

Influence of sintering temperature on electrical properties of $(\text{K}_{0.4425}\text{Na}_{0.52}\text{Li}_{0.0375})(\text{Nb}_{0.8825}\text{Sb}_{0.07}\text{Ta}_{0.0475})\text{O}_3$ ceramics without phase transition induced by sintering temperature

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Abstract: Lead-free $(\text{K}_{0.4425}\text{Na}_{0.52}\text{Li}_{0.0375})(\text{Nb}_{0.8825}\text{Sb}_{0.07}\text{Ta}_{0.0475})\text{O}_3$ (KNLNST) piezoelectric ceramics are synthesized by the conventional solid-state reaction method. The sintering temperature and poling temperature dependence of ceramic properties are investigated. Previous studies have shown that variation of sintering temperature can cause phase transition, similar to the morphotropic phase boundary (MPB) behavior induced by composition changes in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT). And the best piezoelectric performance can be obtained near the phase-transition sintering temperature. In this research, phase transition induced by sintering temperature cannot be detected and excellent piezoelectric properties can still be obtained. The sintering temperature of the largest piezoelectric coefficient of such composition is lower than that of the highest density, which is considered in composition segregation as a result of intensified volatilization of alkali metal oxides. Combined with the effect of poling temperature, the peak values of the piezoelectric properties are $d_{33}=313$ pC/N, $k_p=47\%$, $\varepsilon_r=1825$, $\tan\delta=0.024$, $T_{o-t}=88$ °C, and $T_C=274$ °C.

Keywords: tetragonal; piezoelectric properties; sintering temperature; doped; poling temperature

1 Introduction

The speedy development of piezoelectric devices urgently calls for environment-friendly materials as substitutes for the widely-used lead zirconate titanate ($\text{Pb}(\text{Zr,Ti})\text{O}_3$, PZT). Among the various lead-free piezoelectric materials, alkali niobate ($\text{K,Na})\text{NbO}_3$ (KNN) is considered one of the most promising

candidates for lead-free piezoelectric ceramics due to its high Curie temperature (about 420 °C) and strong ferroelectricity [1–5]. However, the high volatility of alkaline elements at high temperature makes it difficult to achieve the densification and obtain well-sintered KNN ceramics from pure KNN ceramics using ordinary sintering process, which has hindered the research for a long time [2,6]. Thus far, pure KNN ceramics prepared by conventional solid-state reaction method have poor d_{33} values of 80 pC/N and low densities of 4.2 g/cm³ [7]. Various fabricating techniques, such as hot-pressed sintering [8], spark-plasma sintering [9], microwave sintering [10],

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two-step sintering [11] and hydrothermal synthesis [12], have been utilized to improve the properties of lead-free piezoelectric ceramics. However, all of these techniques are unsuitable in industrial applications.

The addition of a small amount of sintering aid (CuO [13], MnO₂ [14], AgTaO₃ [15], SnO₂ [16], ZnO [17], and BiMnO₃ [18]) is an effective method to reduce the sintering temperature and enhance the density. However, the piezoelectric properties of the ceramics could also obviously decrease. Recent studies have shown that Li/Ta/Sb doping can increase the sintering density of KNN ceramics and significantly improve its piezoelectric properties. Saeri *et al.* [19] investigated the effects of Li doping on the property of KNN lead-free ceramics, which exhibit $d_{33} = 215$ pC/N and $\epsilon_r = 560$. Su *et al.* [20] reported that (K_{0.7}Na_{0.3})(Nb_{0.95}Sb_{0.05})O₃ lead-free piezoelectric powders are successfully synthesized by hydrothermal treatment. Saito *et al.* [21] used reactive template growth method to investigate (Na,K)NbO₃–Li(Ta,Sb)O₃. The as-obtained ceramics exhibited piezoelectric properties as high as 416 pC/N, which is comparable to that of PZT ceramics. Partial substitutions of Li at the A-site and Sb and/or Ta at the B-site could induce a sharp change in the lattice parameters of KNN and hence lead to phase transition. However, Pang *et al.* [22] reported a similar phase transition of (K,Na,Li)(Nb,Sb,Ta) ceramics by varying the sintering temperature from 1110 °C to 1140 °C. The peak value of the piezoelectric coefficient (d_{33}) can be obtained while the sintering temperature is close to the phase-transition sintering temperature.

