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Physical and electric properties of lead-free $(Na_{0.5}K_{0.5})NbO_3$–$Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics

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Extending the investigations on $(Na_{0.5}K_{0.5})NbO_3$-based solid solution for lead-free piezoelectric ceramics, this paper consider the complex solid–solution system $(Na_{0.5}K_{0.5})NbO_3$–$Ba(Zr_{0.04}Ti_{0.96})O_3$ [NKN–BZT]. $(Na_{0.5}K_{0.5})NbO_3$ with 0–10 mol% $Ba(Zr_{0.04}Ti_{0.96})O_3$ has been prepared following the conventional mixed oxide process. X-ray diffraction analysis revealed that, during sintering, all of the $Ba(Zr_{0.04}Ti_{0.96})O_3$ diffuses into the lattice of $(Na_{0.5}K_{0.5})NbO_3$ to form a solid solution. Only a orthorhombic phase with a perovskite structure was found in this system. It was found that the samples with a low content of $Ba(Zr_{0.04}Ti_{0.96})O_3$ exhibit relatively good physical and electric properties. For 0.98 $(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics, the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.26 and 0.52, respectively, at the sintering of 1100°C for 2 h. The ratio of thickness coupling coefficient to planar coupling coefficient is 2. For $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ ceramics, the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.3 and 0.55, respectively, at the sintering of 1100°C for 5 h. With suitable $Ba(Zr_{0.04}Ti_{0.96})O_3$ concentration and sintering condition, good physical and electric properties were obtained. Our results show that $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ solid solution ceramics are one of the promising lead-free ceramics for high frequency electromechanical transducer applications.

Key-words : Lead-free ceramics, Piezoelectric, Dielectric, Sintering

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1. Introduction

At present, the most widely-used piezoelectric materials are $Pb(Zr,Ti)O_3$ (PZT)-based ceramics because of their superior piezoelectric properties. However, high volatilization and its toxicity of PbO during firing process can contaminate the environment and damage human health. In recent years, lead-free piezoelectric ceramics have attracted considerable attentions as one of important piezoelectric materials because of its outstanding advantages in free control atmosphere and no lead pollution. Lead-free piezoelectric materials such as sodium potassium niobate-based oxides, bismuth layer structure oxides and sodium bismuth titanate oxides have been studied in order to replace PZT-based ceramics. $(Na_{0.5}K_{0.5})NbO_3$ (NKN) ceramic has been considered a good candidate for lead-free piezoelectric ceramics because of its strong piezoelectricity and ferroelectricity.

The hot pressed NKN ceramics (~99% of theoretical density) have been reported to possess large piezoelectric longitudinal response (d_{33} ~160 pC/N), high planar coupling coefficient (kp ~45%) and high phase transition temperature (T_c = 420°C).[1] NKN ceramics sintered by ordinary sintering show relatively lower properties (k_p = 25%) due to difficulty in the processing of dense ceramics by ordinary sintering.[2] It has received a lot of attention and been thoroughly investigated.[3),4] Nevertheless, dense NKN ceramic is difficultly obtained since their phase stability is limited to 1140°C close to the melting point.[5),6] Many researchers used hot pressing or spark plasma sintering (SPS) techniques to yield better quality ceramics.[7] Recently, an efficient solution to improve foregoing problems is realized by utilizing some additives in NKN ceramics, such as ZnO,[8] $BaTiO_3$,[9] $LiNbO_3$,[10] $LiTaO_3$,[11] $SrTiO_3$,[12),13] $CaTiO_3$,[14),15] etc. The comparison of properties of $(Na_{0.5}K_{0.5})NbO_3$ ceramics based on the previous reports of various groups are demonstrated in **Table 1**. Thus, adding some perovskite compounds to form solid solutions with NKN or synthesizing by Spark Plasma Sintering (SPS) has been made to obtain lead-free materials suitable for industrial applications. Some studies show that the substitution of Ti^{+4} in $BaTiO_3$ with quadrivalence ions (such as Zr^{4+}) can significantly improve the overall properties of the material. For example, $BaZr_xTi_{1-x}O_3$ (BZT) has a small leakage current as a result of its better chemical stability of Zr^{+4} than Ti^{+4}.[16] $Ba(Zr_{0.04}T_{i0.96})O_3$ ceramics are known to have high piezoelectric and dielectric properties.[17] Some studies[18] have reported the effect of adding $Ba(Zr_{0.04}T_{i0.96})O_3$ on the properties of $(Na_{0.5}Bi_{0.5})TiO_3$ ceramics and demonstrated that $Ba(Zr_{0.04}T_{i0.96})O_3$ addition could enhance the piezoelectric properties of the ceramics. However, there have been few studies on the properties of NKN ceramics modified with $Ba(Zr_{0.04}T_{i0.96})O_3$.

