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Effect of Calcination Temperature on the Structural and Electrical Properties of Low-Temperature-Sintered $(Na_{0.52}K_{0.44}Li_{0.04})(Nb_{0.88}Sb_{0.08}Ta_{0.04})O_3$ Ceramics

D.Y. Lv*[1], Z. Liu[1], W.W. Jin[1], Z. Ye[1], F. Hua[1], K. Wu[1]

[1]Institute of Materials Science, Wuhu Institute of Technology, Wuhu, 241003, Anhui, P.R. China
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Abstract

Low-temperature-sintered lead-free 1.5 mol%-Na_2O-excess $(Na_{0.52}K_{0.44}Li_{0.04})(Nb_{0.88}Sb_{0.08}Ta_{0.04})O_3$ (NKN-LST) ceramics were calcined at 500 ~ 950 °C. At 500 °C, a perovskite structure of the calcined powders without crystallinity was obtained. As the calcination temperature increased, an orthogonal structure began to form. And at 750 °C, the NKN-LST powders have a single orthogonal structure. The NKN-LST powders form a tetragonal structure when the calcination temperature ≥ 800 °C. Therefore, in the calcination temperature range of 800 ~ 900 °C, the NKN-LST powders have two orthogonal and tetragonal structures. However, it can be seen that a two-phase coexistence zone of orthogonal and tetragonal structure exists in all the ceramics sintered in air at 1 020 °C for 3 h. Moreover, with increasing calcination temperature, the tetragonal phase increases. There is also an increase in the abnormal grains with increasing the calcination temperature, which may be attributable to a decrease in the critical driving force. At the same time, it has been found that the composition and structure determine the properties of NKN-LST ceramics. The optimum electrical properties of NKN-LST ceramics with a d_{33} of 384 pC/N, a k_p of 0.53, and an $\varepsilon_{33}{}^T$ of 2 735, were obtained when the ceramics were calcined at 700 °C. These properties indicated that the ceramics studied have the potential to replace lead-based ceramics in device applications. Therefore, the reduction of the calcination temperature leads to a significant improvement of 1.5 mol%-Na_2O-excess NKN-LST piezoelectric ceramics.

Keywords: Lead-free piezoelectric ceramics, low-temperature sintering, calcination, electrical properties

I. Introduction

It is known that the sintering performance of $(Na,K)NbO_3$ (NKN)-based ceramics in traditional atmospheric sintering can be significantly improved with the addition of Li, Ta and/or Sb [1–3]. NKN ceramics doped with Li, Ta and/or Sb have been found to exhibit piezoelectric properties comparable to those of lead-zirconate-titanate-based ceramics [4–5]. Research has so far been focused on designing different components [6,7], inhibiting the volatilization of the alkali elements [8], preventing the formation of secondary phase [9], and improving polarization [10].

From the industrial perspective, sintering in air is essential for mass production in order to save costs. However, for NKN-based ceramics, sintering under atmospheric pressure is exceedingly difficult. Therefore, other perovskite materials and sintering aids have been added to NKN ceramics to inhibit volatilization and improve their sintering performance [11–14].

Min-Soo Kim found that 1 mol%-Na_2O-excess NKN-5LT ceramics sintered at 1 050 °C for 4 h in air exhibited the highest properties with a d_{33} of 230 pC/N and a k_p of 0.43, respectively [15]. Generally, the calcination temperature of NKN-based ceramics is 850 °C. But after the addition of Na_2O excess, is this calcination temperature too high?

In this study, 1.5 mol% Na_2O was added as a sintering aid to $(Na_{0.52}K_{0.44}Li_{0.04})(Nb_{0.88}Sb_{0.08}Ta_{0.04})O_3$ (NKN-LST) ceramics. In our previous research, we showed that with this content of Na_2O in NKN-LST ceramics, the ceramics exhibit optimum electrical properties. The effect of the calcining temperature on the structures and properties of 1.5 mol%-Na_2O-excess NKN-LST ceramics was studied.