The superior properties of KNN-based ceramics are generally attributed to the presence of phase structure similar to the morphotropic phase boundary (MPB). Accordingly, it is significant to investigate whether such a similar MPB behavior induced by different sintering temperatures could impact the properties of KNN-based ceramics.

In this paper, the ceramic (K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.8825}Sb_{0.07}Ta_{0.0475})O₃ (KNLNST) was chosen to investigate the effects of the variation of sintering temperature from 1110 °C to 1150 °C on the ceramic phase structure and piezoelectric properties.

2 Experimental procedure

K₂CO₃ (99%), Na₂CO₃ (99.8%), Li₂CO₃ (98%), Nb₂O₅ (99.5%), Ta₂O₅ (99.99%), and Sb₂O₃ (99.5%) were

used as raw materials to prepare KNLNST ceramics by conventional mixed-oxide method. The stoichiometric powders were mixed in ethanol by ball-milling for 12 h, and then dried and calcined at 900 °C for 5 h. The calcined powders were then mixed with 3 wt% polyvinyl alcohol (PVA) solution and uniaxially pressed into pellets with a diameter of 1.5 cm under 300 MPa pressure. After burning out the PVA, the green disks were sintered in air at selected temperatures (1110–1150 °C) for 3 h. The microstructure was observed by a scanning electron microscope (SEM, JSM-5610LV/Noran-Vantage). Powder X-ray diffraction (XRD, D8 Advance) was utilized to identify the crystal structures and phases. Silver paste electrodes were formed at the two circular surfaces of the disk-shaped specimens after firing at 700 °C for 10 min to measure the dielectric and piezoelectric properties. The piezoelectric constant d_{33} was measured using a static piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, Beijing, China). Dielectric properties as functions 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). The measurement of piezoelectric and electromechanical properties was only carried out 24 h after a poling process.

3 Results and discussion

Figure 1(a) shows the XRD patterns of the samples sintered from 1110 °C to 1150 °C. The enlarged XRD patterns of the ceramics in the range of 2θ from 44° to 48° are shown in Fig. 1(b). All the ceramics show a tetragonal phase, and the phase transition does not occur as the sintering temperature increases. A secondary phase is detected in all doped samples when 2θ is approximately 28.5°. The secondary phase could be assigned to the tetragonal tungsten–bronze (TTB) type structure phase, which does not disappear as the composition changes. The occurrence of the TTB secondary phase is attributed to the volatilization and segregation of the alkali elements during the sintering process for Li/Ta-modified KNN material [23], which induces B-site ion excess that is accommodated through TTB phase formation. With the increase in temperature, the (002) and (200) peaks shift toward lower angles, which is attributed to the easy

volatilization of sodium and potassium during high-temperature sintering. Sodium volatilizes faster than potassium, resulting in the presence of a niobium-rich phase [24]. The lattice parameters increase (Fig. 2) because the radius of K^+ (1.38 Å) is larger than that of Na^+ (1.02 Å), which could lead to the gradual increase in space distance. According to Bragg's equation, $2d\sin\theta = \lambda$, $\lambda = 1.5416 \text{ \AA}$, increasing d leads to a decrease in θ .

Figure 3 depicts the micrographs of the KNLNST ceramics sintered at different temperatures. All the ceramics show a bimodal distribution with many fine grains located at the boundaries of the coarse grains. Most figures demonstrate apparent square grains,

except for Fig. 3(a). The boundaries of the grains are ambiguous, and the shape of the grains is not structured according to the KNLNST ceramics sintered at 1110 °C. Figure 3(a) illustrates that sintering temperature of 1110 °C is unsuitable to obtain square grains. When the sintering temperature is increased from 1120 °C to 1150 °C, the shape of matrix grains exhibits more tacticity, but no significant change in the size of grain occurs. A comparison among Figs. 3(b) to 3(e) shows that the shape and tetragonality of the grains are the best in Figs. 3(d) and 3(e). The grains in Fig. 3(e) are more uniform than the grains in Fig. 3(d).

