

PHASE TRANSITION AND ELECTRICAL PROPERTIES OF NEW LEAD-FREE $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-Ba}(\text{Ti}_{0.95}\text{Hf}_{0.05})\text{O}_3$ SOLID SOLUTION CERAMICS

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New lead-free piezoelectric ceramics $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-xBa}(\text{Ti}_{0.95}\text{Hf}_{0.05})\text{O}_3$ (NKN-xBTH) doped with 0.8 mol.% CuO have been successfully fabricated by traditional solid state sintering. Owing to complex atomic occupation at A-sites and B-sites, the ferroelectric phase transition of NKN becomes more and more diffuse with increasing BTH content. On the other hand, it was found that the addition of a small amount of BTH shifts an orthorhombic-tetragonal polymorphic phase transformation of pure NKN composition downwards to room temperature. The two-phase transition zone was identified approximately at $0.04 < x < 0.06$ and the ceramic with $x = 0.06$ possesses obviously enhanced electrical properties: $d_{33} = 185$ pC/N, $k_p = 0.38$, $\epsilon_{33}^T = 1690$, $Q_m = 108$ and $T_c = 267$ °C, compared to pure NKN.

INTRODUCTION

$(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN) as a typical lead-free piezoelectric composition has attracted much attention in recent years because of its relatively good piezoelectric properties, together with a high Curie temperature [1]. However, compared to conventional $\text{Pb}(\text{Zr,Ti})\text{O}_3$ compositions it has a few shortcomings such as difficulty in sintering, inferior piezoelectric properties and so on. It is well known that pure NKN compositions are difficult to densify by ordinary sintering. A few routes such as pressure-assisted sintering [2, 3], stoichiometric control [4-6], alkaline-or rare-earth elements doping [7-10], and sintering aids [11-14], have been so far attempted to improve their densification behavior.

Additionally, piezoelectric properties of pure NKN ceramics could be improved by forming solid solutions with other ferroelectric compositions such as LiNbO_3 [15-17], BaTiO_3 (BT) [18], $\text{A}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (A = Na, K, Li,) [19-21], BiMeO_3 (Me = Mn, Ga, In, Y, Yb, Fe, Sc) [22-24] and even modified BT [25]. The mechanism of property improvement is associated with the formation of a possible two-phase coexistence zone by shifting a polymorphic phase transition (PPT) of pure NKN downwards to room temperature, which is believed to promote the piezoelectric activities. Among these typical ferroelectric compositions, the 5 mol.% Zr^{4+} substituted BT ceramics have received renewed attention due to

enhanced piezoelectric properties [26]. Solid solutions between $\text{Ba}(\text{Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3$ and NKN were recently reported, exhibiting improved piezoelectric performances [25]. It was pointed out that Hf^{4+} may play a similar role to Zr^{4+} in inducing the phase transition and improving piezoelectric properties of BT. $\text{Ba}(\text{Ti}_{0.95}\text{Hf}_{0.05})\text{O}_3$ (BTH) single crystals were reported to have excellent electrical properties [27]. It was also found that BTH ceramics possess a high d_{33} value (305 pC/N) [28]. Therefore, Hf^{4+} doped BT is expected to provide a new alternative to effectively improve the piezoelectric properties of pure NKN. In this work, the $(1-x)\text{NKN-xBTH}$ solid solution ceramics have been for the first time fabricated by ordinary sintering. Their phase transition behavior and various electrical properties were investigated in detail.

EXPERIMENTAL

$(1-x)\text{NKN-xBTH}$ ($x = 0, 0.02, 0.04, 0.05, 0.06, 0.07, 0.08, 0.1$) were synthesized by means of a conventional mixed-oxide route. High-purity oxides and carbonates, Na_2CO_3 (99.8%), K_2CO_3 (99.0%), BaCO_3 (99.99%), Nb_2O_5 (99.5%), TiO_2 (99.99%), HfO_2 (99.9%), were used as starting materials which had been treaded carefully by a special drying process before use, particularly for sodium/potassium carbonates. The weighed powders were mixed by a planetary ball mill in anhydrous alco-

hol for 8 h. After drying, the calcination was done twice at 850 °C for 3 h. The calcined powders were ball milled again with 0.8 mol% CuO and a PVB binder solution for 24 h. The purpose of the CuO addition in this study is to aid sintering. The dried powders were then compacted into disk samples with desired aspect ratios and then sintered in air at 1090-1180 °C for 6 h. Silver paste was coated and then fired on major surfaces at 550 °C for 30 min as electrodes for dielectric and piezoelectric measurements. The ceramics were poled under a dc field of 5-6 kV/mm at 110 °C in a silicone oil bath for 30 min.

