Sintering, microstructure and piezoelectric properties of CuO and SnO$_2$ co-modified sodium potassium niobate ceramics

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ABSTRACT

The CuO and SnO$_2$ co-modified Na$_{0.52}$K$_{0.48}$NbO$_3$ ceramics were prepared by a conventional mixed oxide method. Densification can be further improved but the grain growth is inhibited as a small amount of SnO$_2$ is added into 1% CuO doped Na$_{0.52}$K$_{0.48}$NbO$_3$. The results indicate that the physical and various electrical properties of CuO and SnO$_2$ doped Na$_{0.52}$K$_{0.48}$NbO$_3$ ceramics significantly depend on sintering conditions and the content of dopants. The ceramics doped with 1 mol% CuO and 1 mol% SnO$_2$ sintered at 1070 °C for 3 h show improved dielectric and piezoelectric properties: d_{33} = 120 pC/N, k_p = 0.38, Q_m = 1040, ε_r = 710 and tanδ = 0.013 (1 kHz), in comparison with un-doped or CuO doped compositions.

1. Introduction

It is known that there exists a morphotropic phase boundary between tetragonal antiferroelectric and orthorhombic ferro-electric phases in a pure Na$_y$K$_{1-y}$NbO$_3$ (NKN$_y$) as y = 0.5 [1]. Moreover, the mass of A-site atoms (K and Na) significantly differs from that of B-site atoms (Nb) in ABO$_3$ perovskite structure [2,3]. These similarities to conventional Pb(Zr,Ti)O$_3$ allow ceramists to anticipate excellent ferroelectric and piezoelectric properties from it. However, difficulties in sintering have probably concealed its optimum piezoelectric properties. Although much progress in modified NKN compositions has been achieved by shifting a polymorphic phase transition (PPT) between orthorhombic and tetragonal phases close to room temperature [4–6], yet significant thermal instability of electrical properties has been an obstacle to future device applications [7].

By comparison, pure NKN compositions exhibit relatively good temperature stability up to nearly 200 °C at which PPT lies. Therefore, it might be of great interest to further deeply investigate pure NKN compositions or ones modified with a small amount of dopants. It seems undesirable that NKN ceramics only show a d_{33} of ∼100 pC/N by ordinary sintering [8], and ∼160 pC/N by cold-isostatic pressing which is the highest value reported for it to date [9], indicating that experimental results concerning NKN still have a distance from theoretical values [2,3].

As far as electrical properties are concerned, NKN ceramics seem to exhibit softening characteristics (a higher remnant polarization P_r ∼15 pC/N, a lower coercive field E_c ∼1 kV/mm and a larger loss value ∼0.05 [9]. It appears difficult for them to be used for high-power device application. Copper oxide (CuO) proved to be an effective acceptor dopant to induce hardening features in NKN compositions [10]. In addition, it is also a helpful sintering aid to greatly promote the densification of NKN based on the formation of liquid phases during sintering [11]. Although the addition of a small amount of CuO greatly enhances Q_m and improves densification of NKN (∼98% theoretical density), the d_{33} value remains low (mostly <100 pC/N). Furthermore, an obvious grain growth (>10 μm) was often induced as CuO is added, which could degrade mechanical properties of the ceramics. Of course, too big grain size tends to be adverse to piezoelectric properties. Noticeably, exaggerated grain growth tends to degrade the hardening effect from CuO doping, which was often found in Li modified NKN compositions where Q_m was not significantly enhanced [12,13].

The purpose of this study is thus to investigate the effect of CuO and SnO$_2$ co-doping on the sintering, microstructure and piezo-electric properties of NKN ceramics, considering that SnO$_2$ is known to be an inhibitor of grain growth for some compositions [8,14]. The co-doping effect from SnO$_2$ and CuO in NKN was for the first time reported. As the content of CuO is fixed, the densification behavior, microstructure and various electrical properties were investigated as a function of SnO$_2$ content. The relationship of the processing, structure and properties was discussed. Because the location of MPB for NaNbO$_3$–KNbO$_3$ system was recently revised

[16], Na$_{0.52}$K$_{0.48}$NbO$_3$ (abbreviated as NKN$_{0.48}$) was thus used in this study.