In this paper, we report our work on the preparation and characterization of $(1-x)$ $(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}T_{i0.96})O_3$ [$(1-x)$NKN–xBZT] ($x \leq 0.1$) ceramics. The effect of sintering time on the physical and electric properties of $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramic is also discussed.

2. Experimental procedure

The $(1-x)$ $(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics (abbreviated NKN–BZT) were prepared by solid-state reaction method. Starting materials were K_2CO_3, Na_2CO_3, $BaCO_3$, Nb_2O_5, TiO_2, ZrO_2 with purities of at least 99.5% and weighted according to the stoichiometric composition (x = 0.02, 0.04, 0.06, 0.08 and 0.10). The powders were calcined at 950°C for 10 h. The cal-

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Table 1. Comparison of Properties of $(Na_{0.5}K_{0.5})NbO_3$ Ceramics Based on the Previous Reports of Various Groups

Composition	Density (g/cm^3)	Relative density (%)	K_o	k_p	k_t	k_t/k_p	*Ref.*
NKN	4.34	96.4	—	0.295	0.41	1.39	9
NKN–ZnO	4.26	94.5	500	0.4	—	—	8
0.98NKN–0.02$BaTiO_3$	4.44	98.4	—	0.29	0.38	1.31	9
0.995NKN–0.005$SrTiO_3$	4.44	98.4	412	0.325	0.44	1.35	13
0.94NKN–0.06$LiNbO_3$	4.35	96.5	—	0.42	0.48	1.14	10
0.94NKN–0.06$LiTaO_3$	—	—	570	0.36	—	—	11
0.995NKN–0.005$CaTiO_3$	4.4	97.6	553	0.42	0.38	1.1	14
0.98NKN–0.02 $Ba(Zr_{0.04}Ti_{0.96})O_3$	4.28	95.1	875	0.30	0.55	1.83	Our sample

cined powders were pressed (CIP) at 180 MPa into pellets with 15 mm in diameter. The disc samples were sintered in platinum crucible at 1100°C for 2–8 h in air atmosphere. To measure relevant piezoelectric properties, the prepared ceramic samples were polarized in silicon oil at 100°C under the electric field of 4 kV/mm for 30 min. An X-ray diffractometer (Seimens D5000) using Cu Kα radiation was used to evaluate the crystal structure of the sintered ceramics. The room temperature dielectric constant was measured by LCR meter (Angilent 4284A) at about 1 kHz. The piezoelectric properties were measured by a resonance-antiresonance method based on IEEE standards[19] using an impedance/gain-phase analyzer (Angilent 4194). Samples for observations of the microstructure were polished and thermal etched. The microstructures were observed by a scanning electron microscope (SEM). The mean grain size was calculated by the line intercept method.[20] The density was measured by Archimedes method.

3. Results and discussion

In this system, all of the samples showed no deliquescence when exposed under water for a long period, indicating no existence of the unstable second phase. **Figure 1** shows the X-ray diffraction (XRD) patterns of $(1-x)(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics for x = 0.02, 0.04, 0.06, 0.08 and 0.10. All of the compositions are sintered in an air environment at 1100°C for 5 h. The orthorhombic symmetry of 0.98NKN–0.02BZT ceramics at room temperature is characterized on the XRD patters in the 2θ ranges of 44–48°. The BZT appears to have diffused into the NKN lattice to form a solid solution, in which Ba occupies $(Na_{0.5}K_{0.5})$ lattice and $(Zr_{0.04}Ti_{0.96})$ enters Nb sites of NKN. **Figure 2** shows the XRD patterns of $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics sintered 1100°C for different sintering time (2 h, 5 h and 8 h). The XRD analysis of sintered samples shows that 0.98NKN–0.02BZT ceramics are sure of a single phase and forms a solid solution. Only a orthorhombic phase with a perovskite structure was found in this system. The temperature dependence of the dielectric constant at 1 kHz for $xBa(Zr_{0.04}Ti_{0.96})O_3$–$(1-x)(Na_{0.5}K_{0.5})NbO_3$ ceramics is shown in **Fig. 3**. For pure NKN, two sharp phase transitions are reported at 420°C and 200°C, corresponding to the phase transitions of paraelectric (cubic)–ferroelectric (tetragonal; T_c) and tetragonal–orthorhombic(T_{T-O}), respectively.[9] With increasing BZT content, the paraelectric (cubic)–ferroelectric (tetragonal) and tetragonal-orthorhombic transition temperatures all shift to lower temperatures.