II. Experimental Procedure

The 1.5-mol%-Na_2O-excess, lead-free NKN-LST ceramics were fabricated by means of traditional atmospheric sintering. The raw materials comprised Na_2CO_3, K_2CO_3, Li_2CO_3, Nb_2O_5, Ta_2O_5, and Sb_2O_3. The powders were mixed, dried and then calcined twice at 550 °C – 950 °C for 3 h. After being ground in a ball mill for 24 hours, the dried powders were compacted into disk samples and sintered at 1 020 °C for 3 h in air. Silver paste was fired onto the main surfaces as electrodes at 550 °C for 30 min. The samples were poled with the application of a dc field of 3 kV/mm for 15 min at 110 °C in silicone oil.

The phase composition and microstructure of the samples were measured by means of X-ray diffraction (D8 Ad-

* Corresponding author: dan20031274@163.com

vance, Bruker, Germany) using CuKα radiation and scanning electron microscopy (SEM, SU3900, Hitachi, Japan), respectively. Dielectric curves of the ceramics were measured with the dielectric temperature spectrum testing system (GW-1H, Agilent4980a, USA). The d_{33} was measured with a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p was determined with a resonance-antiresonance method with an impedance analyzer (PV70A, China).

III. Results and Discussion

Fig. 1(a) shows the XRD patterns of 1.5 mol%-Na_2O-excess NKN-LST powders calcined twice at 550 °C – 950 °C for 3 h. A single perovskite structure is found in all compositions, indicating the formation of a series of NKN-LST powders. In addition, it was found that the calcination temperature changes the crystal structure of NKN-LST powders. NKN-LST powders have a perovskite structure when calcined twice at 550 °C, but the crystallinity of the powders was poor. With a further increase in the calcination temperature, the orthogonal phase of NKN-LST powders increased. When the calcination temperature was 750 °C, the NKN-LST powders exhibited a single orthogonal structure. The change in crystal structure can be more clearly seen from the variation of peaks from 44° to 47°, as shown in Fig. 1(b). 1.5 mol%-Na_2O-excess NKN-LST powders formed a tetragonal structure when the calcination temperature ≥ 800 °C. Therefore, it was determined that a two-phase coexistence structure exists in the calcination temperature range of 800 ~ 900 °C. Moreover, with increasing calcination temperature, the tetragonal phase of the powders increased, and when the calcination temperature reached 950 °C, the 1.5 mol%-Na_2O-excess NKN-LST powders had an almost tetragonal structure. Fig. 1(c) shows the XRD patterns of 1.5 mol%-Na_2O-excess NKN-LST ceramics that had been sintered at 1 020 °C for 3 h. It can be seen that a two-phase coexistence zone of orthogonal and tetragonal structure exists in all ceramics. Moreover, with the increase in calcination temperature, the tetragonal phase increased. This can be due to the size effect of crystal growth. This is consistent with the SEM images shown in Fig. 2.

The effect on the grain growth of 1.5 mol%-Na_2O-excess NKN-LST ceramics is shown in Fig. 2. The 1.5 mol%-Na_2O-excess NKN-LST samples sintered at 1 020 °C for 3 h obtained a high density at all calcination temperatures. The microstructure of all samples showed equiaxed matrix grains and large abnormal grains. All the abnormal and the matrix grains have faceted interfaces. The number of abnormal grains increased as the calcination temperature increased. At a calcination temperature of 750 °C, the abnormal grain size decreased because of the large grains impinging on each other, limiting further growth. The microstructure calcined at 950 °C consisted mostly of large equiaxed grains. This was the typical grain growth behavior and may be due to the change in critical driving force for rapid grain growth, resulting in the changes in the microstructure. Similar behavior has been observed in NKN-5LT ceramics with 1 mol% Na_2O and 2 mol% Na_2O [15].

