Article

Structural and Electric Properties of MnO₂-Doped KNN-LT Lead-Free Piezoelectric Ceramics

Yunfeng Deng ¹, Junjun Wang ^{1,2,*} , Chunxiao Zhang ¹, Hui Ma ¹, Chungeng Bai ¹, Danqing Liu ³, Fengmin Wu ^{1,2,*} and Bin Yang ⁴

¹ Department of Physics, School of Science, Harbin University of Science and Technology, Harbin 150080, China; dyf61859@163.com (Y.D.); zhangchunxiao0711@163.com (C.Z.); 18845155892@163.com (H.M.); chungengbai@163.com (C.B.)

² Heilongjiang Provincial Key Laboratory of Quantum Manipulation & Control, Harbin University of Science and Technology, Harbin 150080, China

³ School of Chemical and Environmental Engineering, Harbin University of Science and Technology, Harbin 150080, China; danqingliu76@163.com

⁴ Condensed Matter Science and Technology Institute, The School of Instrumentation Science and Engineering, Harbin Institute of Technology, Harbin 150080, China; binyang@hit.edu.cn

* Correspondence: wangjunjun8689@hrbust.edu.cn (J.W.); fmwu@hrbust.edu.cn (F.W.)

Received: 30 June 2020; Accepted: 12 August 2020; Published: 15 August 2020

Abstract: Structural, ferroelectric, dielectric, and piezoelectric properties of K_{0.5}Na_{0.5}NbO₃-LiTaO₃-xmol%MnO₂ lead-free piezoelectric ceramics with 0.0 ≤ x ≤ 0.3 were studied. The ceramic samples were synthesized through the conventional solid-state reaction method. The MnO₂ 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}NbO₃-LiTaO₃-xMnO₂ were improved ($d_{33} = 251$ pC/N) when x = 0.1. In addition, KNLNT-xMnO₂ ceramics have larger P_r (20.59~21.97 μC/cm²) and smaller E_c (10.77~6.95 kV/cm), which indicates MnO₂ has excellent softening property, which improves the ferroelectric properties of KNLNT ceramics. This work adds relevant information regarding of potassium sodium niobate K_{0.5}Na_{0.5}NbO₃ (KNN) when doped Li, Ta, Mn at the B-site.

Keywords: KNLNT ceramics; MnO₂ doped; ferroelectricity; piezoelectricity

1. Introduction

Potassium sodium niobate K_{0.5}Na_{0.5}NbO₃ (KNN) has been investigated as a candidate lead-free piezoelectric material owing to its high Curie temperature ($T_c \sim 420$ °C), good ferroelectric and piezoelectric properties ($d_{33} \sim 80$ 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 (K₃Li₂Nb₅O₁₅) 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}O₃ ceramics, and 0.5 mol% (NT)⁵⁺ excess in KN(NT)_{1+x} ceramics sintered at 1120 °C showed the optimum electric performances: $d_{33} = 167$ 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 Ta⁵⁺ 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 Ta⁵⁺ 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 BaTiO₃, SrTiO₃, KNbO₃ and KTaO₃, 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}) 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, MnO₂ 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- x MnO₂ 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}NbO₃-LiTaO₃- x MnO₂ ($x = 0.0, 0.1, 0.2, 0.3$) ceramics were synthesized by the conventional solid-state reaction. For the synthesis, Na₂CO₃ (99.50%), K₂CO₃ (99.00%), Nb₂O₅ (99.90%), Li₂CO₃ (99.99%), Ta₂O₅ (99.50%), and MnO₂ (99.00%) were prepared as raw materials (The supplier of all the raw materials is Aladdin in Shanghai, China). Firstly, according to the stoichiometric formula, the raw materials were weighed, and then the absolute alcohol was added into the raw materials and the mixture was ball-milled for 12 h. Secondly, the mixture was calcined at 900 °C for 4 h after drying. The calcined powder was mixed with MnO₂ of different concentrations ($x = 0.0, 0.1, 0.2, 0.3$ mol%) (abbreviated as KNLNT- x Mn). Sintering temperatures of KNLNT- x MnO₂ ($x = 0.0, 0.1, 0.2, 0.3$) ceramics is listed in Table 1. For KNLNT component ceramic, we sintered six KNLNT ceramic pieces at 1174 °C, 1176 °C, 1178 °C, 1180 °C, 1182 °C, and 1184 °C, respectively, and we found that the optimum sintering temperature for KNLNT component ceramics was 1178 °C. For Mn-doped KNLNT ceramics, each Mn-doped component was sintered at 1126 °C, 1128 °C, 1130 °C, and 1132 °C, respectively. Through research on the ceramic properties at different temperatures, we found that the optimum sintering temperatures of Mn-doped component were 1126 °C ($x = 0.1$), 1128 °C ($x = 0.2$), 1132 °C ($x = 0.3$), respectively.