Figure 4 shows the microstructure of $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics sintered at 1100°C for different time (a) 2 h (b) 5 h and (c) 8 h. It can be seen that the

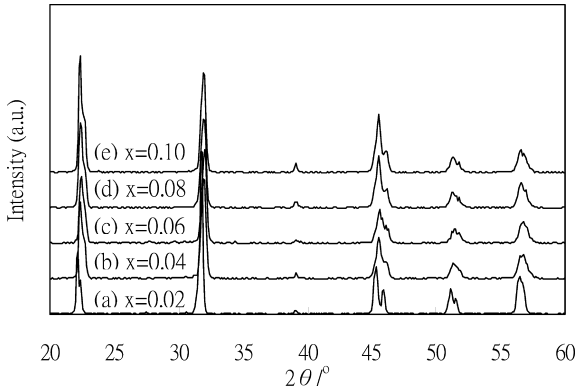


Fig. 1. XRD Patterns of $xBa(Zr_{0.04}Ti_{0.96})O_3$–$(1-x)(Na_{0.5}K_{0.5})NbO_3$ ceramics system with different BZT content (a) x = 0.02, (b) x = 0.04, (c) x = 0.06, (d) x = 0.08, (e) x = 0.10.

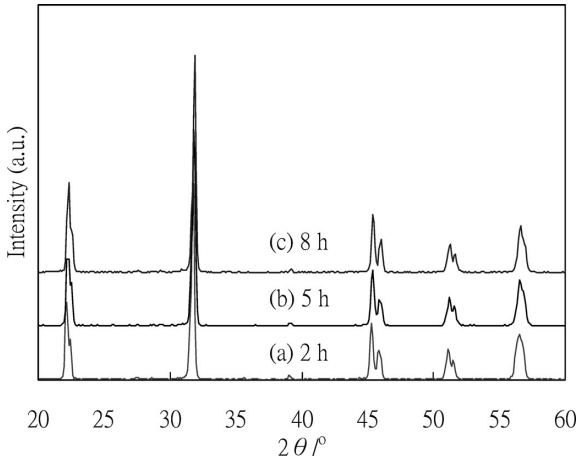


Fig. 2. XRD Patterns of $0.02Ba(Zr_{0.04}Ti_{0.96})O_3$–$0.98(Na_{0.5}K_{0.5})NbO_3$ ceramics system sintered 1100°C for different sintering time (a) 2 h, (b) 5 h, (c) 8 h.

$0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics consist of small grains, with a loose structure, and a high porosity in Fig. 4(a). However, the $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramic sintered for 5 h are more dense, with low porosity, and exhibit a more homogeneous and grain size of ~1.5 μm in Fig. 4(b). It may be explained by the sintering model of Coble[21] that small grain size will promote the densification and grain boundary offer a sink of defect or vacancy in sintering leading to the

