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Structural and Electric Properties of MnO$_2$-Doped KNN-LT Lead-Free Piezoelectric Ceramics

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Abstract: Structural, ferroelectric, dielectric, and piezoelectric properties of K$_{0.5}$Na$_{0.5}$NbO$_3$-LiTaO$_3$-$x$mol%MnO$_2$ lead-free piezoelectric ceramics with $0.0 \leq x \leq 0.3$ were studied. The ceramic samples were synthesized through the conventional solid-state reaction method. The MnO$_2$ addition can reduce the sintering temperature of KNLNT ceramics. Compared with undoped KNLNT ceramic, the piezoelectric measurements showed that piezoelectric properties of K$_{0.5}$Na$_{0.5}$NbO$_3$-LiTaO$_3$-$x$MnO$_2$ were improved ($d_{33} = 251 \text{ pC/N}$) when $x = 0.1$. In addition, KNLNT-$x$MnO$_2$ ceramics have larger $P_r$ ($20.59~21.97 \mu \text{C/cm}^2$) and smaller $E_c$ ($10.77~6.95 \text{ kV/cm}$), which indicates MnO$_2$ has excellent softening property, which improves the ferroelectric properties of KNLNT ceramics. This work adds relevant information regarding potassium sodium niobate K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN) when doped Li, Ta, Mn at the B-site.

Keywords: KNLNT ceramics; MnO$_2$ doped; ferroelectricity; piezoelectricity

1. Introduction

Potassium sodium niobate K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN) has been investigated as a candidate lead-free piezoelectric material owing to its high Curie temperature ($T_c \sim 420 \degree C$), good ferroelectric and piezoelectric properties ($d_{33} \sim 80 \text{ pC/N}$), and high radial coupling coefficient ($k_r \sim 48\%$) [1]. In recent years, KNN based piezoelectric ceramics are studied in different compositions to improve electric properties [2,3]. It was reported that the piezoelectric properties are improved when the Li$^+$ content is increased from 4 mol% to 20 mol%, but it is also shown that an additional phase (K$_3$L$_2$Nb$_3$O$_{15}$) begins to form when the content of Li$^+$ exceeds 8 mol% [4]. It was systematically investigated that the phase structure, microstructure, and piezoelectric properties of B-site non-stoichiometric (K$_{0.5}$Na$_{0.5}$)(Nb$_{0.9}$Ta$_{0.1}$)$_{1+x}$O$_3$ ceramics, and 0.5 mol% (NT)$_{5+}$ excess in KN(NT)$_{1+x}$ ceramics sintered at 1120 °C showed the optimum electric performances: $d_{33} = 167 \text{ pC/N}$, $k_p = 0.41$, and $\tan \delta = 3.2\%$ [5]. A research shows that the electromechanical quality factor and phase transition temperature can be reduced by adding Ta$^{5+}$ into KNN [6]. The grain size of KNN ceramics decreases due to the high temperatures required for the sintering [7]. However, there is a need to improve the electric properties of KNN ceramics for the use in device fabrication to replace Lead Zirconium Titanate (PZT) ceramics.
A significant improvement in the piezoelectric properties was achieved by Li and Ta modification for KNN ceramics in Qin’s study, where the KNN-Li\(_x\) ceramic with \(x = 0.035\) shows the highest piezoelectric properties, with \(d_{33}\) and \(k_p\) being on the order of 260 pC/N and 48%, respectively, which is due to the fact that the orthorhombic-tetragonal polymorphic phase transition temperature of KNNT-Li\(_{0.035}\) is around the room temperature [8]. However, the improvement of piezoelectric properties by Li\(^+\) and Ta\(^{5+}\) doping is far from enough for the use in device fabrication to replace PZT ceramics. KNN ceramics exhibit low density and high defect concentration, which is caused by the volatility of KNN. Although the conductivity is enhanced, the ferroelectric behavior is adversely affected [9,10]. Actually, in undoped KNN ceramics and KNN doped with Li and Ta, values for remnant polarization is affected by the leakage current [11,12]. Generally speaking, when the leakage current in the material is relatively small, the piezoelectric performance will be better, while the larger leakage current will have a great adverse effect on the polarization process, which is not suitable for industrial application [13]. Lead-based ceramics are usually doped with manganese to improve mechanical quality factor (\(Q_m\)) and reduce dielectric losses (\(tan \delta\)) [14–16]. Moreover, Mn plays an indispensable role in lead-free materials such as BaTiO\(_3\), SrTiO\(_3\), KNbO\(_3\) and KTaO\(_3\), which can increase the density, dielectric loss, and electromechanical properties of ceramics [17–21]. It is reported that the dopant Mn can reduce the leakage current in KNN based ceramics. What’s more, the phase transition temperature from orthorhombic to tetragonal (T\(_O\)-T\(_T\)) and the Curie temperature can be slightly influenced with Mn doped in KNN ceramics [22,23]. A lot of studies have reported KNN based systems, but there are few reports on the effect of Mn, Li, and Ta co-doping on the structure and electrical properties of KNN based ceramics.

