Preparation and piezoelectric properties of CuO-doped $(Na_{0.5}K_{0.5})NbO_3$ ceramics by the citrate precursor method

Hongqiang Wang · Ruzhong Zuo · Li Wang ·
Jian Fang · Xiaohui Wang · Longtu Li

Abstract A low-cost citrate so-gel route was investigated to synthesize nano-sized crystalline powders (<100 nm) of 1 mol% CuO modified $(Na_{0.5}K_{0.5})NbO_3$ compositions. It was found that amorphous gels can be transformed into crystallite powders with single-phase perovskite structure when calcined at 500–600 °C for 3 h. The transmission electron microscopy observation showed that the particles are column-like and well dispersed, depending on the calcination condition. The as-pressed samples exhibit improved densification behavior and finer grain morphology after sintering. Electrical properties of the samples sintered at 1,060 °C are as follows: dielectric constant $\varepsilon_r = 605$, piezoelectric constant $d_{33} \sim 117$ pC/N, planar electromechanical coupling factor $k_p \sim 0.38$ and mechanical quality factor $Q_m \sim 725$.

1 Introduction

Lead free $(Na_{0.5}K_{0.5})NbO_3$ (NKN) compositions have attracted much attention in the last few years for their good piezoelectric and electromechanical properties and relatively high Curie temperature (~ 420 °C) [1], becoming an important candidate material for replacing conventional lead based piezoelectric materials. Unfortunately, it was well-known that pure NKN ceramics are difficult to get dense by ordinary sintering under atmospheric pressure [2–5]. A few pressure-assisted sintering techniques were applied to make dense NKN ceramics such as hot pressing, hot isostatic pressing or spark plasma sintering [6–8]. Hot-pressed NKN ceramics were reported to show high density (4.46 g/cm³, 98.9% theoretical density, TD) and excellent piezoelectric properties ($d_{33} = 160$ pC/N and $k_p = 45\%$) [6]. However, these methods cost much and restrict the sample sizes as well. Thus, a number of studies on pressureless sintering have been carried out to improve the densification and piezoelectric properties of NKN ceramics either by forming new solid solutions or by using sintering additives [9–12]. However, the use of sintering aids tends to cause the degradation of electrical properties and coarsening of the microstructure in some cases. Some new attempts such as the control of heating schedules and milling process were adopted in a conventional pressureless sintering technique [3, 13, 14].

On the other hand, wet chemical techniques, including hydrothermal and sol–gel methods have advantages in stoichiometric control and homogeneous mixing at the molecular level in order to synthesize fine oxide ceramic powders over the conventional mixed oxide route, where commercially available inorganic powders such as oxides, carbonates, and hydroxides are used as the starting chemicals. The problem is that niobium alkoxides $(C_nH_{2n+1}O)_5Nb$ used in conventional sol–gel processing are expensive and easy to hydrolyze. It will be a key issue how the cost can be reduced significantly if such wet chemical routes are used to make oxide powders. Few attempts have been made to prepare NKN powders via a citrate precursor method by dissolving Nb_2O_5 into HF solution [15–17]. Niobium oxide as Nb source was also tried to make Li doped NKN powders but the densification

H. Wang · R. Zuo (✉) · L. Wang
Institute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of Technology, 230009 Hefei, People's Republic of China
e-mail: piezolab@hfut.edu.cn

J. Fang · X. Wang · L. Li
State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, 100084 Beijing, China

behavior and piezoelectric properties of these powder compacts were not given in the Ref. [18].

In this study, a modified citrate sol–gel process using Nb_2O_5 as Nb source was employed to synthesize 1 mol% CuO doped NKN (NKN-Cu) superfine powders. A small amount of CuO was used as an acceptor dopant in order to make hard NKN ceramics [19–21]. The citrate precursors were formed by chelating niobium hydroxide with citric acid. The sintering behavior, microstructure and various electrical properties of ceramic samples from as-prepared powders were investigated in detail.