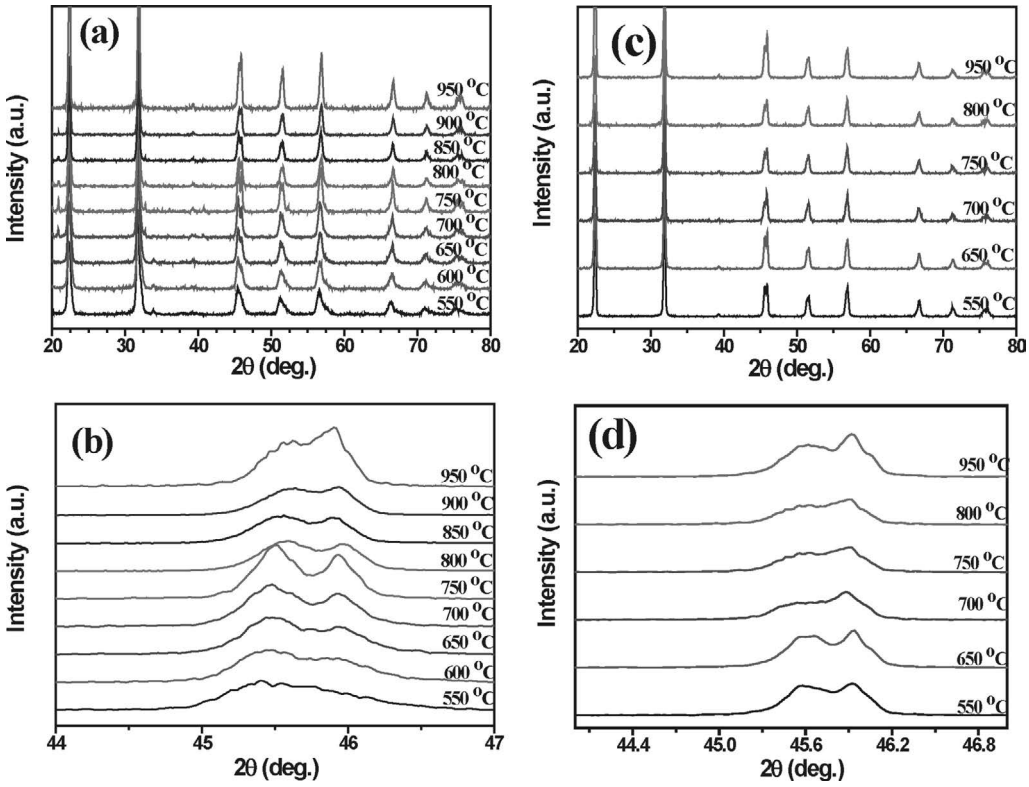

Fig. 1: (a) and (b) show the XRD patterns of 1.5 mol%-Na_2O-excess NKN-LST powders calcined twice at 550 °C ~ 950 °C for 3 h. (c) and (d) show the XRD patterns of 1.5 mol%-Na_2O-excess NKN-LST ceramics sintered at 1 020 °C for 3 h.

