

## Performance Improvement of LiF/ZnO Codoped Lead-Free Piezoelectric Ceramics

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In this study, a series of  $\text{Li}_{0.058}(\text{Na}_{0.535}\text{K}_{0.480})_{0.966}(\text{Nb}_{0.90}\text{Ta}_{0.10})\text{O}_3$  (LNKNT) +  $(x)\text{ZnO}$  +  $(y)\text{LiF}$  ( $x = 0, 0.4,$  and  $0.6$  wt%;  $y = 0$  and  $0.2$  wt%) lead-free piezoelectric ceramics were fabricated by a conventional solid-state reaction method. The codoping of ZnO and LiF could significantly improve the sintering ability of LNKNT ceramics by reducing the optimal sintering temperature from 1090 to 990 °C. The crystal phases and microstructures were analyzed by X-ray diffraction (XRD) and scanning electronic microscopy (SEM), respectively. The dielectric characteristics, electromechanical coupling factors, piezoelectric constants, and  $P$ – $E$  curves were also measured and investigated. From the results, as 0.6 wt% ZnO and 0.2 wt% LiF were added into pure LNKNT ceramics, uniform and condensed grains can be obtained easily, and thus the sintering temperature can be decreased from 1090 °C (pure LNKNT) to 990 °C. Compared with pure LNKNT, ZnO/LiF codoped LNKNT has better orthorhombic and tetragonal coexistence phases. In this study, the optimal  $d_{33}$  values were improved from 279 pC/N (pure LNKNT) to 304 pC/N (LNKNT-6Z2LF), and  $k_p$  were improved from 0.46 (LNKNT) to 0.48 (LNKNT-6Z2LF). Hence, the codoping of ZnO and LiF can improve the sintering ability of the LNKNT ceramics effectively.

### 1. Introduction

Lead-free piezoelectric materials that are environmentally friendly from the viewpoint of sustainable development have attracted attention in recent years.<sup>(1,2)</sup> Among them,  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$  (KNN)-based piezoelectric ceramics are considered promising candidates because of their markedly enhanced piezoelectric properties.<sup>(3–5)</sup> An important key approach for improving the electrical properties of KNN ceramics is to lower the tetragonal–orthorhombic phase transition ( $T_{\text{O-T}}$ ), producing a coexistence of the tetragonal and orthorhombic phases at low temperature. In addition, Matsubara *et al.*<sup>(6,7)</sup> reported that, for KNN ceramics, the partial substitution of Li for A site ions and Ta for B site ions enhances their dielectric and piezoelectric properties considerably. Recently, by

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introducing LiNbO<sub>3</sub> into the KNN ceramics with the nominal optimal K:Na ratio of 0.480:0.535, an exact morphotropic phase boundary (MPB) separating orthorhombic and tetragonal phases has been determined, in which a  $d_{33}$  of 314 pC/N has been obtained in the nonstoichiometric composition of  $\text{Li}_{0.058}(\text{Na}_{0.535}\text{K}_{0.480})_{0.942}\text{NbO}_3$ .<sup>(8)</sup>

Furthermore, some dopants such as ZnO, SnO<sub>2</sub>, and Yb<sub>2</sub>O<sub>3</sub> were found to promote densification as well.<sup>(9,10)</sup> An ideal sintering aid should effectively lower the sintering temperature while maintaining the piezoelectric properties as best as possible. Caballero *et al.*<sup>(11)</sup> and Kim *et al.*<sup>(12)</sup> reported that ZnO has been successfully used to reduce the dielectric losses in different materials. It has been shown that the addition of ZnO helps to increase the density of the material and avoids deliquescence.