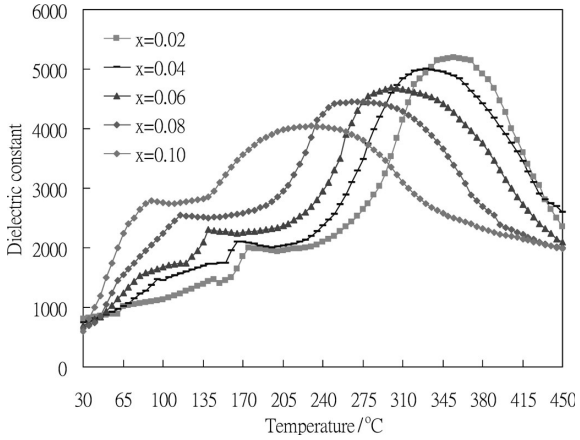
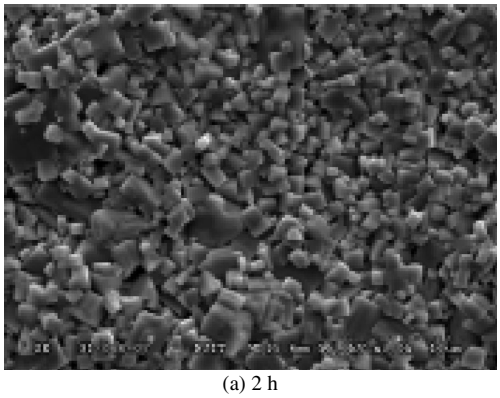
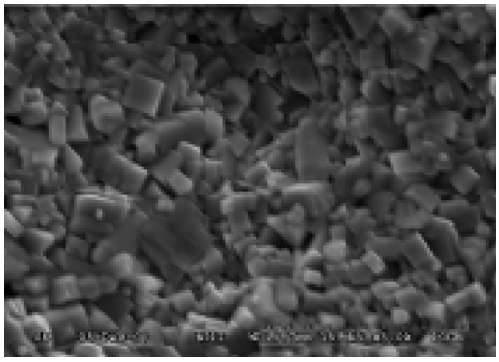


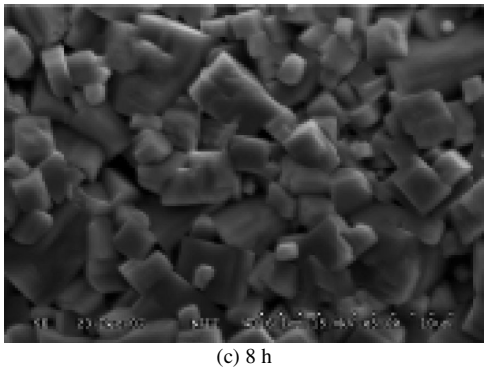
Fig. 3. Temperature dependence of dielectric constant of xBa$(Zr_{0.04}Ti_{0.96})O_3$–$(1–x)(Na_{0.5}K_{0.5})NbO_3$ ceramics at 1 kHz.



(a) 2 h



(b) 5 h



(c) 8 h

Fig. 4. SEM images of $0.02Ba(Zr_{0.04}Ti_{0.96})O_3$–$0.98(Na_{0.5}K_{0.5})NbO_3$ ceramics sintered at 1100°C for different time (a) 2 h, (b) 5 h, (c) 8 h.

increase of the density. In Fig. 4(c), a longer sintering time may cause excessive NKN loss and a resultant variation in composition, which leads to an inhomogeneous microstructure. This may increase the porosity, attributed to a greater rate of evaporation of NKN compared to that recondensed.

Figure 5 to **Fig. 6** show the physical and electrical properties of $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ (x = 0.02, 0.04, 0.06, 0.08 and 0.10) sintered at 1100°C for 5 h. The measured density and dielectric constant of $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$x$Ba $(Zr_{0.04}Ti_{0.96})O_3$ ceramics are shown as a function of BZT composition in Fig. 5. The measured density of the sintered samples is 90–96% of the theoretical density. The measured density and dielectric constant increase with an increase of BZT composition. The highest dielectric constant of $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$x$Ba $(Zr_{0.04}Ti_{0.96})O_3$ ceramics is found at x = 0.02. For $0.98(Na_{0.5}K_{0.5})$ NbO_3–$0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ ceramics, the value of the dielectric constant K^T_{33} is 875 at the sintering of 1100°C for 5 h. The planar coupling factor (k_p) and thickness coupling factor (k_t) of $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics are shown as a function of BZT composition in Fig. 6. The electromechanical coupling factor is related to different BZT composition. The

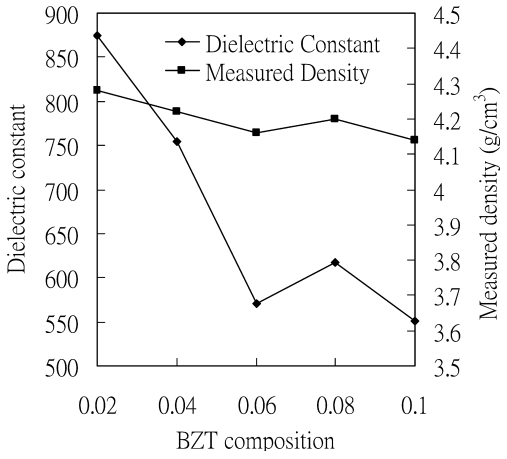


Fig. 5. Measured density and dielectric constant of $(1–x)$ $(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics are shown as a function of BZT composition.

