°C for 2 h, the sintering procedure is programmed from 900°C to the first-step sintering temperature  $T_1$ °C with a rapid heating rate 10°C/min. The temperature is held at  $T_1$ °C for a short time  $t_1$  min, and then rapidly cooled to a lower second-step temperature  $T_2$  at 10°C/min, then held for a long time  $t_2$  h. After that, it follows the furnace cooling. For the conventional sintering process, the heating rate maintains 3°C/min, and the cooling rate also follows the furnace cooling. Furthermore, the symbols “ $T$ °C for  $t$  h” and “ $T_1/t_1/T_2/t_2$ ” are used to indicate conventional sintering and two-step sintering, respectively.

For electrical measurements, silver paste was screen printed on both sides of the disk samples. Electric poling was conducted at 110°C in a silicone oil bath by applying a dc field of  $\sim 2$  kV/mm for 30 min. The crystal structures were determined by XRD with a CuK $\alpha$  radiation (D/max-rB, Rigaku, Tokyo, Japan). The Piezoelectric coefficient  $d_{33}$  was measured 24 h later after poling by a quasistatic piezoelectric coefficient testing meter (PM300, PIE-ZOTEST, London, UK) and the planar electromechanical coupling factor  $K_p$  were tested by the resonance-antiresonance method with an impedance analyzer (HP4192A, HP, Santa Clara). The dielectric properties at room temperature were determined by a capacitance meter (HP4278A) at 1 kHz and the ferroelectric hysteresis loops were measured at room temperature using a ferroelectric tester (RT6000HVA, Radiant Technologies, NM). The bulk densities were obtained by the Archimedes method and the microstructures were observed by an SEM (Leo-1530, Oberkochen, Germany).

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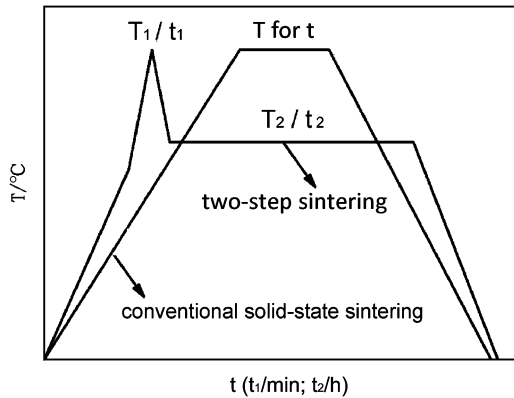


Fig. 1. The sketch of conventional sintering and two-step sintering.

### III. Results and Discussions

Figure 2 indicates that all the KNN-LTS ceramics sintered under different conditions exhibit perovskite phases. As shown in Fig. 2(a), the phase structure of the ceramic sintered by the conventional sintering changes with the increase of sintering temperature  $T$ , from a polymorphic phase transition (PPT)<sup>3</sup> to a tetragonal symmetry. However, the phase structures of the ceramics sintered by two-step sintering seem to have little relevance to the change of sintering temperature. As shown in Figs. 2(b) and (c), the ceramics always maintain PPT with the increase of the first-step sintering temperature  $T_1$  from 1100° to 1160°C and the second-step sintering temperature  $T_2$  from 1000° to 1075°C, respectively. Furthermore, Fig. 2(d) shows that changing dwelling time  $t_2$  also has a limited effect on the phase structures of the ceramics sintered by two-step sintering.

The surface and corresponding cross-section (inset) SEM images of the KNN-LTS ceramics sintered under different conditions are shown in Fig. 3. It can be found that the microstructures of the ceramics sintered by conventional sintering are strongly dependent on the sintering temperature. Figure 3(a) shows that the ceramic sintered at 1075°C for 4 h has a porous microstructure with small grains. With the increase of sintering

temperature, the microstructure firstly become dense, and then porous again, meanwhile, grains grow and abnormal grains increase, as shown in Figs. 3(b) and (c). Furthermore, Fig. 3(d) shows that too long dwelling time in conventional sintering results in a seriously porous microstructure with large grains, which may be due to the volatilization of alkali elements. However, the microstructures sintered by two-step sintering seem to have little relevance to the change of sintering temperature. All the ceramics sintered by two-step sintering exhibit dense microstructures with bimodal grain size distributions. Besides, properly increasing dwelling time  $t_2$  can eliminate pores and improve density accordingly, as shown in Figs. 3(e) and (f).