2. Experimental

High-purity raw chemicals, K$_2$CO$_3$ ($\geq$99.0%), Na$_2$CO$_3$ ($\geq$99.8%), Nb$_2$O$_5$ ($\geq$99.5%), CuO ($\geq$99.0%) and SnO$_2$ ($\geq$99.5%) were used in this study. NKN$_{0.48}$ powder was prepared through the following steps. After weighing, powders were mixed by a planetary ball mill using anhydrous ethanol as the media. The dried powder was calcined at 850 °C twice. The powder was re-milled between two calcinations in order to improve chemical homogeneity. Subsequently, the dopants (CuO and SnO$_2$) were added according to the formula: NKN$_{0.48}$ + 1 mol% CuO+ x mol% SnO$_2$ (x = 0, 0.25, 0.5, 1, 1.5 and 2) (NKN$_{0.48}$ + 1 + x). After milling for 24 h, the resultant powder was pressed into disk specimens. Sintering was carried out in the temperature range of 1010–1090 °C for up to 7 h. The Archimedes method was used to measure the sample density. The crystal structure was examined by an X-ray diffractometer (XRD, D/Mzx-rB, Rigaku, Japan) using a Cu Kα radiation. The microstructure was observed by means of a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan).

For electrical measurements, silver paste was coated on major surfaces and then fired at 550 °C for 30 min. The electric poling was performed at 120 °C in a silicone oil bath by applying a dc field of 4.5–5 kV/mm for 20 min and the electric field was maintained during cooling. Dielectric properties were measured as a function of temperature by an LCR meter (Agilent E4980A, Santa Clara, CA) equipped with a temperature box. The piezoelectric strain constant d_{33} was measured by a Berlincourt-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 (Impedance Analyzer, PV70A, Beijing, China).

3. Results and discussion

Fig. 1 indicates that the CuO and SnO$_2$ co-modified NKN$_{0.48}$ samples exhibit single perovskite structure with an orthorhombic symmetry, except for NKN$_{0.48}$ + 1 + 1.5 ceramics which start to have a tiny amount of second phases (indexed as Sn$_2$Nb$_2$O$_7$). Because the ionic size of Sn^{4+} (0.71 Å) is similar to that of Nb^{5+} (0.69 Å), it is difficult to see the change of lattice constants from the diffraction angles. This implies that Sn^{4+} should occupy B-site to substitute for Nb^{5+} because smaller B-site ions at the center of cubic cells will not induce obvious lattice distortions. Moreover, it is indicated that only a small amount of SnO$_2$ can enter the lattice of 1 mol% CuO doped NKN$_{0.48}$ owing to the solubility limit ($<$1.5%).
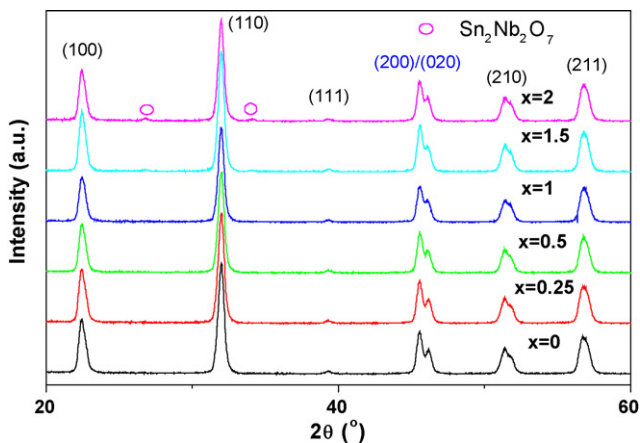
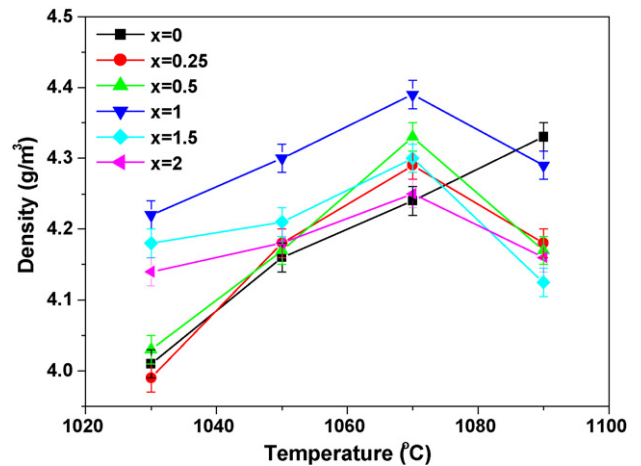**Fig. 1.** X-ray diffraction patterns of NKN$_{0.48}$ + 1 + x ceramics.