The crystal structure was examined by an X-ray diffractometer (XRD, D/Mzx-rB, Rigaku, Tokyo, Japan) using a Cu *K* α radiation. The microstructure was observed by a scanning electron microscope (SEM, JEOL JSM-6335F, Japan). Dielectric properties were measured as a function of temperature by an LCR meter (Agilent E4980A, USA). The piezoelectric constant d_{33} was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p and the mechanical quality factor Q_m were determined by a resonance-antiresonance method with an impedance analyzer (PV70A, China).

RESULTS AND DISCUSSION

Figure 1a shows XRD patterns of (1-x)NKN-xBTH ceramics sintered at 1100 °C for 6 h. All compositions show a single perovskite structure, indicating the formation of a series of solid solutions. In addition, it was found that the addition of a small amount of BTH changes the crystal structure of pure NKN. Similar to pure NKN [1], (1-x)NKN-xBTH ceramics have an orthorhombic structure at room temperature when $x < 0.04$. With further increasing BTH content, the ceramic undergoes an orthorhombic to tetragonal phase

transition. When $x > 0.06$, it becomes a single tetragonal phase. The change in crystal structure can be more clearly seen from the variation of (200) peaks in Figure 1b. Therefore, it turns out that there exists a two-phase coexistence zone in the composition range of $0.04 < x < 0.06$. Moreover, it can be seen that the tetragonal phases remain unchanged when $0.07 < x < 0.1$, however the tetragonality c/a seems to decrease with increasing the amount of BTH. When $x = 0.1$, the c/a value is equal to approximately 1.009. The compositions with $x > 0.1$ were not reported in this study because the materials possess very low Curie temperatures.

The SEM images on free surfaces of the samples at the optimal temperature are shown in Figure 2. The addition of BTH not only changes the crystal structures of NKN compositions but also influences their densification behavior. BTH-added NKN solid solution ceramics may have relatively high sintering temperature. It can be seen that the grains are faceted and the average grain size drops down with increasing x . It is $\sim 5 \mu\text{m}$ for pure NKN ceramics, decreases to $\sim 1 \mu\text{m}$ for the 6% BTH substituted NKN ceramics, and becomes even smaller for the 8% BTH substituted NKN ceramics. In addition, the sinterability of NKN ceramics has been slightly improved when BTH is $\leq 6\%$ and the 8% BTH substituted NKN ceramics start to become difficultly densified.

Dielectric constant of (1-x)NKN-xBTH ceramics as a function of temperature is shown in Figure 3a and the variation of the phase transition temperature with x is summarized in Figure 3b. When $x = 0$, the ceramic undergoes two phase transitions: the paraelectric cubic to ferroelectric tetragonal phase transition at 420 °C (T_c), and the ferroelectric tetragonal to ferroelectric orthorhombic phase transition at 201 °C (T_{o-t}). Obviously, these two transition peaks are simultaneously shifted

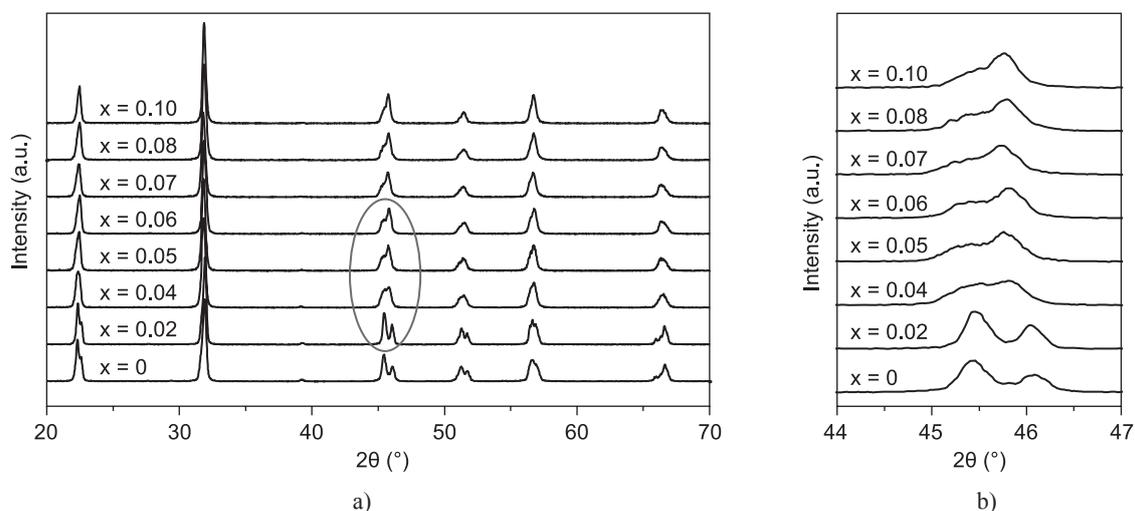


Figure 1. X-ray diffraction patterns of (1-x)NKN-xBTH ceramics with different x as a) indicated and b) locally magnified (200) diffraction peaks for each composition.