Figure 4 shows the piezoelectric properties, dielectric properties, and relative densities of the KNN-LTS ceramics sintered under different conditions. It can be seen that the various properties of the ceramics sintered by the conventional sintering are strongly dependent on the sintering temperature. The  $d_{33}$ ,  $K_p$ ,  $\epsilon_{33}^T/\epsilon_0$ , and relative density increase with an increase of sintering temperature, reaching a maximum around 1100°C, and then rapidly decline with a further increase of sintering temperature. Meanwhile, the  $\tan \delta$  undergoes an opposite process, and reaches a minimum around 1105°C. Therefore, the sintering temperature range of the KNN-LTS ceramics prepared by conventional sintering is limited in a narrow temperature range from 1090° to 1105°C. However, the ceramics sintered by two-step sintering exhibit significantly different temperature dependences. The ceramics sintered under the conditions “ $T_1/20$  or  $0/1050/12$ ” and “ $1120/0/T_2/12$  or  $24$ ” maintain excellent properties over wide temperature ranges of  $T_1$  from 1100° to 1160°C and  $T_2$  from 1000° to 1075°C, respectively. Furthermore, the properties of the ceramics sintered by two-step sintering can also be improved by the increase of the dwelling time  $t_2$ . As the ceramics sintered under the condition “ $1120/0/1050/t_2$ ,” the  $d_{33}$ ,  $K_p$ ,  $\epsilon_{33}^T/\epsilon_0$ , and relative density increase with an increase of the dwelling time  $t_2$ , and the  $\tan \delta$  almost maintains unchanged.

Figure 5 shows the  $P$ - $E$  hysteresis loops of the ceramics sintered under different conditions and their corresponding remnant polarizations ( $P_r$ ) and coercive fields ( $E_c$ ). As shown in Figs. 5(b)-(d), well-saturated  $P$ - $E$  hysteresis loops are observed for the ceramics sintered by two-step sintering. Meanwhile, Fig. 5(e) shows

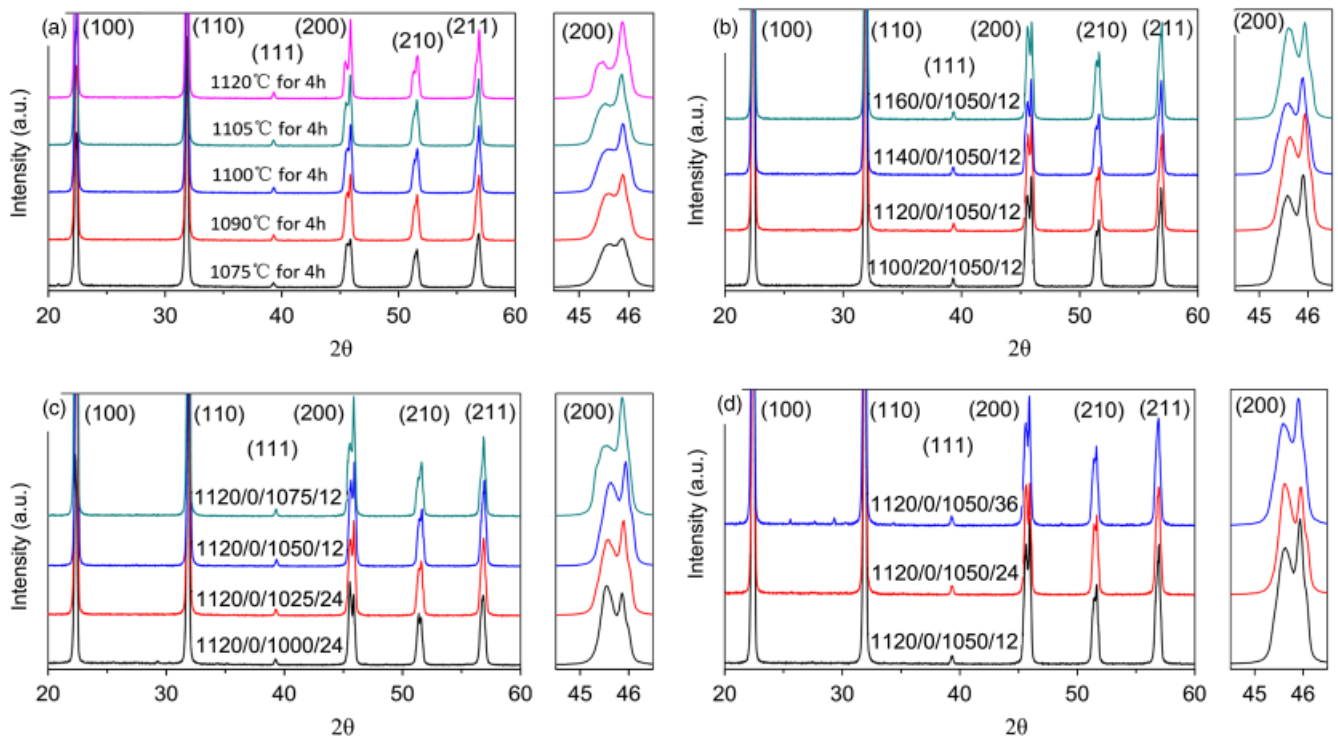
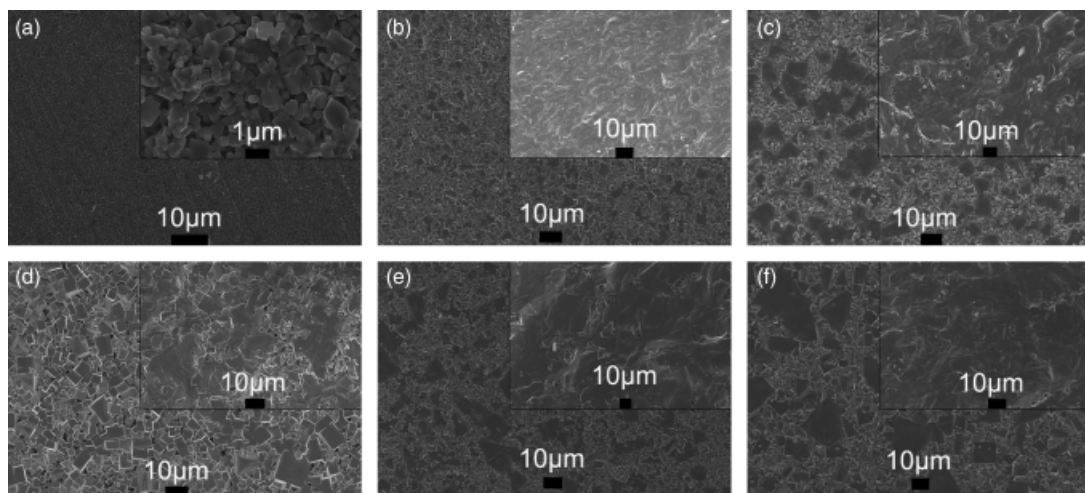