Fig. 2. Densities of NKN$_{0.48}$ + 1 + x ceramics sintered at different temperatures for 3 h.

Isothermal sintering behavior of NKN$_{0.48}$ + 1 + x compositions as a function of temperature is shown in Fig. 2. Sample densities first increase and then start to decrease after a maximum value. All doped compositions reach the best densification at 1070 °C, almost independent of the SnO$_2$ content. The composition with x = 0 seems to have relatively high sintering temperature. Although the addition of CuO can improve sintering of NKN [10], the results in this study demonstrate that the co-doping of CuO and SnO$_2$ can more effectively promote sintering. On the other hand, it can be seen that the highest density of NKN$_{0.48}$ samples sintered at 1070 °C depends on the content of SnO$_2$, reaching the maximum for NKN$_{0.48}$ + 1 + 1 sample. The reason could be attributed to the temperature at which the liquid phase is formed, the amount of formed liquid phases and the grain growth. It is known that CuO as a sintering aid can promote sintering of NKN by forming a liquid phase K$_4$CuNb$_8$O$_{23}$. The addition of SnO$_2$ could further decrease the melting point of liquid phases, leading to a relatively low sintering temperature, and increase the quantity of liquid phases, thus more effectively promoting densification. However, too much liquid phase and resultant grain growth tend to decrease the driving force of mass transportation. As indicated in Fig. 3, grains slightly grow with increasing temperature but are significantly coarsened at 1090 °C. Fig. 4 shows the density change of NKN$_{0.48}$ + 1 + x samples sintered at 1070 °C as a function of holding time. All compositions show a typical profile with holding time, reaching a plateau at 3 h. Therefore, the optimum sintering condition can be set as 1070 °C for 3 h at which NKN$_{0.48}$ + 1 + 1 samples can achieve a density of 97% of theoretical density.