to lower temperatures with the addition of BTH. Only cubic-tetragonal phase transition can be seen above room temperature when $x > 0.06$. Furthermore, it can be seen that the corresponding dielectric peaks become broader

and broader with increasing BTH content. As shown in Figure 3b, T_c decreases almost linearly with increasing x from 420 °C to 176 °C at an average rate of 23 °C/mol%, and T_{o-t} decreases from 201 °C to 41 °C at an average

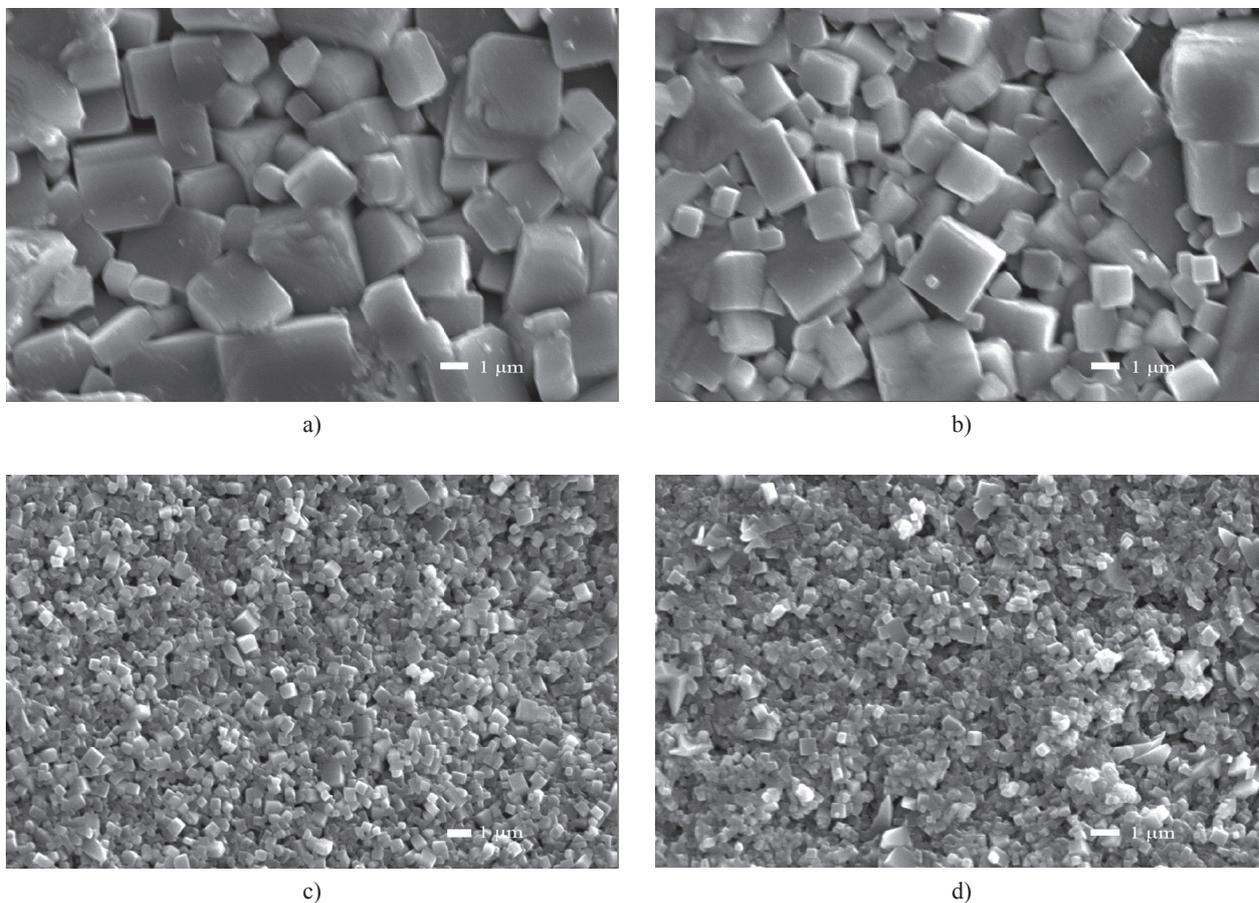


Figure 2. SEM images on natural surfaces of $(1-x)\text{NKN-xBTH}$ ceramics: (a) $x = 0$ and (b) $x = 0.02$, sintered at 1100 °C for 3 h, (c) $x = 0.06$, sintered at 1130 °C for 3 h and (d) $x = 0.08$, sintered at 1150 °C for 3 h.