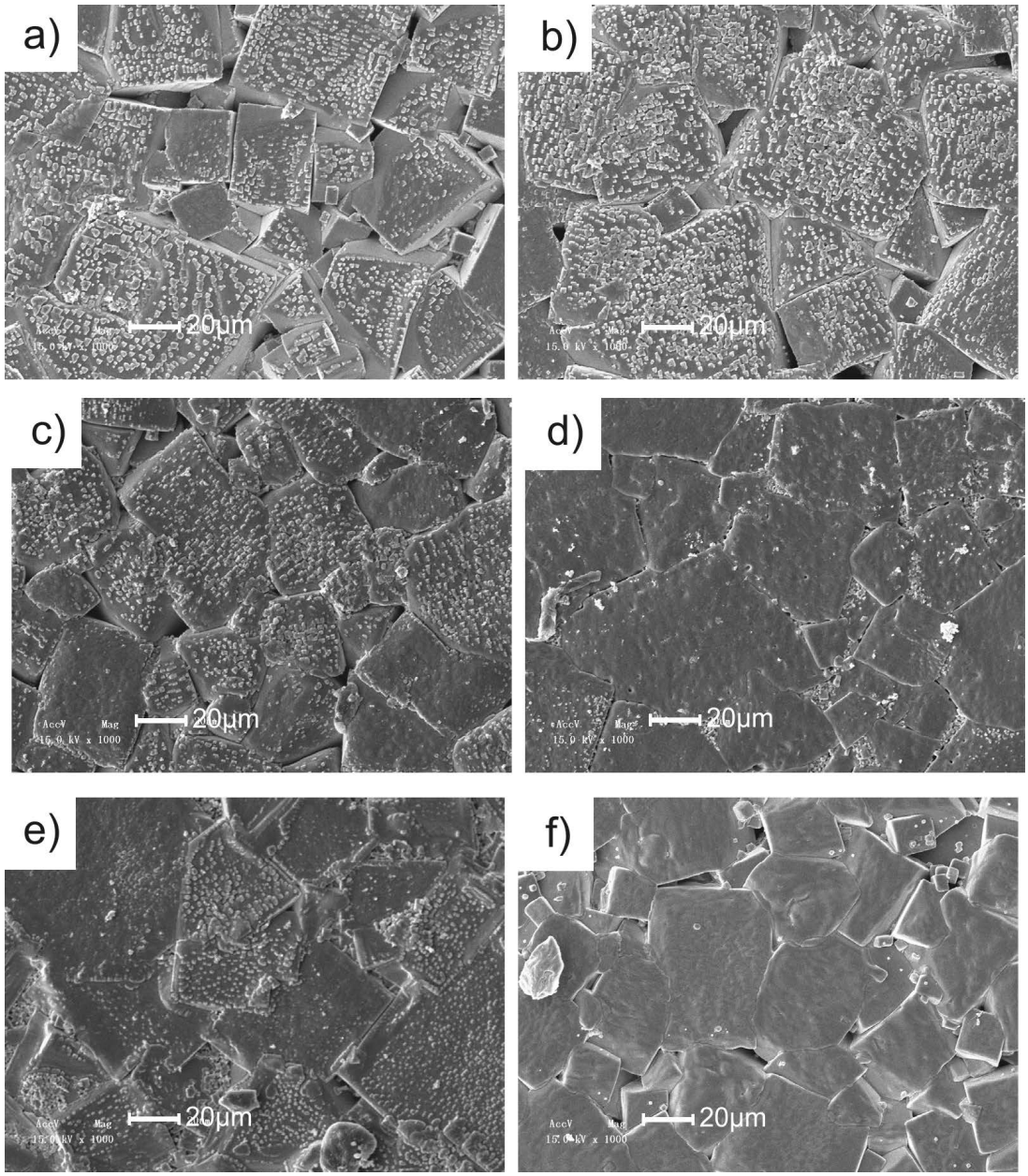

Fig. 2: Microstructures of 1.5 mol%-Na_2O-excess NKN-LST ceramics sintered at 1020 °C for 3 h. (a) calcinated at 550 °C; (b) calcinated at 650 °C; (c) calcinated at 700 °C; (d) calcinated at 750 °C; (e) calcinated at 800 °C; (f) calcinated at 950 °C.

Fig. 3 shows the dielectric temperature spectrum of the NKN-LST samples measured at 10 kHz. The tetragonal-cubic ferroelectric phase transition (T_c) and the orthorhombic-tetragonal ($T_{O\text{-}T}$) were observed for all samples. An inset shows the phase transition at $T_{O\text{-}T}$. With the increase in calcination temperature, the value of $T_{O\text{-}T}$ was shifted to room temperature, possibly because of the formation of the two-phase coexistence zone. At 700 °C, the similar phenomenon was most obvious. When calcination temperature > 700°C, the NKN-LST ceramics changed to tetragonal phase, therefore, the $T_{O\text{-}T}$ values shifted to a higher temperature. On the other hand, increasing the calcination temperature pushed T_C slightly towards a higher temperature. This probably has something to do with the increase in tetragonality as shown in Fig. 1(d). The sample calcined at 950 °C had a T_C of 261 °C approximately.