The grain morphology of NKN$_{0.48}$ + 1 + x samples sintered at 1070 °C for 3 h is shown in Fig. 5. With the addition of SnO$_2$, the average grain size was clearly reduced up to x = 1 ($\sim$12 μm for NKN$_{0.48}$ + 1 + 0 sample, $\sim$7 μm for NKN$_{0.48}$ + 1 + 0.5 sample and $\sim$3 μm for NKN$_{0.48}$ + 1 + 1 sample). Simultaneously, the sample density becomes higher (Fig. 2); therefore, a small amount of SnO$_2$ together with CuO can promote sintering of NKN, and effectively restrict the grain growth at the same time. The formation of liquid phases and the inhibition of grain growth together improve densification by means of increasing the driving force of sintering. For CuO-doped NKN samples, obvious grain growth frequently happens particularly when the CuO content is higher [13]. It is known that the grain-coarsened piezoelectric ceramics tend to have lower mechanical strength. Additionally, it is found from the literature that it is difficult to manufacture high-Q_m alkaline niobate based lead-free piezoelectric ceramics. According to the domain stabilization mechanism in ferroelectric perovskites, less bias field tends to be formed in samples with a larger grain size
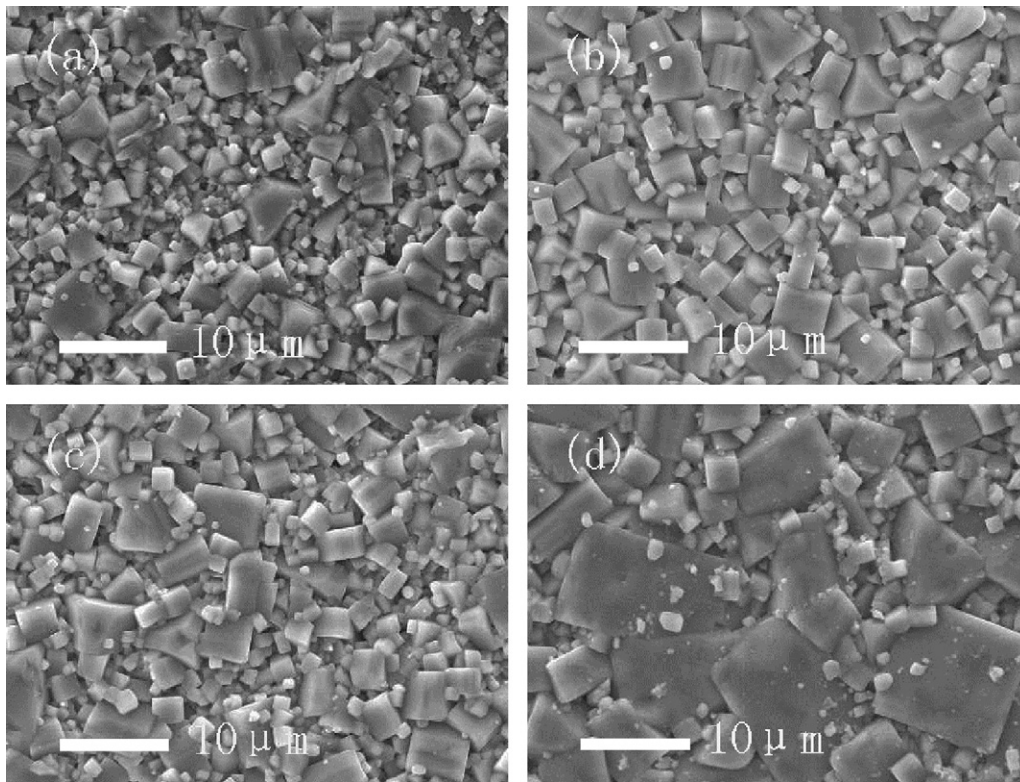
Fig. 3. SEM images of NKN$_{0.48}$ + 1 + 1 ceramics sintered at different temperatures for 3 h: (a) 1030 °C, (b) 1050 °C, (c) 1070 °C and (d) 1090 °C.

because a long-range diffusion is needed across bigger domains of piezoelectric ceramics [15]. Therefore, it makes senses to co-dope CuO and SnO$_2$ to make fine-grained low-temperature firable NKN based ceramics since SnO$_2$ as a grain growth inhibitor and CuO as a sintering aid can interact with each other. However, grains become bigger as the content of SnO$_2$ is more than 1 mol%. More liquid phase is prone to promote the grain growth. In addition, lattice defects formed due to the substitution of Sn^{4+} for Nb^{5+} may also promote the grain growth.

The dielectric constant ε_r at 1 kHz of NKN$_{0.48}$ + 1 + x samples was measured with changing temperature, as shown in Fig. 6. All compositions show two phase transitions with temperature: orthorhombic to tetragonal transition (T_{o-t}) and tetragonal to cubic transition (T_c), similar to undoped NKN ceramics. From insets of Fig. 6, it can be seen that the addition of SnO$_2$ causes a change of both temperatures. T_c decreases with increasing the content of SnO$_2$ but T_{o-t} slightly increases. The change of these two phase transition temperatures implies that Sn^{4+} really enters the lattice of NKN compositions. However, both T_c and T_{o-t} do not linearly change with increasing x, probably owing to the solubility limit of Sn^{4+} in NKN and the degree of lattice distortion.