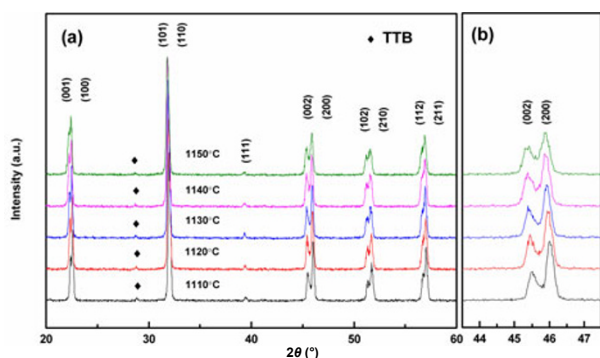


Fig. 1 XRD patterns of the KNLNST ceramics sintered at different temperatures in the range of 2θ : (a) from 20° to 60°; (b) from 44° to 48°.

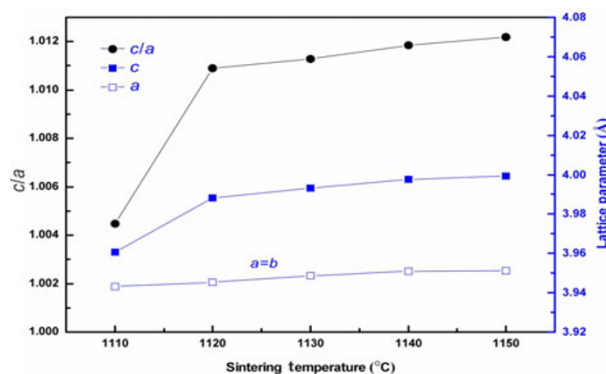


Fig. 2 Lattice parameter evolutions as functions of sintering temperature.

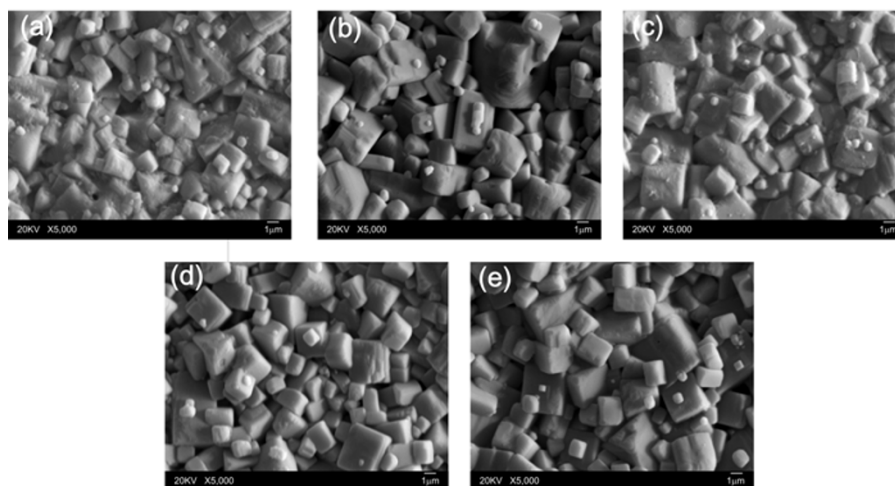


Fig. 3 SEM images of the KNLNST ceramics sintered at different temperatures: (a) 1110 °C, (b) 1120 °C, (c) 1130 °C, (d) 1140 °C, and (e) 1150 °C.

Figure 4 displays the measured density of KNLNST as a function of sintering temperature. The measured density of the KNLNST samples increases from 4.33 g/cm^3 to 4.52 g/cm^3 , while the sintering

temperature increases by a scope of 30 °C from 1110 °C to 1140 °C. The highest density is obtained for the KNLNST sample sintered at 1140 °C, and then tends to decrease as the temperature exceeds 1140 °C.

A relatively higher temperature is helpful in achieving higher density, but may also lead to higher volatilization of K and Na for KNN-based ceramics. So when the effect of temperature on density increase cannot compensate the volatilization of alkali metal, the density decreases.