Fig. 2. XRD patterns of the KNN-LTS ceramics sintered under different conditions, “ $T$ °C for 4 h” (a), “ $T_1/20$  or  $0/1050/12$ ” (b), “ $1120/0/T_2/12$  or  $24$ ” (c), and “ $1120/0/1050/t_2$ ” (d).

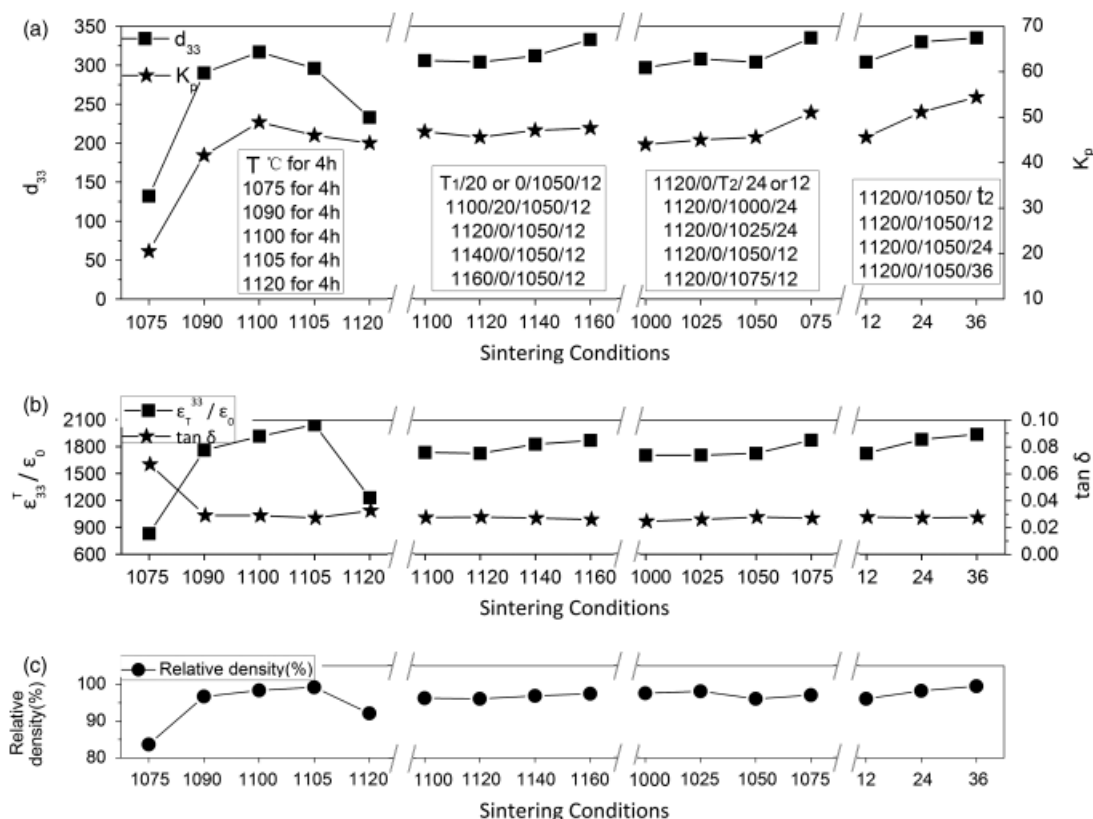


**Fig. 3.** Surface and corresponding cross-section (inset) SEM images of the KNN-LTS ceramics sintered under different conditions, “1075°C for 4 h”, (a) “1100°C for 4 h”, (b) “1120°C for 4 h”, (c) “1100°C for 24 h”, (d) “1120/0/1050/12 h”, and (e) “1120/0/1050/24 h” (f).

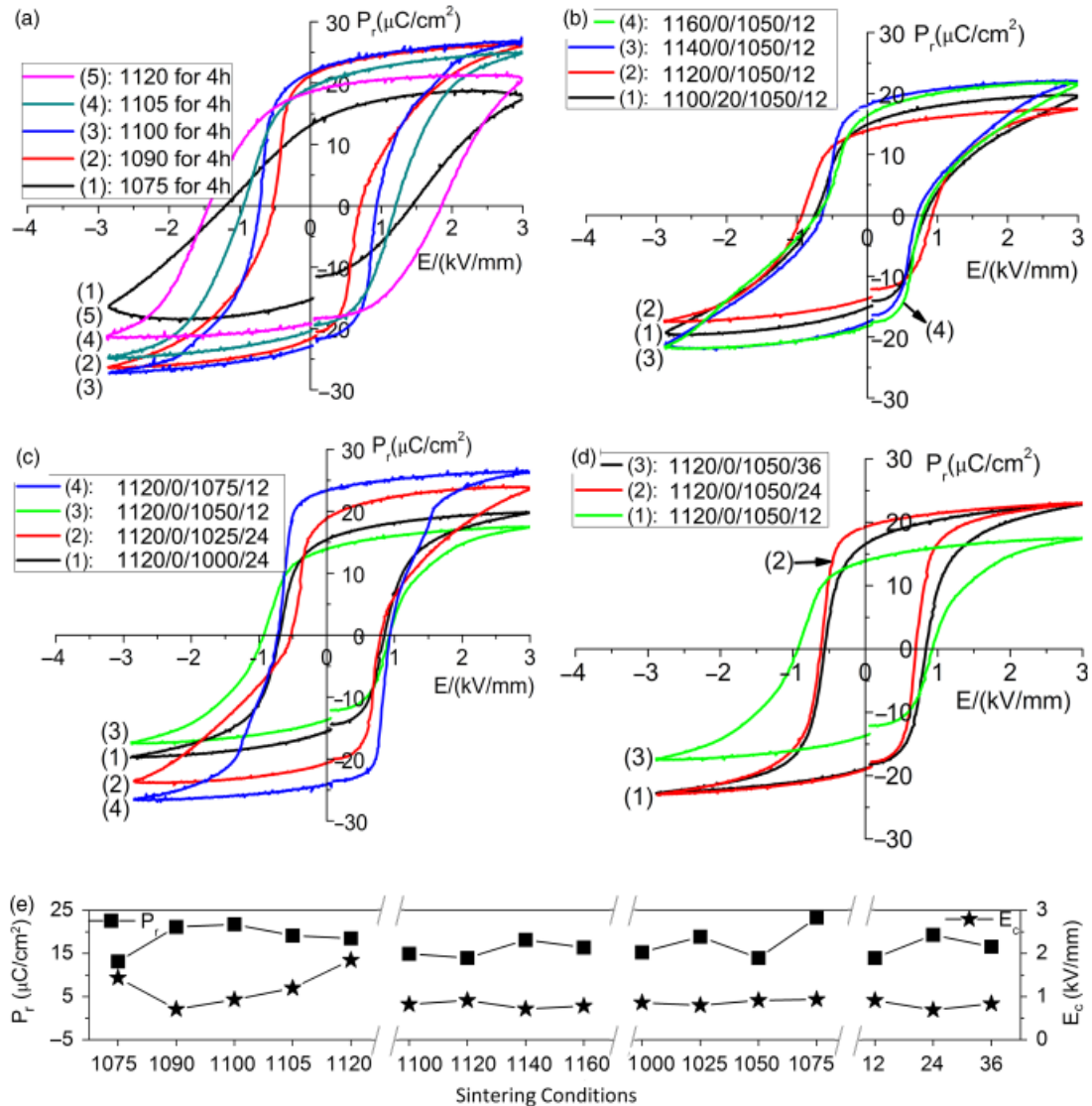
that the ceramics maintain relatively high  $P_r$  and low  $E_c$  over wide temperature ranges. However, as shown in Figs. 5(a) and (e), sintering temperature has an obvious influence on the ferroelectric properties of the samples sintered by conventional sintering. A round-shaped  $P$ - $E$  hysteresis loop is obtained in the sample sintered at 1075°C for 4 h, due to a large leakage current, which suggests that its sintering temperature is not sufficiently high to obtain a dense ceramic. With the increase of sintering temperature, the  $P$ - $E$  hysteresis loops of the ceramics gradually become well-saturated. However, the  $E_c$  increases at the same time, especially for the sample sintered at 1120°C for 4 h. This may be due to the increasing of oxygen vacancy caused by the volatilization of A-site cations such as Na and K, which enhance the pinning effects and decrease domain wall mobility correspondingly.<sup>8</sup>