Because LiF exhibits a low melting point of 845 °C, it is commonly used in the synthesis of molten salts. The low melting point of LiF indicates that it may form a liquid phase during the sintering process, which may promote densification and grain growth of KNN-based piezoceramics. Hence, in this study, to improve the sintering ability and piezoelectric characteristics of  $\text{Li}_{0.058}(\text{Na}_{0.535}\text{K}_{0.480})_{0.966}(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_3$  (denoted as LNKNT) piezoceramics, small amounts of ZnO and LiF were added to LNKNT piezoceramics at the same time and with the composition of  $\text{Li}_{0.058}(\text{Na}_{0.535}\text{K}_{0.480})_{0.966}(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_3 + (x)\text{ZnO} + (y)\text{LiF}$  (denoted as LNKNT-*xZyLF*). The effect of codoped LiF/ZnO on the phase structure as well as the microstructure of LNKNT ceramics was systematically investigated.

## 2. Experimental Procedure

From the composition of  $\text{Li}_{0.058}(\text{Na}_{0.535}\text{K}_{0.480})_{0.966}(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_3$  and by the conventional solid-state reaction method, proportional high-purity (>99.5%) raw materials (Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, and Ta<sub>2</sub>O<sub>5</sub>) were used. After mixing, grinding, and 850 °C / 2 h calcination, commercially available ZnO and LiF (>99.5%) sintering promoters were then introduced into LNKNT with the formula of LNKNT + (x)ZnO + (y)LiF ( $x = 0, 0.4, \text{ and } 0.6 \text{ wt\%}$ ;  $y = 0 \text{ and } 0.2 \text{ wt\%}$ ), mixed, ball-milled for 10 h in ethanol, and dried. After adding 5 wt% polyvinyl alcohol (PVA) as binder, the resulting powders were ground again, dried, and pressed into pellets 12 mm in diameter under a pressure of 150 MPa. Finally, these samples were debindered and sintered in air between 950 and 1120 °C for 2 h. The crystal structure of the sintered samples was analyzed by X-ray diffraction (XRD) using CuK<sub>α</sub> radiation ( $2\theta = 20\text{--}60^\circ$ ), and their microstructures were characterized by scanning electron microscopy (SEM). After painting the electrodes and polarizing (3.5 kV/mm) in 140 °C silicon oil for 30 min, the piezoelectric constant ( $d_{33}$ ) was measured using a  $d_{33}$  meter, and by using the impedance analyzer (HP4294A), the electromechanical coupling factors ( $k_p$ ) were determined by the resonance and antiresonance method according to IEEE standards. The polarization–electric field ( $P$ – $E$ ) hysteresis loops were measured using a ferroelectric tester, and the remanent polarizations ( $P_r$ ) and coercive fields ( $E_c$ ) were then obtained.

## 3. Results and Discussion

Figure 1 shows the XRD patterns ( $2\theta = 20\text{--}60^\circ$  and  $44\text{--}47^\circ$ ) of the LNKNT + (x)ZnO + (y)LiF ( $x = 0, 0.4, \text{ and } 0.6 \text{ wt\%}$ ;  $y = 0 \text{ and } 0.2 \text{ wt\%}$ ) ceramics sintered at 990 °C for 2 h. The SEM images of the LNKNT-*xZyLF* (sintered at 990 °C for 2 h) ceramics are shown in Fig. 2. It can be seen that the peaks of ZnO and LiF are not clear owing to their small concentrations. No clear second phases can

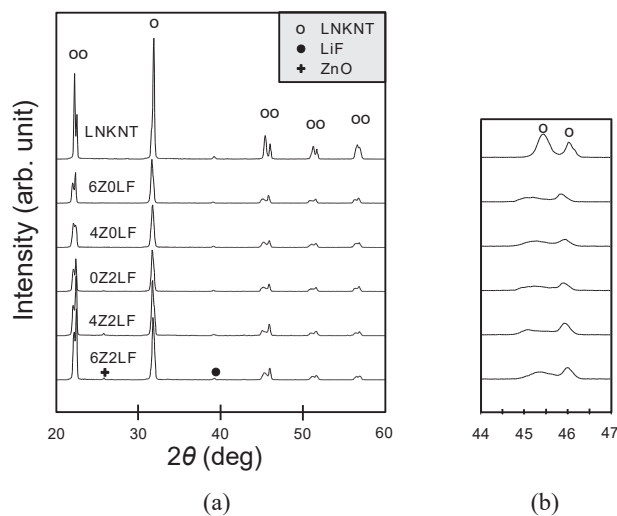


Fig. 1. XRD patterns of the LNKNT- $x$ Z $y$ LF ceramics sintered at 990 °C for 2 h. (a)  $2\theta = 20\text{--}60^\circ$  and (b)  $2\theta = 44\text{--}47^\circ$ .