Figures 5(a) and 5(b) show the piezoelectric property (d_{33}) and electromechanical coupling factor (k_p). As the sintering temperature increases, both d_{33}

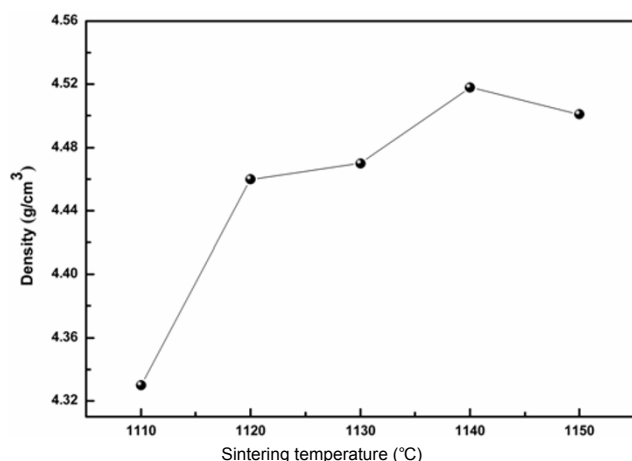


Fig. 4 Dependence of measured density as a function of sintering temperature.

and k_p initially increase rapidly from 230 pC/N to 313 pC/N and from 0.32 to 0.47, respectively. The further increase of the sintering temperature leads to obvious decreases in d_{33} and k_p which are partly caused by the volatilization of Na and K during high-temperature sintering. The peak value of d_{33} appears when the sintering temperature is 1130 °C. Although phase transition does not occur in the sintering temperature range of 1110 °C to 1150 °C, excellent piezoelectric properties like those mentioned in previous reports can still be obtained, indicating that the excellent piezoelectric property does not result from phase transition caused by the variation in sintering temperature. Mechanical quality factor (Q_m) (seen in Fig. 5(c)) reveals an opposite trend to d_{33} , showing an obvious “valley” region within the sintering temperature range of 1120 °C to 1140 °C. The lowest value of Q_m (29) appears at 1130 °C corresponding to the highest value of d_{33} . The relative permittivity (ϵ_r) value variation of KNLNST ceramics can be seen in Fig. 5(d). It shows that the influence of sintering temperature on ϵ_r is similar to d_{33} , increasing with increasing sintering temperature, reaching the peak value of 1825 at 1130 °C. Over the peak value, ϵ_r value decreases sharply to 1567 at 1140 °C. While the