Table 1. Sintering temperature of KNLNT- x MnO₂ ($x = 0.0, 0.1, 0.2, 0.3$) ceramics.

x mol% MnO ₂	0.0	0.1	0.2	0.3
Sintering temperature (°C)	1178	1126	1128	1132

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 CuK α as a radiation source ($\lambda = 1.5418\text{\AA}$). 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 ϵ_r , and dielectric loss $\tan \delta$, with temperature was determined. We used a quasi-static Berlincourt Meter to measure piezoelectric constant d_{33} . 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 (d_{33}) were calculated by the following formula [24]:

$$\frac{1}{k_p^2} = 0.395 \times \frac{f_r}{f_a - f_r} + 0.574 \quad (1)$$

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]:

$$d_{33} = 2\epsilon_r\epsilon_0Q_{11}P_r \quad (2)$$

where ϵ_r is dielectric constant, ϵ_0 is vacuum dielectric constant, Q_{11} is Electrostriction coefficient, P_r is remnant polarization.

3. Results and Discussion

X-ray diagrams of sintered KNLNT-*x*Mn ($x = 0.0, 0.1, 0.2, 0.3$) 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⁺ ($r = 0.78\text{\AA}$) is larger than those both the Mn³⁺ ($r = 0.72\text{\AA}$) and Mn⁴⁺ ($r = 0.67\text{\AA}$) ions, but slightly smaller than the radius of Mn²⁺ ($r = 0.81\text{\AA}$) [26].

Figure 2 displays the SEM of KNLNT-*x*Mn ($x = 0.0, 0.1, 0.2, 0.3$) 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- x Mn ($x = 0.0, 0.1, 0.2, 0.3$) ceramics: (a) 20–60°, (b) 44–47°.

Table 2. Lattice parameters and unit cell volume of KNLNT- x MnO₂ ($x = 0.0, 0.1, 0.2, 0.3$) ceramics.

x mol% MnO ₂	0.0	0.1	0.2	0.3
a (Å)	3.9998	3.9961	3.9943	3.9925
b (Å)	3.9785	3.9765	3.9735	3.9713
c (Å)	3.9929	3.9885	3.9814	3.9721
Vol (Å ³)	63.54	63.38	63.19	62.98

Figure 2. SEM of KNLNT- x Mn (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 $\mu\text{C}/\text{cm}^2$ and E_c of 13.67 kV/cm. Compared with undoped sample, with the increase in MnO₂ 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 $\mu\text{C}/\text{cm}^2$, 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- x Mn ($x = 0.1, 0.2, 0.3$) ceramics have larger P_r and smaller E_c , which indicates that MnO₂ 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- x MnO₂ ceramics: (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$.

In order to better study the reason of 'shrinking' P - E loops, the J - E curves of KNLNT- x MnO₂ 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 MnO₂ concentration increasing, the value of E_c gradually decreases and the reverse depolarization current tends to be larger and larger. The addition of MnO₂ 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 ϵ_r , and dielectric loss $\tan \delta$, measured at the frequency of 1 kHz for poled KNLNT- x Mn ($x = 0.0, 0.1, 0.2, 0.3$) ceramics at the temperature range 50~450 $^{\circ}\text{C}$ are presented in Figure 4. As can be seen, there is only one abnormal dielectric peak across the curve from 50 $^{\circ}\text{C}$ to 450 $^{\circ}\text{C}$, which corresponds to the Curie temperature T_C (333 $^{\circ}\text{C}$) for undoped ceramic. The orthorhombic-tetragonal transition temperature T_{O-T} , is lowered to near room temperature due to the doping of Li⁺ and Ta⁵⁺. However, with the increase in MnO₂ 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- $x\text{Mn}$ ($x = 0.1, 0.2, 0.3$) 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 ϵ_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 ϵ_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 ϵ_r , and (b) dielectric loss $\tan \delta$, measured at a frequency of 1 kHz for poled KNLNT- $x\text{Mn}$ ($x = 0.0, 0.1, 0.2, 0.3$) ceramics.