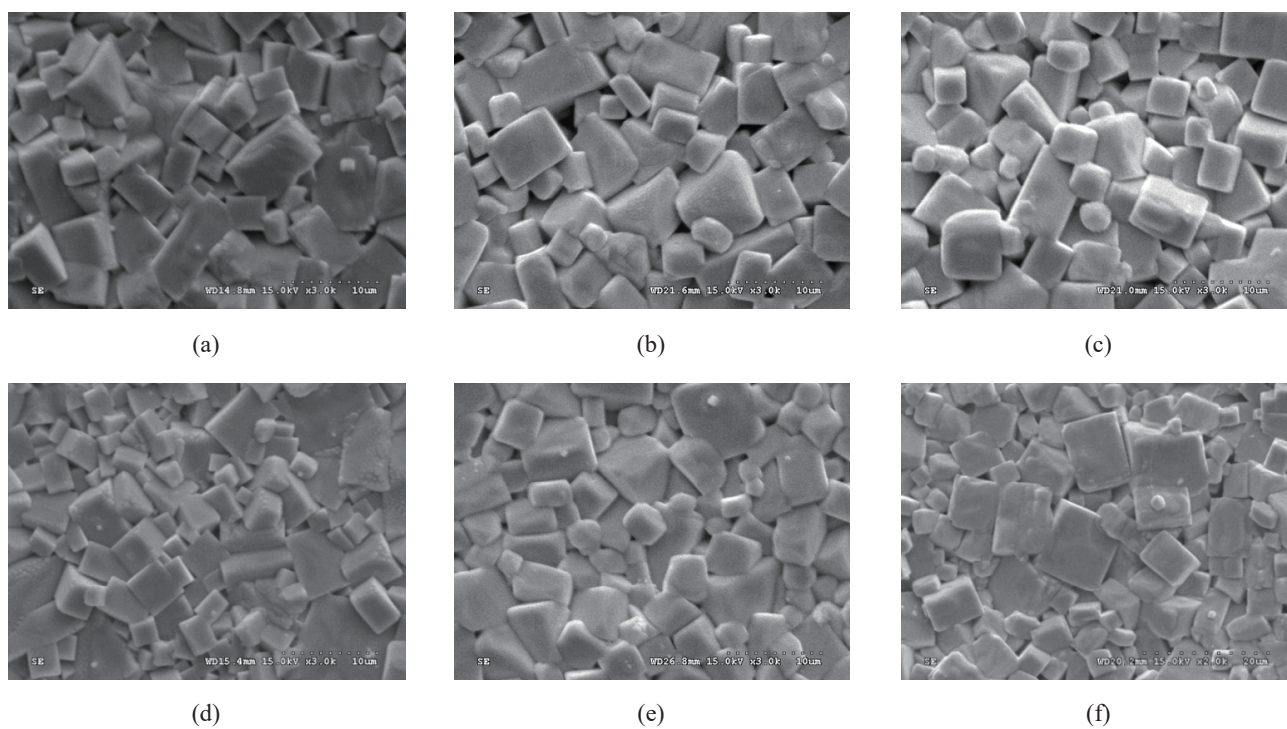


Fig. 2. SEM images of LNKNT- $x$ Z $y$ LF sintered at 990 °C. (a) 6Z0LF, (b) 4Z2LF, (c) 6Z2LF, (d) 4Z0LF, (e) 0Z2LF, and (f) pure LNKNT.

be found, and all specimens reveal pure perovskite structures with cubic-type grains. Furthermore, from the 44–47° figure presented, we can observe that, compared with the pure LNKNT, the ZnO/LiF codoped LNKNT reveals better orthorhombic and tetragonal coexistent phases.