In this paper, MnO\(_2\) was used as the dopant to modify KNLNT ceramics, which was synthesized by the conventional solid-state reaction. The effects of the concentration of Mn doped at the B-site on piezoelectric properties, ferroelectric properties and dielectric properties of KNLNT-xMnO\(_2\) ceramics were investigated. Moreover, the impact of phase structure on piezoelectric properties is discussed in detail.

### 2. Materials and Methods

Lead-free K\(_{0.5}\)Na\(_{0.5}\)NbO\(_3\)-LiTaO\(_3\)-xMnO\(_2\) (\(x = 0.0, 0.1, 0.2, 0.3\)) ceramics were synthesized by the conventional solid-state reaction. The effects of the concentration of Mn doped at the B-site on piezoelectric properties, ferroelectric properties and dielectric properties of KNLNT-xMnO\(_2\) ceramics were investigated. Moreover, the impact of phase structure on piezoelectric properties is discussed in detail.

**Table 1.** Sintering temperature of KNLNT-xMnO\(_2\) (\(x = 0.0, 0.1, 0.2, 0.3\)) ceramics.

<table>
<thead>
<tr>
<th>(x%) MnO(_2)</th>
<th>0.0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintering temperature (°C)</td>
<td>1178</td>
<td>1126</td>
<td>1128</td>
<td>1132</td>
</tr>
</tbody>
</table>
Therefore, the obtained undoped KNLNT powder was uniaxially pressed into disks and sintered for 5 h, at 1178 °C. The obtained KNLNT-0.1MnO₂ powder was uniaxially pressed into disks and sintered for 5 h at 1126 °C. The obtained KNLNT-0.2MnO₂ powder was uniaxially pressed into disks and sintered for 5 h at 1128 °C. The obtained KNLNT-0.3MnO₂ powder was uniaxially pressed into disks and sintered for 5 h at 1132 °C. Then, the surfaces of polished ceramics were uniformly coated with silver paste by a homogenizer and burned at 550 °C for 40 min. Finally, the ceramic samples can be tested after polarization in silicone oil and the polarization voltage is 5 kV.

The crystal structure of the materials was studied by X-ray diffraction (XRD) with CuKα as a radiation source (λ = 1.5418Å). The P-E hysteresis loops was measured by ferroelectric tester precision (premier II, Radiant Tech, Albuquerque, New Mexico, USA) The dielectric properties were obtained using LCR test instrument (Agilent, E4980A, Santa Clara, CA, USA). Variation of relative permittivity εᵣ, and dielectric loss tan δ, with temperature was determined. We used a quasi-static Berlincourt Meter to measure piezoelectric constant d₃₃. On the basis of IEEE standards, the electromechanical coupling coefficients were determined by using an impedance analyzer (HP4294A) at room temperature. The electromechanical coupling factor in planar (k_p) mode and piezoelectric constant (d₃₃) were calculated by the following formula [24]:

\[
\frac{1}{k_p^2} = 0.395 \times \frac{f_r}{f_a - f_r} + 0.574
\]

where f_r is the resonant frequency; f_a is the anti-resonant frequency. The intrinsic piezoelectric and dielectric responses are related through the following equation [25]:

\[
d_{33} = 2\varepsilon_r\varepsilon_0 Q_{11} P_r
\]

where ε_r is dielectric constant, ε₀ is vacuum dielectric constant, Q₁₁ is Electrostriction coefficient, Pᵣ is remnant polarization.

3. Results and Discussion

X-ray diagrams of sintered KNLNT-xMn (x = 0.0, 0.1, 0.2, 0.3) samples are shown in Figure 1. Figure 1a shows that all samples show pure perovskite phases and there are no obvious traces of impurities. For further analysis on the phase structure of samples, as shown in Figure 1b, we amplify (200) and (002) diffraction peaks. Figure 1b clearly depicts that the ratio of the two peaks of KNLNT sample slightly greater than 1, while the ratio of the two peaks is about 2:1 when x = 0.1, 0.2, 0.3, which indicates that the doped ceramics are randomly oriented and have orthorhombic symmetry at room temperature.

In addition, the two diffraction peaks of MnO₂-doped KNLNT ceramics undergo a slight shift toward higher angles, which suggests that the lattice parameters decrease. The lattice parameters and volume of the unit cell are calculated from the XRD patterns after refinement by jade 6.5 software (XRD Pattern Processing & Identification) and are presented in Table 2. This shift could be attributed to the replacement of the B-site Nb⁵⁺ [Coordination Number (CN) = 6] by a manganese ion of a different valence. In this process, it is worth reminding that the ionic radius of Nb⁵⁺ (r = 0.78Å) is larger than those both the Mn³⁺ (r = 0.72Å) and Mn⁴⁺ (r = 0.67Å) ions, but slightly smaller than the radius of Mn²⁺ (r = 0.81Å) [26].

Figure 2 displays the SEM of KNLNT-xMn (x = 0.0, 0.1, 0.2, 0.3) ceramics. The results show that the best sintering temperature of KNLNT is 1178 °C, while that of MnO₂ doped samples is 1126 °C, 1128 °C, 1132 °C, respectively. It can be seen from the Figure 2 that the addition of Mn to KNLNT ceramics slightly improves the density of undoped ceramics. With the increase of x, the crystalline grains gradually decrease, and the surface is smoother and close to the liquid phase. Due to the doping of MnO₂, it reduces the sintering temperature of the ceramics, which is lower than actual firing temperature. Finally, it results in the formation of the liquid phase in the sintering process. In KNN
based ceramics, the appearance of the liquid phase in the sintering process will promote the abnormal growth of the crystalline grains, resulting in the uneven distribution of the crystalline grains.

Figure 1. XRD pattern of KNLNT-xMn (x = 0.0, 0.1, 0.2, 0.3) ceramics: (a) 20–60°, (b) 44–47°.

Table 2. Lattice parameters and unit cell volume of KNLNT-xMnO₂ (x = 0.0, 0.1, 0.2, 0.3) ceramics.