The influence of sintering temperature on physical and electrical properties of NKN$_{0.48}$ + 1 + 1 ceramics is shown in Fig. 7. The optimum electrical properties were reached when the sample was sintered at 1070 °C mostly because the sample has the highest density at that temperature. In addition, the grain morphology may play another key role in various electrical properties. At higher sintering temperature, an obvious grain growth tends to decrease the driving force of densification. The Q_m value slightly decreases with increasing sintering temperature, probably owing to the grain growth as well, as discussed above. The grain size can be correlated with the sample density, domain size and the fraction of boundary phases. The tanδ value just shows an opposite tendency to Q_m since higher Q_m implies a lower energy loss from internal friction. As extrinsic factors, the density, grain

size, domain size and even defect type together decide the dielectric and piezoelectric properties of samples.

Fig. 8 shows the influence of SnO$_2$ content on various electrical properties of NKN$_{0.48}$ + 1 + x ceramics. As discussed above, the content of SnO$_2$ has an obvious effect on the densification and grain growth. When it is below 1 mol%, the improved sample density and the reduced grain size benefit to various electrical properties. Sn^{4+} and Cu^{2+} act as an acceptor dopant by substituting for B-site Nb^{5+}, making NKN$_{0.48}$ + 1 + x compositions electrically harder. Because the addition of a small amount of SnO$_2$ tends to inhibit the grain growth to a certain degree, the Q_m value can be further enhanced. As x = 1, various electrical properties reach the optimum values: d_{33} = 120 pC/N, k_p = 0.38, Q_m = 1040, ε_r = 710 and tanδ = 0.013. With further increasing the content of SnO$_2$, they start to decline
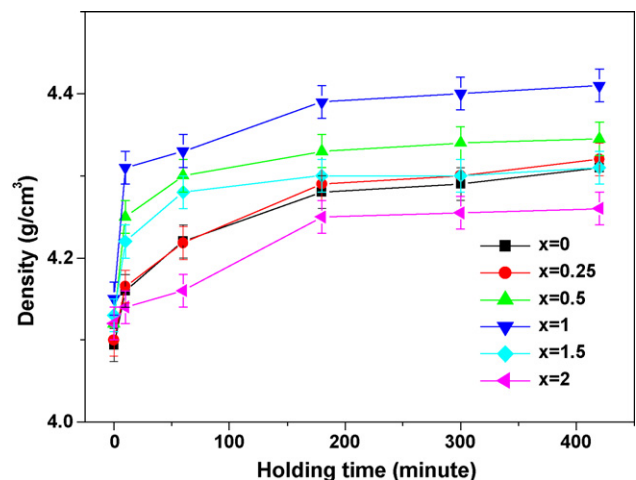