Figure 3 shows the relative dielectric constants and dielectric loss variations of the LNKNT- $x$ Z $y$ LF ceramics as a function of sintering temperature. From the relative dielectric constants

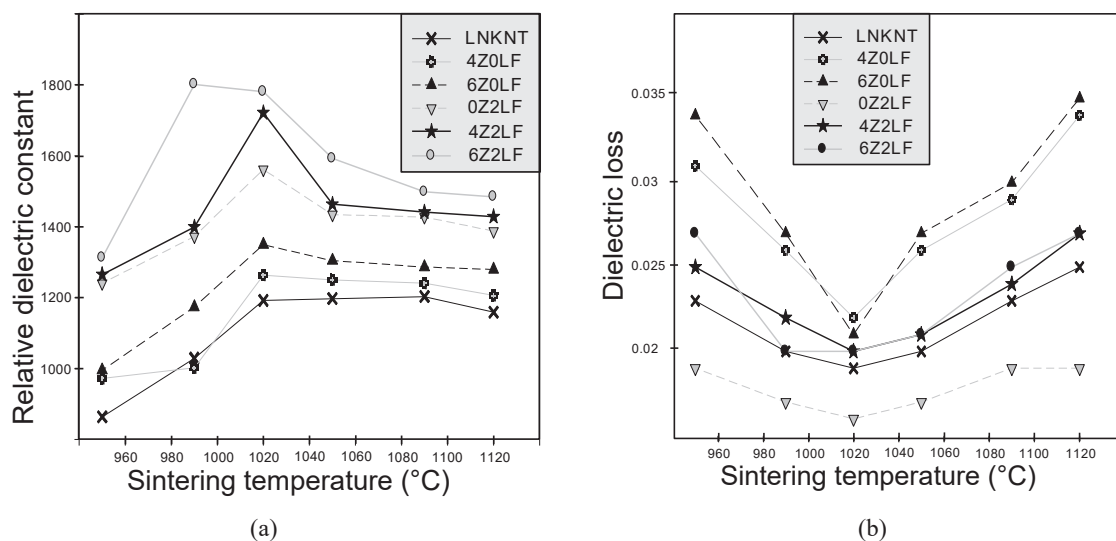


Fig. 3. (a) Relative dielectric constants and (b) dielectric losses of LNKNT- $x$ Z $y$ LF ceramics.

shown, it can be observed that pure LNKNT reveals lower relative dielectric constants than the others. Moreover, as the sintering temperature increases from 950 to 1120 °C, all the relative dielectric constants increase to a maximum value gradually and then decrease. However, except for the pure LNKNT specimens (obtained at 1090 °C) and LNKNT-6Z2LF specimens (obtained at 990 °C), all the maximum dielectric constants are obtained at 1020 °C. The maximum relative dielectric constants are about 1200 for pure LNKNT and 1800 for LNKNT-6Z2LF. This means that the additions of ZnO and LiF have obvious effects, i.e., (1) increasing the dielectric constant and (2) decreasing the sintering temperature. However, the dielectric loss variation shown in Fig. 3(b) decreases to a minimum value and then increases with increasing sintering temperature for all the specimens, and all the minimum dielectric losses occur at 1020 °C. In particular, for the LNKNT-0Z2LF specimens, the dielectric loss reveals a lower value ( $<0.02$ ) than those of the others, and LiF-doped specimens reveal larger dielectric constants and lower dielectric losses. This means that LiF dopants can improve the dielectric properties of LNKNT ceramics effectively.