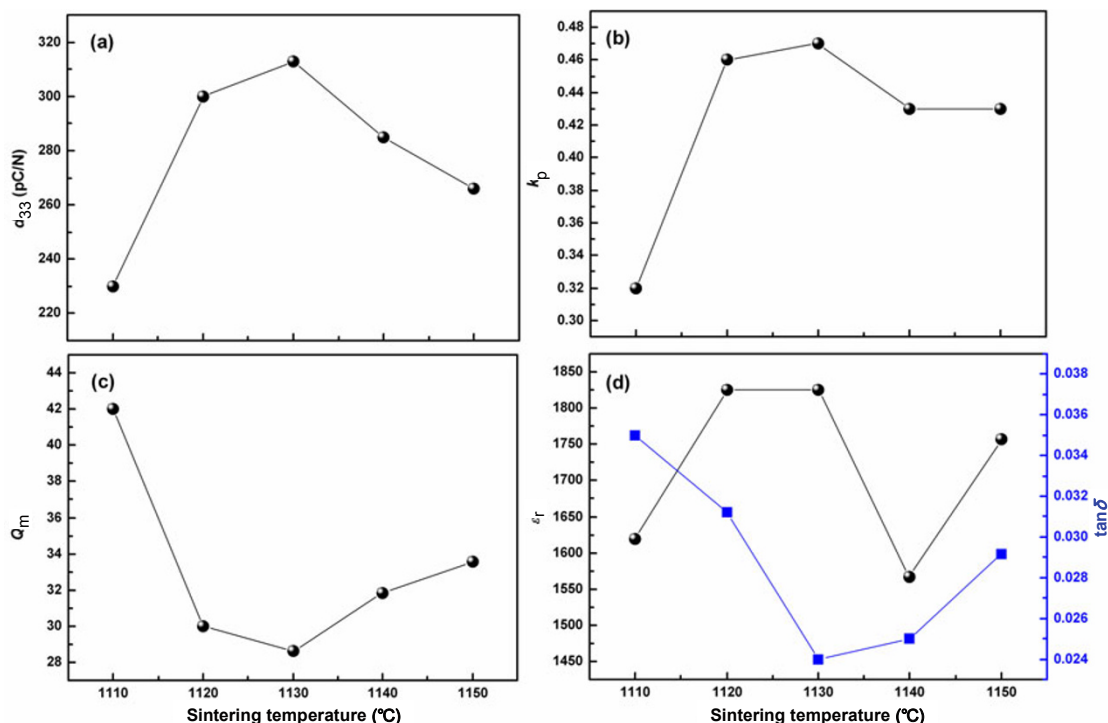


Fig. 5 Dependence of electrical properties of the KNLNST ceramics sintered at different temperatures: (a) piezoelectric coefficient (d_{33}), (b) planar mode electromechanical coupling coefficient (k_p), (c) mechanical quality factor (Q_m), and (d) relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$).

sintering temperature reaches 1150 °C, ϵ_r value again exhibits a significant increase from 1567 to 1757. This abnormal variation is not well-understood at present, and needs to be studied further. Dielectric loss ($\tan\delta$) exhibits normal variation process, decreasing incipiently and then gradually increasing with the sintering temperature exceeding 1130 °C. The minimal $\tan\delta$ appears at 1130 °C, indicating that the ceramic owns fewer defects. Therefore, the optimum sintering temperature for KNLNST ceramics is 1130 °C, and the properties are $d_{33}=313$ pC/N, $\epsilon_r=1825$, $k_p=0.47$, $Q_m=29$, and $\tan\delta=0.024$.

Figure 6(a) shows the P - E hysteresis loops of the KNLNST ceramics as functions of the sintering temperature from 1110 °C to 1150 °C. It shows that all the P - E loops are well saturated. Remanent polarization P_r produces slight fluctuation as the sintering temperature varies, and the value of P_r settles into the 15.5 $\mu\text{C}/\text{cm}^2$ to 16.3 $\mu\text{C}/\text{cm}^2$ range (as shown in Fig. 6(b)). The varying trend of coercive field E_c (Fig. 6(c)) is similar to that of P_r , exhibiting inactivity as the sintering temperature changes. The sample sintered at 1150 °C shows the lowest E_c , which is distinct from the E_c of other sintering temperatures.

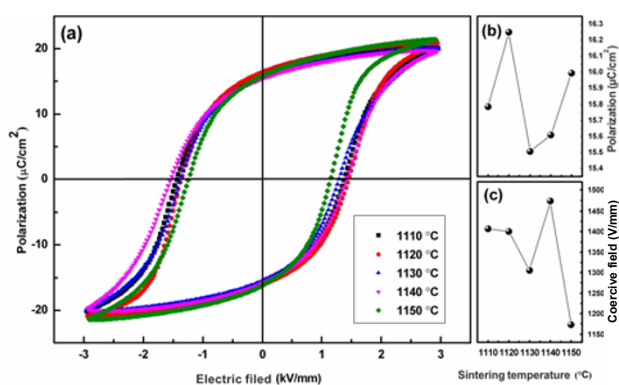


Fig. 6 (a) Polarization–electric field hysteresis loops of the KNLNST ceramics sintered at different temperatures; (b) the variation of polarization (P_r) value as a function of sintering temperature; and (c) the coercive field (E_c) value of KNLNST ceramics sintered at different temperatures.

Figure 7(a) shows the temperature dependence of the dielectric constant (measured at 10 kHz) for the KNLNST ceramics with different sintering temperatures. The two peaks can be detected in the temperature ranges of 40 °C to 110 °C and 250 °C to 300 °C, respectively. These peaks correspond to the transition from the orthorhombic phase to the

tetragonal phase (T_{o-t}), and from the tetragonal phase to the cubic phase (T_C), respectively. T_{o-t} fluctuates with the increase of the sintering temperature, shifting to higher temperature. T_{o-t} for all samples synthesized at 1110 °C, 1130 °C, and 1150 °C are 47 °C, 88 °C, and 101 °C, respectively (as shown in Fig. 7(b)). T_C shows the same variation trend, shifting to higher temperature but changing slightly. The maximum dielectric constant at T_C can be obtained at 1130 °C. The values of T_C are 271 °C, 274 °C, and 287 °C, respectively (seen in Fig. 7(c)). Referring to a previous study, T_C decreases as a result of Ta/Sb doping. However, Choi *et al.* [25] pointed out that the T_C value of ceramics can be improved by enhancing the tetragonality of the ceramics, which is decided by the lattice ratio of c/a . The illustration of the lattice parameters of the different sintering temperatures shows that the value of c/a increases with temperature. Therefore, the variation trend of T_C is more complicated, which may be decided by two factors, namely, Ta content and tetragonality. For the stability of the Ta content, the change in the tendency of T_C is decided by the tetragonality of the ceramics. In addition, no apparent broadening of the dielectric constant can be observed in the figure, indicating that the ceramics do not possess relaxation properties.