Piezoelectric constant d_{33} , planar electromechanical coupling factor k_p , relative permittivity ϵ_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 $\mu\text{C}/\text{cm}^2$ to 21.97 $\mu\text{C}/\text{cm}^2$ 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 3. Piezoelectric constant d_{33} , planar electromechanical coupling factor k_p , dielectric constant ϵ_r , remnant polarization P_r and electrostriction coefficient Q_{11} for KNLNT ceramics at different MnO_2 concentration.

$x\text{mol}\% \text{MnO}_2$	d_{33} (pC/N)	k_p (%)	ϵ_r (1kHz)	P_r ($\mu\text{C}/\text{cm}^2$)	Q_{11} (10^9)
0.0	165	36.3	74.95	13.66	9.65
0.1	251	29.5	839.7	20.59	0.87
0.2	170	35.6	1302	21.85	0.36
0.3	197	29.4	1214	21.97	0.44

4. Conclusions

In summary, KNLNT- $x\text{Mn}$ ($x = 0.0, 0.1, 0.2, 0.3$) ceramics were prepared by traditional solid-state reaction method. The effect of MnO_2 -doping on KNLNT ceramics 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.

Author Contributions: Data curation, Y.D., J.W. and C.Z.; Formal analysis, Y.D. and D.L.; Investigation, J.W., C.Z., H.M. and C.B.; Writing—original draft, J.W.; Writing—review & editing, F.W. and B.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Natural Science Foundation of Heilongjiang Province under Grant No. E2018049 and the National Natural Science Foundation of China under Grant No. 51402075.

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

References

1. Jaeger, R.E.; Egerton, L. Hot Pressing of Potassium-Sodium Niobates. *J. Am. Ceram. Soc.* **1962**, *45*, 209–213. [\[CrossRef\]](#)
2. Guo, Y.; Kakimoto, K.; Ohsato, H. Structure and Electrical Properties of Lead-Free $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ - BaTiO_3 Ceramics. *Jpn. J. Appl. Phys.* **2004**, *43*, 6662–6666. [\[CrossRef\]](#)
3. Choi, C.H.; Ahn, C.W.; Nahm, S.; Hong, J.O.; Lee, J.S. $(1-x)\text{BaTiO}_3$ - $x(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ ceramics for multilayer ceramic capacitors. *Appl. Phys. Lett.* **2007**, *90*, 132905. [\[CrossRef\]](#)
4. Guo, Y.; Kakimoto, K.I.; Ohsato, H. Phase transitional behavior and piezoelectric properties of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ - LiNbO_3 ceramics. *Appl. Phys. Lett.* **2004**, *85*, 4121–4123. [\[CrossRef\]](#)
5. Du, J.; Zheng, L.; Xu, Z. Properties of B-site non-stoichiometric $(\text{K}_{0.5}\text{Na}_{0.5})(\text{Nb}_{0.9}\text{Ta}_{0.1})_{1+x}\text{O}_3$ lead-free piezoelectric ceramics. *J. Mater. Sci. Mater. Electron.* **2013**, *25*, 1085–1088. [\[CrossRef\]](#)
6. Mgbemere, H.E.; Schneider, G.A.; Stegk, T.A. Effect of Antimony Substitution for Niobium on the Crystal Structure, Piezoelectric and Dielectric Properties of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ Ceramics. *Funct. Mater. Lett.* **2010**, *3*, 25–30. [\[CrossRef\]](#)
7. Zuo, R.; Fu, J.; Su, S.; Fang, X.; Cao, J.L. Electrical Properties of Manganese Modified Sodium Potassium Lithium Niobate Lead-free Piezoelectric Ceramics. *J. Mater. Sci. Mater. Electron.* **2009**, *20*, 212–216. [\[CrossRef\]](#)
8. Qin, Y.; Zhang, J.; Tan, Y.; Yao, W.; Wang, C.; Zhang, S. Domain configuration and piezoelectric properties of $(\text{K}_{0.50}\text{Na}_{0.50})_{1-x}\text{Li}_x(\text{Nb}_{0.80}\text{Ta}_{0.20})\text{O}_3$ ceramics. *J. Eur. Ceram. Soc.* **2014**, *34*, 4177–4184. [\[CrossRef\]](#)
9. Irle, E.; Blachnik, R.; Gather, B. The phase diagrams of Na_2O and K_2O with Nb_2O_5 and the ternary system Nb_2O_5 - Na_2O - Yb_2O_3 . *Thermochim. Acta* **1991**, 157–169. [\[CrossRef\]](#)
10. Rubiomarcos, F.; Ochoa, P.; Fernandez, J.F. Sintering and properties of lead-free $(\text{K},\text{Na},\text{Li})(\text{Nb},\text{Ta},\text{Sb})\text{O}_3$ ceramics. *J. Eur. Ceram. Soc.* **2007**, *27*, 4125–4129. [\[CrossRef\]](#)
11. Mgbemere, H.E.; Hinterstein, M.; Schneider, G.A. Electrical and structural characterization of $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$ ceramics modified with Li and Ta. *J. Appl. Crystallogr.* **2011**, *44*, 1080–1089. [\[CrossRef\]](#)
12. Mgbemere, H.E.; Hinterstein, M.; Schneider, G.A. Structural phase transitions and electrical properties of $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$ -based ceramics modified with Mn. *J. Eur. Ceram. Soc.* **2012**, *32*, 4341–4352. [\[CrossRef\]](#)
13. Rafiq, M.A.; Tkach, A.; Costa, E.; Vilarinho, P.M. Defects and charge transport in Mn-doped $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ceramics. *Phys. Chem. Chem. Phys.* **2015**, *17*, 24403–24411. [\[CrossRef\]](#) [\[PubMed\]](#)
14. He, L.X.; Li, C.E. Effects of addition of MnO on piezoelectric properties of lead zirconate titanate. *J. Mater. Sci.* **2000**, *35*, 2477–2480. [\[CrossRef\]](#)
15. Galassi, C.; Roncari, E.; Capiani, C.; Craciun, F. Processing and characterization of high Qm ferroelectric ceramics. *J. Eur. Ceram. Soc.* **1999**, *19*, 1237–1241. [\[CrossRef\]](#)
16. Yu, C.S.; Hsieh, H.L. Piezoelectric properties of $\text{Pb}(\text{Ni}_{1/3}\text{Sb}_{2/3})\text{O}_3$ - PbTiO_3 - PbZrO_3 ceramics modified with MnO_2 additive. *J. Eur. Ceram. Soc.* **2005**, *25*, 2425–2427. [\[CrossRef\]](#)
17. Wang, X.; Gu, M.; Yang, B. Hall effect and dielectric properties of Mn-doped barium titanate. *Microelectron. Eng.* **2003**, *66*, 855–859. [\[CrossRef\]](#)
18. Tkach, A.; Vilarinho, P.M.; Kholkin, A.L. Structure–microstructure–dielectric tunability relationship in Mn-doped strontium titanate ceramics. *Acta. Mater.* **2005**, *53*, 5061–5069. [\[CrossRef\]](#)