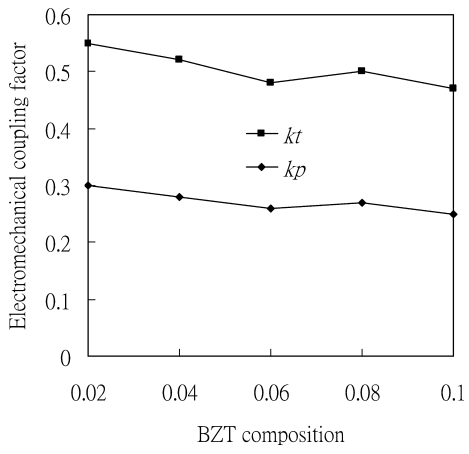


Fig. 6. Planar coupling factor (k_p) and thickness coupling factor (k_t) of $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics are shown as a function of BZT composition.

electromechanical coupling factor has been used extensively as a measure of the piezoelectric response of PZT type ceramics. It was found that the electromechanical coupling factor depended on the material parameters[22] such as grain size, porosity, and chemical composition. Usually, the piezoelectric activity is appreciated by the value of the electromechanically coupling factor in radial mode k_p and in thickness mode k_t. Therefore, k_p and k_t is the figure of merit of the piezoelectric activity and the square of that gives the efficiency of the conversion of electrical-mechanical energy.[23] Usually, the piezoelectric activity increases with the value of the electromechanical coupling factor in radial mode k_p and in thickness mode k_t . The equation for calculating electromechanical coupling factor k_p and k_t is

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

and

$$\frac{1}{k_t^2} = 0.81\frac{f_r}{f_a - f_r} + 0.405, \text{ respectively,}$$

where fr is a resonant frequency and fa is an anti-resonant frequency. The highest coupling factor of $(1–x)(Na_{0.5}K_{0.5})NbO_3–xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics is found at $x = 0.02$. For $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ ceramics, the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.3 and 0.55, respectively, at the sintering of 1100°C for 5 h.

Figure 7 to **Fig. 8** the physical and electrical properties of $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ ceramics sintered at 1100°C for different sintering time (2 h, 5 h and 8 h). The measured density and dielectric constant of $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ sintered 1100°C are shown as a function of sintering time in Fig. 7. The measured density and dielectric constant increase with an increase sintering time until it reaches 5 h, then decreases for 8 h. The dielectric constant K_o (before polarization) and K^T_{33} (after polarization) of $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ ceramic are shown as a function of sintering time in Fig. 7. In piezoelectric ceramics, the properties depend on the composition and crystal structure; the dielectric constant may be increased or decreased through poling treatment. Moreover, the variations of the dielectric constant through poling also rely on the domain alignment. In a orthorhombic phase, the dielectric constant decreases after poling, and the net decrease is owing to the 90° domain reorientation dominating the effect of the removal of compression.[24)–26)] In the orthorhombic phase, K^T_{33} decreases in comparison to K_o as a result of the dielectric anisotropic.

The planar coupling factor (k_p) and thickness coupling factor (k_t) of $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ ceramics are shown as a function of sintering time in Fig. 8. For $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics, the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.26 and 0.52, respectively, at the sintering of 1100°C for 2 h. The ratio of thickness coupling coefficient to planar coupling coefficient is 2 as shown in **Table 2**. The planar coupling factor (k_p) and thickness coupling factor (k_t) increase with increasing sintering time until it reaches 5 h, then decrease for 8 h.

Table 2 shows the physical and electric properties of $(1–x)(Na_{0.5}K_{0.5})NbO_3–xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics sintered 1100°C at different compositions and sintering time. The relative density is the ratio of the measured density to theoretical density. The relative density of $(1–x)(Na_{0.5}K_{0.5})NbO_3–xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics has a maximum value of 95.1% at the sintering of 1100°C for 5 h. In this system, the properties of $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ have better values of k_p and k_t for 5 h of the sintering time at 1100°C. With increasing the BZT content and sintering time, the dielectric loss decreases and the mechanical quality factor Q_m increases in this system.