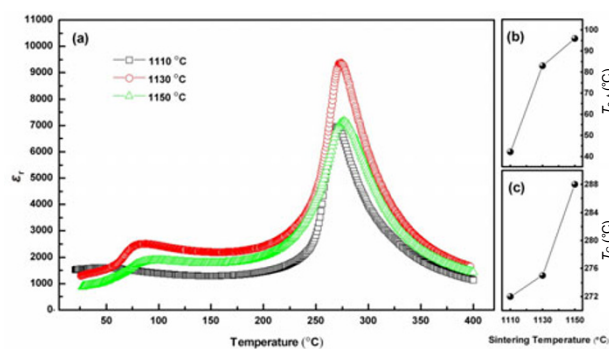


Fig. 7 (a) Temperature dependence of the dielectric constant (ϵ_r) for the KNLNST ceramics sintered at 1110 °C, 1130 °C, 1150 °C for 3 h measured at 10 kHz; (b) the phase transition temperature (T_{o-t}) of KNLNST ceramics sintered at 1110 °C, 1130 °C, 1150 °C; and (c) the Curie temperature (T_C) of KNLNST ceramics as a function of sintering temperature.

The effect of polarization temperature ranging from 30 °C to 150 °C on the value of piezoelectric coefficient (d_{33}) is also investigated (Fig. 8). The optimal d_{33} can be obtained when poling temperature is

70 °C, which approaches T_{0-t} . This finding is attributed to the metastability of the phase structure near the T_{0-t} , where domains possess higher activity and are more likely to reverse. Moreover, d_{33} decreases monotonously from 313 pC/N to 276 pC/N as the polarization temperature continuously increases to 150 °C.

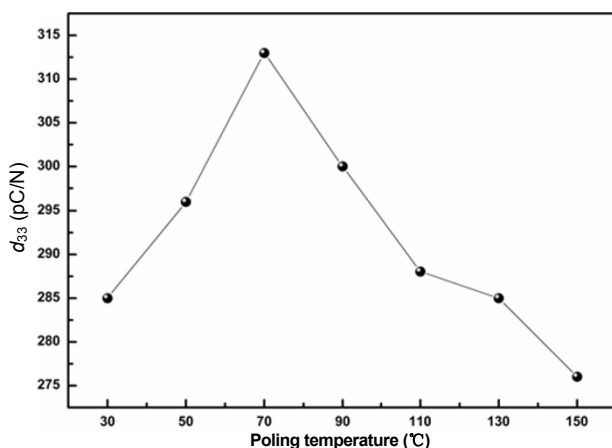


Fig. 8 Poling temperature dependence of the piezoelectric coefficient (d_{33}) for the KNLNST ceramics sintered at 1130 °C for 3 h.

4 Conclusions

The effects of sintering temperature on the microstructure, dielectric, piezoelectric, and ferroelectric properties of KNLNST ceramics were studied. No obvious phase transition behavior for the KNLNST ceramics with Ta = 4.75 mol% was observed with changes in sintering temperature ranging from 1110 °C to 1150 °C. However, excellent piezoelectric properties can still be obtained. Accordingly, the excellent piezoelectric property did not result from such similar MPB behavior caused by the variation in sintering temperature. Moreover, by combining the effect of sintering temperature and poling temperature, the KNLNST ceramics exhibited optimum electrical properties as follows: d_{33} = 313 pC/N, k_p = 0.47, ϵ_r = 1825, $\tan\delta$ = 0.024, T_C = 274 °C, T_{0-t} = 88 °C, P_r = 15.5 $\mu\text{C}/\text{cm}^2$, and E_c = 1316 V/mm.

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