<table>
<thead>
<tr>
<th>x mol% MnO₂</th>
<th>0.0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>3.9998</td>
<td>3.9961</td>
<td>3.9943</td>
<td>3.9925</td>
</tr>
<tr>
<td>b (Å)</td>
<td>3.9785</td>
<td>3.9765</td>
<td>3.9735</td>
<td>3.9713</td>
</tr>
<tr>
<td>c (Å)</td>
<td>3.9929</td>
<td>3.9885</td>
<td>3.9814</td>
<td>3.9721</td>
</tr>
<tr>
<td>Vol (Å³)</td>
<td>63.54</td>
<td>63.38</td>
<td>63.19</td>
<td>62.98</td>
</tr>
</tbody>
</table>

Figure 2. SEM of KNLNT-xMn (a) x = 0.0, (b) x = 0.1, (c) x = 0.2, (d) x = 0.3 ceramics sintered at 1178 °C, 1126 °C, 1128 °C and 1132 °C, respectively.
To investigate ferroelectric properties of undoped and MnO2-doped samples, polarization versus electrical field (P-E) hysteresis loops, measured at room temperature and at the frequency of 0.3 Hz, which is presented in Figure 3, for undoped and Mn-doped KNLNT ceramics. From the curves, undoped KNLNT ceramic exhibits a leaky P-E loop with \( P_r \) of 13.66 \( \mu \)C/cm\(^2\) and \( E_c \) of 13.67 kV/cm. Compared with undoped sample, with the increase in MnO\(_2\) concentration (\( x = 0.1, 0.2, 0.3 \)), the remnant polarization \( P_r \) of ceramics increase with the variation range of 20.59–21.97 \( \mu \)C/cm\(^2\), and the coercive field \( E_c \) gradually decrease with the variation range of 10.77–6.95 kV/cm. Compared with KNLNT ceramic, with the increase of Mn content, the hysteresis loop becomes asymmetrical about the zero electric field point and KNLNT-xMn (\( x = 0.1, 0.2, 0.3 \)) ceramics have larger \( P_r \) and smaller \( E_c \), which indicates that MnO\(_2\) has excellent softening property, which improves the ferroelectric properties of KNLNT ceramics. For undoped KNLNT ceramic, the P-E loop has a typical saturated ferroelectric shape. However, with the increase of Mn content, the area surrounded by P-E loop begins to shrink and the shape of P-E loop becomes more and more ‘slim’.

![Figure 3. P-E loops and J-E curves of KNLNT-xMn ceramics: (a) \( x = 0.0 \), (b) \( x = 0.1 \), (c) \( x = 0.2 \), (d) \( x = 0.3 \).](image)

In order to better study the reason of ‘shrinking’ P-E loops, the J-E curves of KNLNT-xMnO\(_2\) ceramics are calculated as well. Figure 3 shows that the peaks of all J-E curves appear in the similar position of \( E_c \), which means that a larger reverse depolarization current is generated. What’s more, with MnO\(_2\) concentration increasing, the value of \( E_c \) gradually decreases and the reverse depolarization current tends to be larger and larger. The addition of MnO\(_2\) reduces the stability of the domain, and the peak gradually moves towards the direction of zero electric field, resulting in the decrease of \( E_c \) and the formation of ‘shrinking’ P-E loop.

Temperature dependence of dielectric constant \( \varepsilon_{xx} \) and dielectric loss \( \tan \delta \), measured at the frequency of 1 kHz for poled KNLNT-xMn (\( x = 0.0, 0.1, 0.2, 0.3 \)) ceramics at the temperature range 50–450 °C are presented in Figure 4. As can be seen, there is only one abnormal dielectric peak across the curve from 50 °C to 450 °C, which corresponds to the Curie temperature \( T_C \) (333 °C) for undoped ceramic. The orthorhombic-tetragonal transition temperature \( T_{O-T} \), is lowered to near room temperature due to the doping of Li\(^+\) and Ta\(^{5+}\). However, with the increase in MnO\(_2\) concentration, the second
dielectric peak appears in the range of 55~110 °C, which corresponds to the orthorhombic-tetragonal transition temperature \( T_{O-T} \). Moreover, the Curie temperature \( T_C \), of MnO\(_2\)-doped ceramics is in the range of 330~350 °C. Compared with KNLNT ceramic, the orthorhombic-tetragonal transition temperature \( T_{O-T} \) of KNLNT-xMn \( (x = 0.1, 0.2, 0.3) \) has been greatly improved, while the Curie temperature is basically unchanged, which is due to the doping of MnO\(_2\). It is observed that dielectric constant \( \varepsilon_r \), and dielectric loss \( \tan \delta \), of samples with low MnO\(_2\) concentration \( (x = 0.1, 0.2, 0.3) \) are basically unchanged when \( T_{O-T} < T < 280 \) °C, and the ferroelectric domain structure formed in the ceramics is stable, and \( \varepsilon_r \) increases with temperature. The addition of MnO\(_2\) increases the orthorhombic-tetragonal transition temperature and has little effect on the Curie temperature.