Fig. 4. Densities of NKN$_{0.48}$ + 1 + x ceramics sintered at 1070 °C for different holding time.
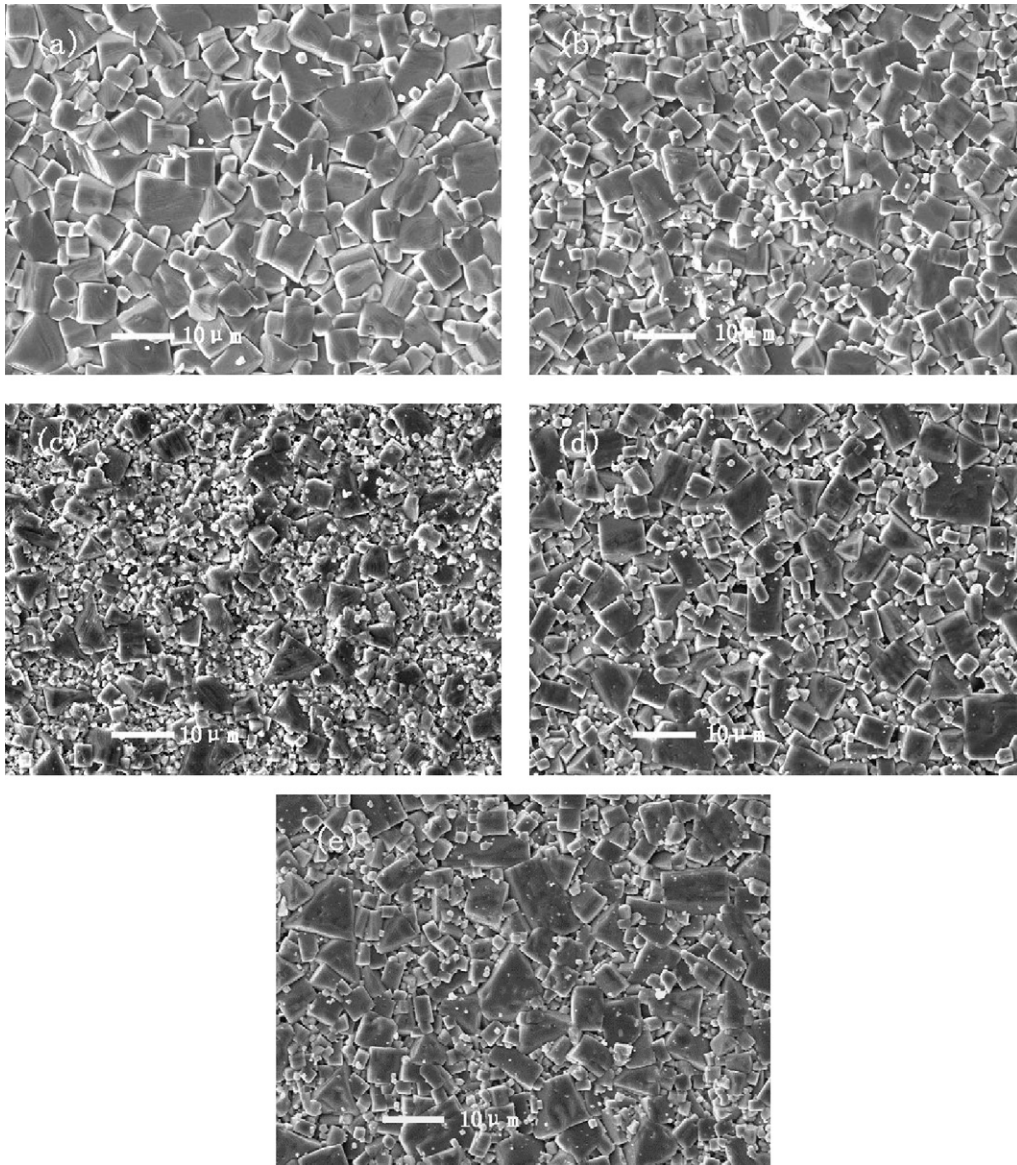
Fig. 5. SEM images of NKN$_{0.48}$ + 1 + x ceramics sintered at 1070 °C for 3 h: (a) x = 0, (b) x = 0.5, (c) x = 1, (d) x = 1.5 and (e) x = 2.
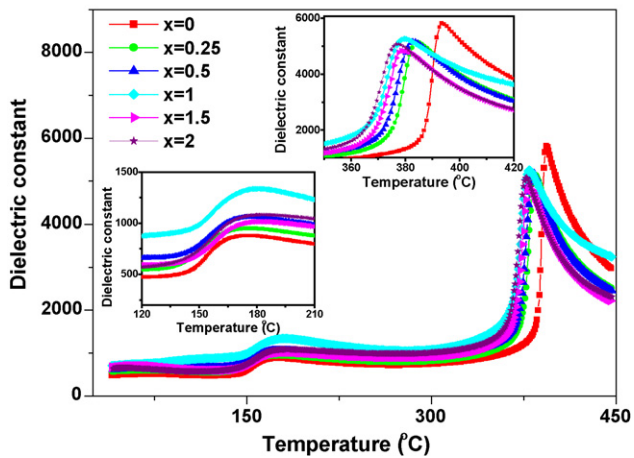