All the previous experiment results suggest that two-step sintering is an effective approach to broaden the sintering tem-

perature range of KNN-based ceramics. And we can tentatively propose that the following factors play important roles. Firstly, dense ceramics can be prepared at a quite low sintering temperature by two-step sintering. Many works<sup>11,13</sup> have pointed out that the volatilization of alkali elements is serious during the high-temperature sintering of KNN-based ceramics. Hence, it can be considered that two-step sintering restrain the volatilization of alkali elements during the process of sintering dense KNN-based ceramics, because the dwelling time at  $T_1$  is so short and the heating-cooling rate is very rapid. The examination of room-temperature phase structures and microstructures offers a good support to the claim in some cases. Secondly, our previous work (J. Fang, X. Wang, R. Zuo, Z. Tian, C. Zhong, and L. Li *et al.*, unpubl. data) has also indicated that compositional segregation become serious in KNN-based ceramics during high-temperature sintering, resulting in a great deviation from the



**Fig. 4.** (a) Piezoelectric properties, (b) dielectric properties, and (c) relative densities of the KNN-LTS ceramics sintered under different conditions.



**Fig. 5.** Ferroelectric properties of the KNN-LTS ceramics sintered under different conditions, “ $T^{\circ}\text{C}$  for 4 h” (a), “ $T_1/20$  or  $0/1050/12$ ” (b), “ $1120/0/T_2/12$  or  $24$ ” (c), “ $1120/0/1050/t_2$ ” (d), and their corresponding  $P_r$  and  $E_c$  (e).

original stoichiometric proportion and a serious degradation in performance consequently. Two-step sintering can considerably avoid the impact of the factor due to its low sintering temperature. However, the case is impossible for conventional sintering.

#### IV. Conclusions

The Li- and Ta/Sb-modified KNN ceramics were fabricated by conventional sintering and two-step sintering, respectively. The phase structures, microstructures, electrical properties, and relative densities of the KNN-based ceramics sintered by conventional sintering are obviously dependent on sintering temperature. However, the ceramics with excellent properties can be prepared by two-step sintering over a wide sintering temperature range. The results reveal that two-step sintering is an effective way to broaden the sintering temperature range of the KNN-based ceramics. And it will be helpful to the application of the KNN-based piezoelectric ceramics.

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