![Figure 4. Temperature dependence of (a) dielectric constant \( \varepsilon_r \), and (b) dielectric loss \( \tan \delta \), measured at a frequency of 1 kHz for poled KNLNT-xMn \( (x = 0.0, 0.1, 0.2, 0.3) \) ceramics.](image)

Piezoelectric constant \( d_{33} \), planar electromechanical coupling factor \( k_p \), relative permittivity \( \varepsilon_r \), and remnant polarization \( P_r \) for KNLNT ceramics at different MnO\(_2\) concentration are presented in Table 3. It is observed that the value of \( P_r \) increases from 13.66 μC/cm\(^2\) to 21.97 μC/cm\(^2\) with the MnO\(_2\) concentration increasing. Equation (2) gives the relationship between piezoelectric response and dielectric response. MnO\(_2\)-doped ceramics has an increased remnant polarization compared with KNLNT ceramics. Throughout all the samples, the dielectric constant near room temperature varied only by about 20%. The values of electrostriction coefficient \( Q_{11} \), calculated by Equation (2) are also listed in Table 1. It can be observed that the value of \( Q_{11} \) decreases with \( x \) increases. Therefore, the increase in \( P_r \) results in the increased \( d_{33} \) value of 0.1 mol% Mn-doped composition. This increased remnant polarization also confirms the enlarged reverse depolarization current by Mn.

<table>
<thead>
<tr>
<th>xmol% MnO(_2)</th>
<th>( d_{33} ) (pC/N)</th>
<th>( k_p ) (%)</th>
<th>( \varepsilon_r ) (1kHz)</th>
<th>( P_r ) (μC/cm(^2))</th>
<th>( Q_{11} ) (10(^6))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>165</td>
<td>36.3</td>
<td>74.95</td>
<td>13.66</td>
<td>9.65</td>
</tr>
<tr>
<td>0.1</td>
<td>251</td>
<td>29.5</td>
<td>839.7</td>
<td>20.59</td>
<td>0.87</td>
</tr>
<tr>
<td>0.2</td>
<td>170</td>
<td>35.6</td>
<td>1302</td>
<td>21.85</td>
<td>0.36</td>
</tr>
<tr>
<td>0.3</td>
<td>197</td>
<td>29.4</td>
<td>1214</td>
<td>21.97</td>
<td>0.44</td>
</tr>
</tbody>
</table>

4. Conclusions

In summary, KNLNT-xMn \( (x = 0.0, 0.1, 0.2, 0.3) \) ceramics were prepared by traditional solid-state reaction method. The effect of MnO\(_2\)-doping on KNLNT ceramic was assessed in this work. The addition of MnO\(_2\) can slightly improve the density of KNLNT ceramic and obviously reduced the sintering temperature of KNLNT ceramic. With MnO\(_2\) content increasing, the ceramics have larger \( P_r \).
and smaller $E_c$, which indicates that MnO$_2$ has excellent softening property. It reduces the stability of domains and enlarges the reverse depolarization current, and increases the orthorhombic-tetragonal transition temperature of KNLNT for the doped MnO$_2$. KNLNT-0.1Mn ceramic presents an improved room temperature hysteretic response and piezoelectric properties ($d_{33} = 251$ pC/N) when compared with samples with higher doping concentration of Mn.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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