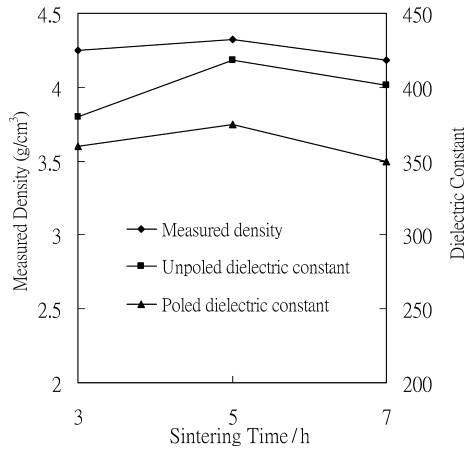


Fig. 7. Measured density and dielectric constant of $0.02Ba(Zr_{0.04}Ti_{0.96})O_3–0.98(Na_{0.5}K_{0.5})NbO_3$ ceramics sintered 1100°C at different time.

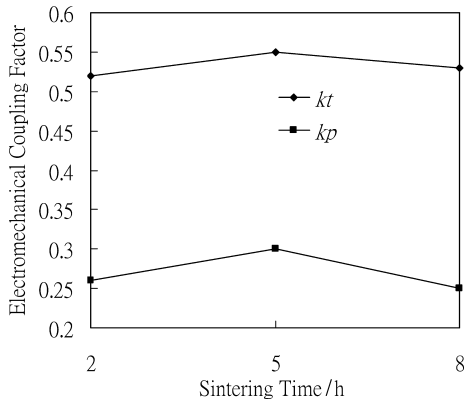


Fig. 8. Planar coupling factor k_p and thickness coupling factor k_t of $0.02Ba(Zr_{0.04}Ti_{0.96})O_3–0.98(Na_{0.5}K_{0.5})NbO_3$ ceramics sintered 1100°C at different time.

Table 2. Physical and Electric Properties of $(1–x)(Na_{0.5}K_{0.5})NbO_3–xBa(Zr_{0.04}Ti_{0.96})O_3$ Ceramics Sintered 1100°C at Different Compositions and Sintering Time

Composition	Sintering time (h)	Relative density	k_p	k_t	k_t/k_p	Q_m	$\tan\delta$
$x = 0.10$	5	92.0%	0.25	0.47	1.88	92	0.058
$x = 0.08$	5	93.3%	0.27	0.50	1.82	85	0.065
$x = 0.06$	5	92.4%	0.26	0.48	1.79	78	0.071
$x = 0.04$	5	93.8%	0.28	0.52	1.86	71	0.082
$x = 0.02$	8	90.2%	0.25	0.53	2.12	68	0.078
$x = 0.02$	5	95.1%	0.30	0.55	1.83	65	0.085
$x = 0.02$	2	87.3%	0.26	0.52	2	55	0.092

4. Conclusion

The $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ solid solution ceramics were prepared by the cold-pressing (CIP) method and the conventional ceramics technique. From the XRD patters, the orthorhombic symmetry of $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics ($x \leq 0.10$) at room temperature was found. In piezoelectric ceramics, depending on the crystalline phase, the dielectric constant may increase or decrease through poling treatment. In this system, the dielectric constant before polarization is larger than that after polarization in orthorhombic phase. The highest coupling factor of $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$xBa(Zr_{0.04}Ti_{0.96})O_3$ ceramics is found at $x = 0.02$. For $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_{0.04}Ti_{0.96})O_3$ ceramics, the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.26 and 0.52, respectively, at the sintering of 1100°C for 2 h. The ratio of thickness coupling coefficient to planar coupling coefficient is 2.

The effects of sintering time on the properties of $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ ceramics were discussed. The physical and electric properties have better values for 5 h of the sintering time at 1100°C. Prolonged sintering time results in an excessive NKN loss and the resultant variation in composition leads to an inhomogeneous and a loose microstructure. For $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Ti_{0.96}Zr_{0.04})O_3$ ceramics, the electromechanical coupling coefficients of the planar mode k_p and the thickness mode k_t reach 0.3 and 0.55, respectively, at the sintering of 1100°C for 5 h. The ratio of thickness coupling coefficient to planar coupling coefficient is 1.83.

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