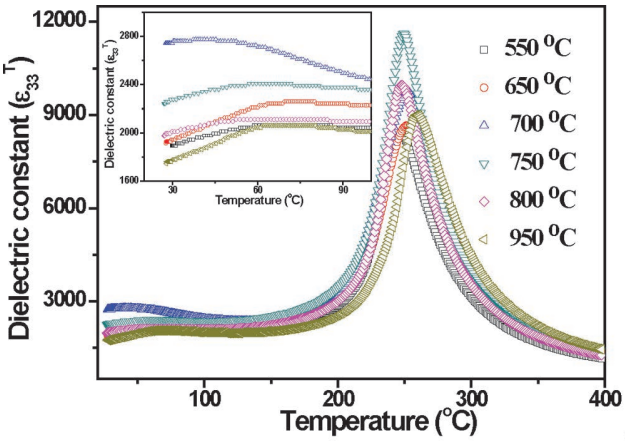

Fig. 3: Temperature dependence of the dielectric constant of 1.5 mol%-Na_2O-excess NKN-LST ceramics (10 kHz). Inset shows the phase transition of orthorhombic-tetragonal at $T_{O\text{-}T}$.

Fig. 4 shows the electrical properties of 1.5 mol%-Na_2O-excess NKN-LST ceramics sintered at 1 020 °C for 3 h, which were calcined at 500 ~ 950 °C. With increasing calcination temperature, the values of d_{33}, k_p and $\varepsilon_{33}{}^T$ increase slightly at first. At 700 °C, the electric properties reach approximately the maxima, and then fall with the further increase in calcination temperature. The dielectric and piezoelectric properties have a strong dependence on the calcination temperature of 1.5 mol%-Na_2O-excess NKN-LST ceramics, whose two ferroelectric phases coexist in all calcination temperature samples, resulting in an increase in the possible polarization states. The 1.5 mol%-Na_2O-excess NKN-LST ceramics calcined at 700 °C obtained the following optimum electrical properties: d_{33} of 384 pC/N, k_p of 0.53, and $\varepsilon_{33}{}^T$ of 2 735, respectively.

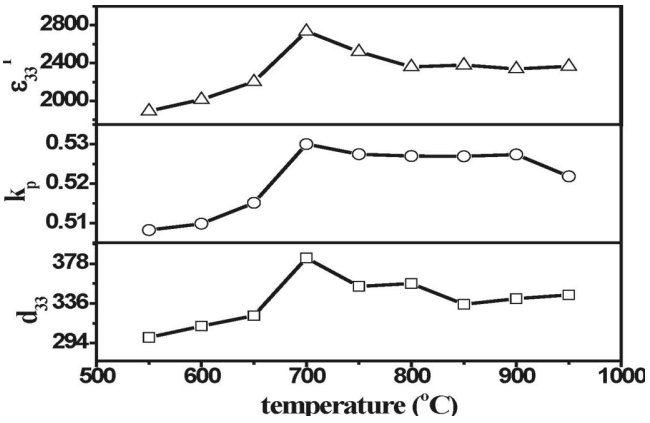

Fig. 4: Electrical properties of 1.5 mol%-Na_2O-excess NKN-LST ceramics sintered at 1 020 °C for 3 h, calcined at 500 ~ 950 °C.

IV. Conclusions

1.5 mol%-Na_2O-excess lead-free NKN-LST ceramics were fabricated by means of low-temperature sintering at 1 020 °C for 3 h; these were calcined at 500 ~ 950 °C. Their phase transition behavior, microstructure and various electrical properties were investigated. A significant improvement in the piezoelectric properties was determined with the reduction in the calcination temperature. This may be attributable to the existence of a two-phase coexistence, which causes a $T_{o\text{-}T}$ close to room temperature, increasing the possibility of polarization. Excellent overall values of d_{33} = 384 pC/N, k_p = 0.53, and $\varepsilon_{33}{}^T$ = 2 735 were obtained in the samples calcined at 700 °C. It indicates that the ceramics studied have the potential to replace lead-based ceramics in device applications.

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