Two  $P$ - $E$  curves of the LNKNT-4Z2LF and LNKNT-6Z2LF specimens for different sintering temperatures are plotted in Fig. 4. In addition, Fig. 5 shows the remanent polarization ( $P_r$ ) and coercive field ( $E_c$ ) variations of the LNKNT- $x$ Z $y$ LF ceramics. As the sintering temperature increases from 950 to 1120 °C, both the  $P_r$  and  $E_c$  values become maximums at first, and then decrease gradually. For the LNKNT-4Z2LF specimens, at a sintering temperature of 1020 °C, we obtain maximum  $P_r$  and  $E_c$  values of 13.52  $\mu\text{C}/\text{cm}^2$  and 2.22 kV/mm, respectively. However, for the LNKNT-6Z2LF specimens, at a sintering temperature of 990 °C, we obtain maximum  $P_r$  and  $E_c$  values of 11.42  $\mu\text{C}/\text{cm}^2$  and 2.22 kV/mm, respectively.

The variations of piezoelectric constants ( $d_{33}$ ) and electromechanical coupling factors ( $k_p$ ) of the LNKNT- $x$ Z $y$ LF ceramics are presented in Fig. 6. It is clear that, for all the specimens, the  $d_{33}$  values first increased, reached a maximum value, and then decreased gradually. The maximum  $d_{33}$  value of LNKNT-6Z2LF is 304 pC/N and its sintering temperature is only 990 °C. However, for pure LNKNT, the maximum  $d_{33}$  value is only 279 pC/N and it is sintered at 1090 °C. Hence, it is clear that, owing to the addition of ZnO and LiF liquid-phase sintering promoters, the optimal sintering temperature of 1090 °C can be reduced significantly to 990 °C by ZnO/LiF codoping, and

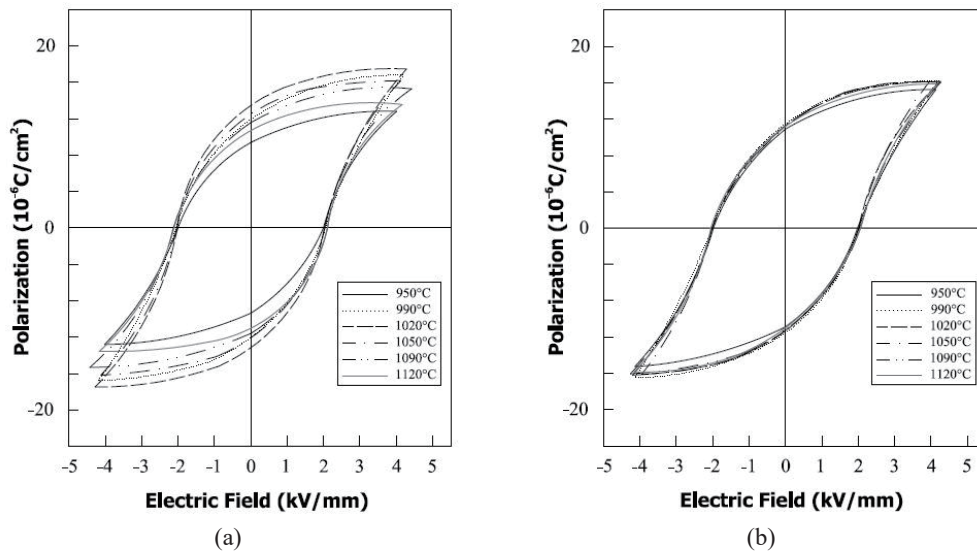


Fig. 4.  $P$ - $E$  curves of LNKNT- $x$ Z $y$ LF ceramics: (a) 4Z2LF and (b) 6Z2LF.