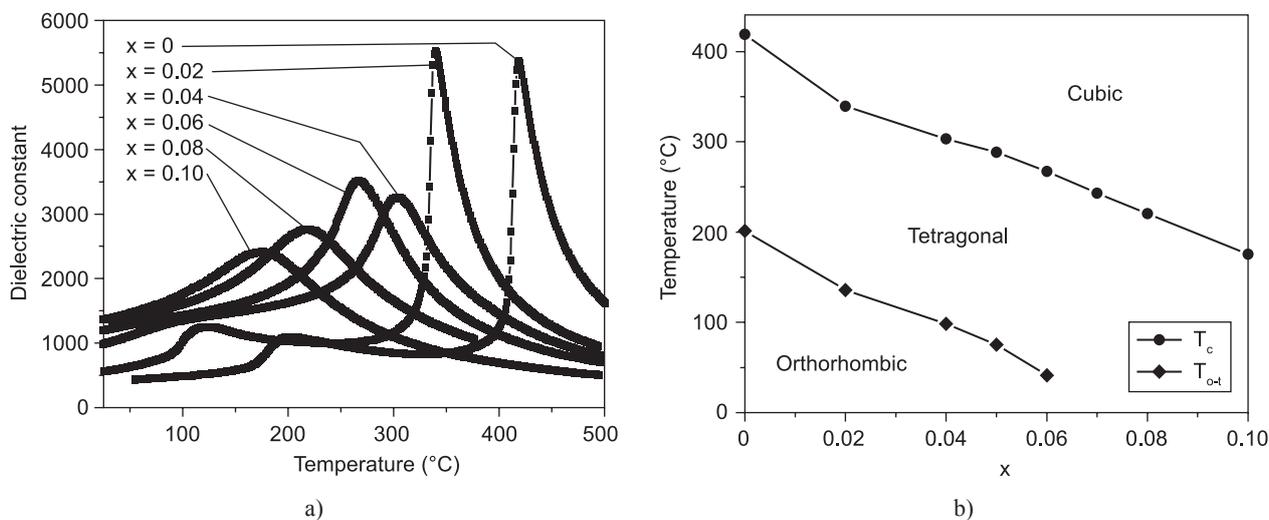


Figure 3. Dielectric constant at 10 kHz of $(1-x)\text{NKN-xBTH}$ ceramics with different x as a) indicated and b) phase transition temperatures of each composition as a function of x .

rate of 25 °C/mol% with increasing x from 0 to 0.06. At $0.04 < x < 0.06$, a diffuse PPT is moved around room temperature such that a two-phase coexistence state can be expected. This observation keeps consistency with the above XRD results.

In addition, as seen in Figure 3a, the cubic-tetragonal phase transition peak becomes broadened, implying that a diffuse ferroelectric phase transition behavior has been induced with increasing the content of BTH. The diffuseness can be described by a modified Curie-Weiss law, $1/\varepsilon - 1/\varepsilon_m = C^{-1}(T - T_m)^\gamma$, where ε_m is the maximum value of dielectric constant ε_r at the phase transition temperature T_m , γ and C are assumed to be constants, and the γ value ranges from 1 for a normal ferroelectric to 2 for an ideal relaxor ferroelectric. The logarithm of $(1/\varepsilon - 1/\varepsilon_m)$ is plotted against the logarithm of $(T - T_m)$ as shown in Figure 4. A linear relationship is observed for the compositions with $x=0, 0.02, 0.06, 0.08$. The slope of the linearly fitted curves is used to determine the γ value. The γ value varies from 1.14 to 1.62, indicating

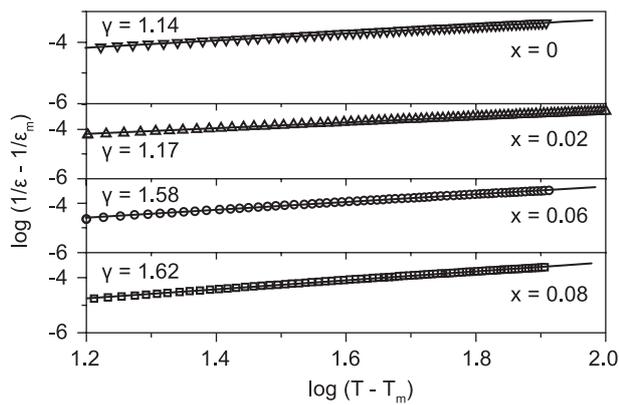


Figure 4. Plots of $\log(1/\varepsilon - 1/\varepsilon_m)$ versus $\log(T - T_m)$ for $(1-x)$ NKN- x BTH ceramics. The different symbols denote the experimental data while the solid lines denote the least-squares fittings according to the modified Curie-Weiss law.