Fig. 6. Dielectric constant at 1 kHz of NKN$_{0.48}$ + 1 + x ceramics sintered at 1070 °C for 3 h. (Insets are locally magnified curves at Curie temperatures (upper right) and PPTs (lower left), respectively.)
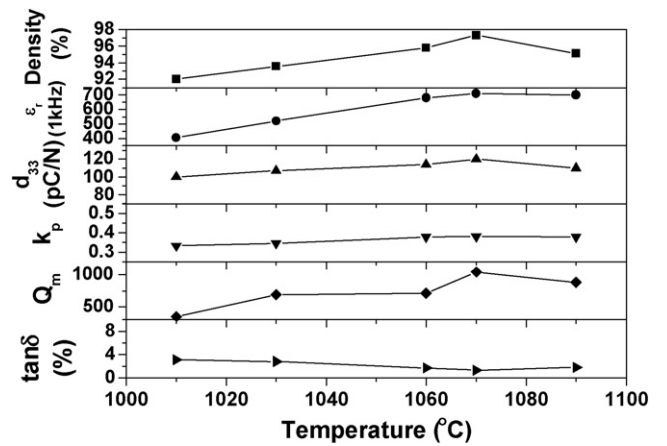

Fig. 7. Physical and electrical properties of NKN$_{0.48}$ + 1 + 1 ceramics sintered at different temperatures for 3 h.
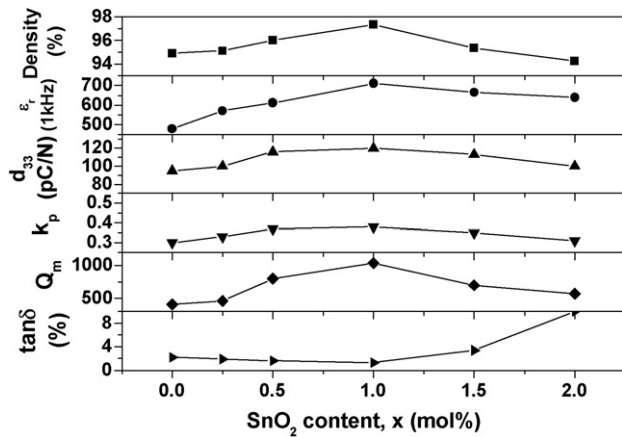
Fig. 8. Physical and electrical properties of $NKN_{0.48} + 1 + 1$ ceramics sintered at 1070 °C for 3 h.

Table 1
Comparison of piezoelectric properties for NKN modified by a small amount of CuO or Cu-containing compounds.

Compositions	d_{33} (pC/N)	k_p	Q_m
NKN + 1 mol% CuO [10]	82	0.39	2500
NKN + 1.5 mol% CuO [17]	80	0.37	844
NKN + 0.75 mol% MnO_2 + 1 mol% CuO [18]	82	0.37	1205
NKN + 0.75 mol% $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ [19]	90	0.41	1530
NKN + 1 mol% CuO + 1 mol% SnO_2 (this study)	120	0.38	1040

because of reduced density, increased grain size and even increased electrical conductivity. A comparison of electrical properties for several compositions is shown in Table 1. It can be seen that the SnO_2 and CuO_2 co-modified NKN ceramics show higher d_{33} and simultaneously maintain a high Q_m value. The contribution of fine grain morphology to the mechanical strength would be another advantage.

4. Conclusions

The influence of SnO_2 and CuO co-doping on the densification, grain growth behavior and various electrical properties of $NKN_{0.48}$

compositions were investigated. It is found that a small amount of SnO_2 plays a role as a grain growth inhibitor, in addition to the improvement of sintering. However, grains start to grow as the content of SnO_2 exceeds 1 mol%, together with a reduced sample density. Compared to CuO-doped compositions, the 1 mol% CuO and 1 mol% SnO_2 co-doped ceramics sintered at 1070 °C for 3 h show improved electrical properties: $d_{33} = 120$ pC/N, $k_p = 0.38$, $Q_m = 1040$, $\varepsilon_r = 710$ and $\tan\delta = 0.013$.

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