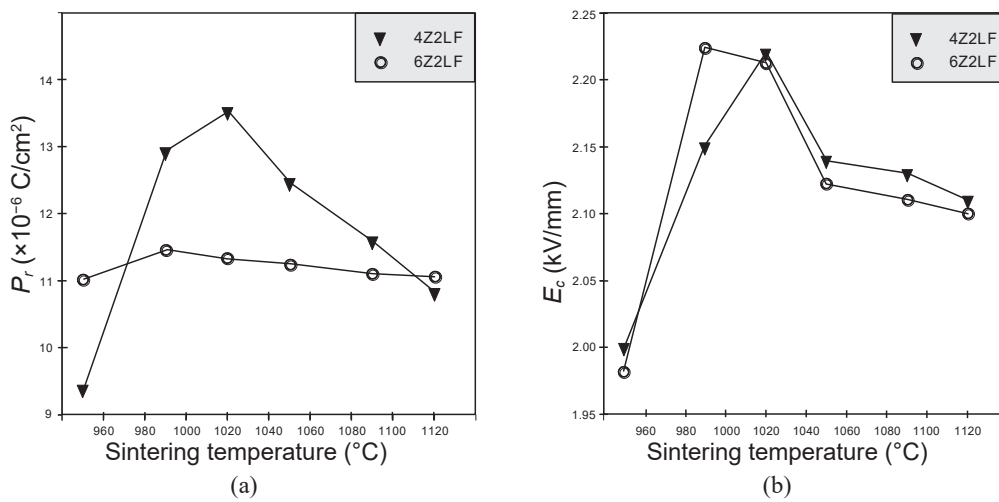


Fig. 5. (a) Remanent polarizations and (b) coercive fields of LNKNT- $x$ Z $y$ LF ceramics.

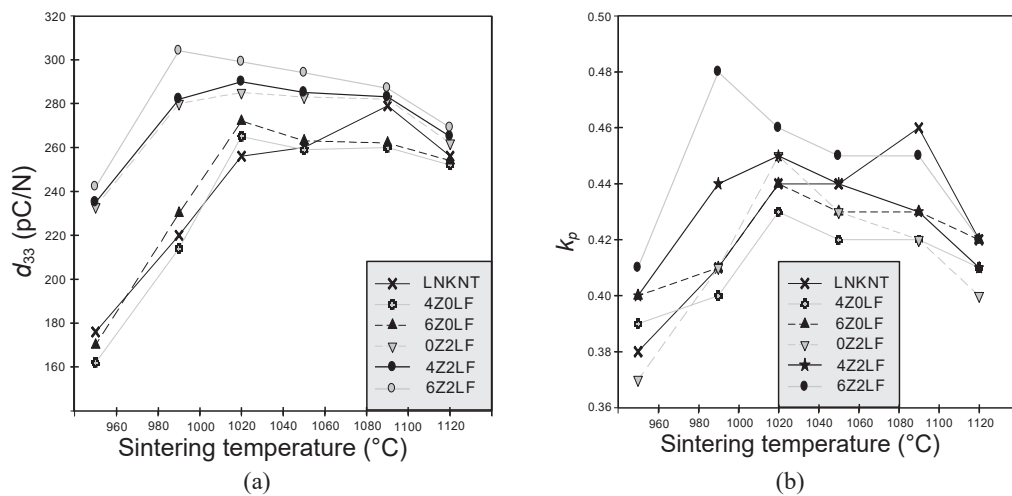


Fig. 6. (a) Piezoelectric constants and (b) electromechanical coupling factors of LNKNT- $x$ Z $y$ LF ceramics.



the piezoelectric characteristics ( $d_{33}$  values) can be improved from 279 to 304 pC/N. Furthermore, for the electromechanical coupling factors ( $k_p$ ) of the LNKNT- $x$ Z $y$ LF ceramics shown in Fig. 6(b), as the sintering temperature increased from 950 to 1090 °C, all the  $k_p$  values reveal a trend similar to the  $d_{33}$  values. Moreover, except for the pure LNKNT specimens (obtained at 1090 °C) and LNKNT-6Z2LF specimens (obtained at 990 °C), all the maximum  $k_p$  values are obtained at 1020 °C. For the pure LNKNT specimens sintered at 1090 °C, the maximum  $k_p$  value is 0.46. However, for LNKNT-6Z2LF specimens sintered at 990 °C, the maximum  $k_p$  value is 0.48.