19. Feng, Z.; Ren, X. Aging Effect and Large Recoverable Electrostrain in Mn-Doped KNbO_3 -Based Ferroelectrics. *Appl. Phys. Lett.* **2007**, *91*, 032904. [[CrossRef](#)]
20. Matsumoto, K.; Hiruma, Y.; Nagata, H. Electric-field-induced strain in Mn-doped KNbO_3 ferroelectric ceramics. *Ceram. Int.* **2008**, *34*, 787–791. [[CrossRef](#)]
21. Ferreira, P.; Castro, A.; Vilarinho, P.M. Electron Microscopy Study of Porous and Co Functionalized BaTiO_3 Thin Films. *Microsc. Microanal.* **2012**, *18*, 115–116. [[CrossRef](#)]
22. Kizaki, Y.; Noguchi, Y.; Miyayama, M. Defect control for low leakage current in $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ single crystals. *Appl. Phys. Lett.* **2006**, *89*, 142910. [[CrossRef](#)]
23. Mgbemere, H.E.; Herber, R.P.; Schneider, G.A. Effect of MnO_2 on the dielectric and piezoelectric properties of alkaline niobate based lead free piezoelectric ceramics. *J. Eur. Ceram. Soc.* **2009**, *29*, 1729–1733. [[CrossRef](#)]
24. Yang, S.L.; Tsai, C.C.; Liou, Y.C. Investigation of CuO-doped NKN ceramics with high mechanical quality factor synthesized by a B-site oxide precursor method. *J. Am. Ceram. Soc.* **2011**, *95*, 1011–1017. [[CrossRef](#)]
25. Zhang, S.T.; Kounga, A.B.; Aulbach, E. Lead-free piezoceramics with giant strain in the system $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - BaTiO_3 - $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. I. Structure and room temperature properties. *J. Appl. Phys.* **2008**, *103*, 034107. [[CrossRef](#)]
26. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767. [[CrossRef](#)]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).