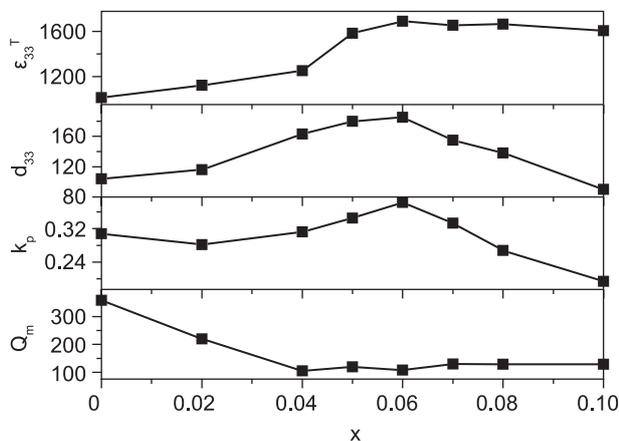


Figure 5. Various electrical properties of poled $(1-x)$ NKN- x BTH ceramics as a function of BTH content.

that a normal ferroelectric NKN changes to a relaxor-like ferroelectric by adding BTH. Considering that Ba^{2+} (1.60 Å, ionic radius) could substitute for Na^+ (1.39 Å) and K^+ (1.64 Å), while Ti^{4+} (0.61 Å) and Hf^{4+} (0.71 Å) could substitute for Nb^{5+} (0.64 Å), multi-ions occupying at A sites or B sites may enhance the degree of disorder or the local compositional fluctuation may increase, thus inducing a relaxor-like phase transition behavior.

The various electrical properties of poled $(1-x)$ NKN- x BTH ceramics as a function of x are shown in Figure 5, showing a strong composition dependence of electrical properties. The dielectric constant ε_{33}^T , the piezoelectric constant d_{33} , and the planar electromechanical coupling coefficient k_p increase with x initially, reach maximum values of $\varepsilon_{33}^T = 1690$, $d_{33} = 185$ pC/N and $k_p = 0.38$ at $x = 0.06$, and then decrease with further increasing x . It is generally thought that the coexistence of two ferroelectric states contributes to the enhancement of piezoelectric and dielectric properties. On the other hand, the mechanical quality factor Q_m decreases from 358 to 105 as x increases from 0 to 0.04, and then remains unchanged at larger BTH contents. The Q_m value for the composition with $x = 0$ seems larger than that of pure NKN ceramics (generally $Q_m = \sim 100$), probably being attributed to the addition of a small amount of CuO as sintering aid. As far as the d_{33} value is concerned, it is a little bit lower than that of BT modified NKN ceramics [18] although BTH may have better piezoelectric properties than BT, probably because of the processing issues such as CuO doping in this study. Hardened piezoelectric ceramics are known to have less d_{33} but higher Q_m . Moreover, compared with a pure NKN ceramic [12], the dielectric and piezoelectric properties of $(1-x)$ NKN- x BTH solid solution ceramics are obviously enhanced. Over the phase boundary approximately at $0.04 < x < 0.06$, the dielectric constant could remain at high values probably because of enhanced diffuseness in ferroelectric phase transitions. However, the piezoelectric and electromechanical coupling properties drop quickly, possibly associated with reduced ferroelectricity, as indicated from decreased Curie temperatures of NKN compositions with higher BTH substitutions.

CONCLUSIONS

New lead-free $(1-x)$ NKN- x BTH solid solution ceramics were fabricated by ordinary sintering with a sintering aid of 0.8 mol.% CuO. The orthorhombic-tetragonal ferroelectric phase transition was shifted around room temperature for compositions with $0.04 < x < 0.06$. The optimum electrical properties of $d_{33} = 185$ pC/N, $k_p = 0.38$, $\varepsilon_{33}^T = 1690$, $Q_m = 108$ and $T_c = 267$ °C appear in the composition with $x = 0.06$. Moreover, the addition of BTH tends to induce a transition of NKN from normal ferroelectric to a relaxor-like

ferroelectric. The results demonstrated that the studied solid solution compositions show advantages over pure NKN for device applications.

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