Previously, Safari and Akdogan<sup>(13)</sup> illustrated the relationship among  $P_r$ ,  $d_{33}$ , and  $\varepsilon_r$  values as

$$d_{33} = 2K\varepsilon_0\varepsilon_r P_r, \quad (1)$$

where  $K$  is a constant between 0.05 and 0.1 m<sup>4</sup>/C<sup>2</sup> for different materials,  $\varepsilon_r$  is the relative permittivity, and  $\varepsilon_0$  is the permittivity of vacuum. Therefore, in Fig. 7, as we choose  $K$  as 0.085 m<sup>4</sup>/C<sup>2</sup> for the LNKNT-6Z2LF ceramic, we reveal a comparison of its measured  $d_{33}$  values, theoretical  $d_{33}$  values [calculated from Eq. (1)], and measured  $P_r$  values. It is clearly found that, as the sintering temperature increased from 950 to 990 °C, these three values (measured  $d_{33}$ , theoretical  $d_{33}$ , and measured  $P_r$ ) reveal the same variation tendency (increase to a maximum and then decrease gradually), which also confirms the relationship between the  $d_{33}$  values and the  $P_r$  values in Eq. (1).

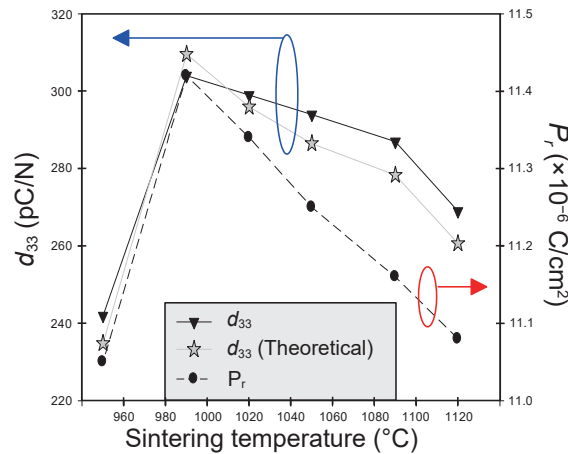


Fig. 7. (Color online) Comparison of measured  $d_{33}$  values, theoretical  $d_{33}$  values, and measured  $P_r$  values of LNKNT-6Z2LF ceramics.

Table 1  
Optimal characteristics of LKNNT- $x$ Z $y$ LF ceramics.

	$d_{33}$ (pC/N)	$k_p$	$\tan\delta$	$\varepsilon_r$	Density (g/cm <sup>3</sup> )	Sintering temperature (°C)
LNKNT	279	0.46	0.019	1203	4.421	1090
LNKNT-0Z2LF	285	0.45	0.016	1561	4.334	1020
LNKNT-4Z0LF	265	0.43	0.022	1263	4.467	1020
LNKNT-6Z0LF	272	0.44	0.021	1349	4.448	1020
LNKNT-4Z2LF	290	0.45	0.020	1721	4.422	1020
LNKNT-6Z2LF	304	0.48	0.020	1801	4.453	990

#### 4. Conclusions

The influences of ZnO and LiF codoped on the phase structure and the dielectric and piezoelectric properties of LNKNT ceramics were investigated. As concluded in Table 1, the optimal sintering temperature was improved from 1090 (pure LNKNT) to 990 °C (LNKNT-6Z2LF) owing to the codoping of ZnO and LiF sintering promoters. Even though the sintering temperature was only 990 °C, the optimal  $d_{33}$  values were improved from 279 pC/N (pure LNKNT) to 304 pC/N (LNKNT-6Z2LF), and  $k_p$  was improved from 0.46 (LNKNT) to 0.48 (LNKNT-6Z2LF). Finally, ZnO and LiF are suitable as sintering promoters of KNN-based piezoelectric ceramics for future applications.

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