2 Experimental

Nb_2O_5 (≥99.5%), K_2CO_3 (≥99.0%), $NaNO_3$ (≥99.0%), KNO_3 (≥99.0%), citric acid (≥99.5%), glycol (≥99.0%), HNO_3 (65.0–68.0%), CuO (≥99.0%) and ammonia (25–28%) were used as raw materials. Firstly, Nb_2O_5 and K_2CO_3 were mixed and calcined at 900 °C for 2 h to form a soluble potassium niobate. Then, the as-prepared potassium niobate was dissolved in distilled water and titrated by nitric acid to obtain a precipitate of niobium hydroxide. After potassium ions were removed by means of washing several times, a soluble niobium precursor was gained, which can be chelated with citric acid. The molar ratio of citric acid to metal cations was 2:1. According to the stoichiometry of NKN-Cu, the niobium hydroxide, KNO_3 and $NaNO_3$ were introduced into the citric acid solution. CuO was firstly dissolved into nitric acid and then added to the solution. The sol was heated at 100 °C to remove redundant solvent and to form gel. Subsequently, the gel was calcined at 400–600 °C for 3 h to obtain the crystallite powders. The powders were pressed into discs and then sintered at 1,000–1,100 °C for 3 h in air. Fired-on silver paste was used as electrodes for the measurement of the electrical properties of sintered samples. The ceramics were poled in silicone oil under a dc electric field of 4–5 kV/mm at 110 °C for 15 min.

Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses of the as-prepared gel were carried out by using a simultaneous thermal analyzer (STA409C, Netzsch, Germany). The calcined powders at different temperatures were characterized by an X-ray diffractometer (XRD, D/MAX2500 VL/PC, Rigaku, Japan) and a transmission electron microscope (TEM, Model H-800, Hitachi, Japan). The microstructure of sintered samples was observed using a scanning electron microscope (SEM, JSM-6490LV, JEOL, Japan). The dielectric properties were measured as a function of temperature by a LCR meter (Agilent E4980A, USA).The piezoelectric constant d_{33} was measured directly on a quasi-static d_{33} meter (YE2730A, Sinocera, China). The electromechanical

coupling coefficient k_p was measured by a high precision impedance analyzer (PV70A, Beijing Band ERA Co., Ltd. China). Polarization versus electric field (P-E) hysteresis loops were measured under an alternating electric field using a ferroelectric measuring system (Precision LC, Radiant Technologies, Inc. USA).

3 Results and discussion

Figure 1 shows TG and DSC curves of the NKN-Cu gel. A faint endothermic peak at ~74 °C is caused by the evaporation of remaining water, and ammonia, resulting in a small weight loss of 6.1% at temperatures up to ~150 °C. There is a gentle exothermic peak at ~349 °C, which is ascribed to the thermal decomposition of excessive citrate acid and citrate complexes, accompanied by a weight loss of 41.8%. The strong exothermic peak at ~501 °C can be related to the combustion of residual organic components, with a weight loss of 19.9%. No further weight loss or peaks can be seen thereafter in the TG and DSC curves, indicating that the thermal decomposition of the NKN-Cu gel is completed before 600 °C.

The XRD patterns of NKN-Cu xerogel powders calcined at different temperatures in the 2θ range of 20° to 60° are shown in Fig. 2. The powders calcined below 400 °C exhibit typical patterns of amorphous phases. After further increasing temperature to 500 °C, the characteristic diffraction peaks of a perovskite structure begin to appear. It was known that NKN is an orthorhombic phase at room temperature, but the diffraction peaks (200) for NKN powders heat treated at 500 °C are broad and not clearly split. However, the diffraction peaks obviously change with increasing the calcination temperature, indicating a grain size induced phase structure transition [22]. Although a single perovskite phase can be formed when the sample was calcined at 500 °C, the calcination temperature of 600 °C was still chosen for the sample preparation, considering the weight loss between 500 and 600 °C as seen
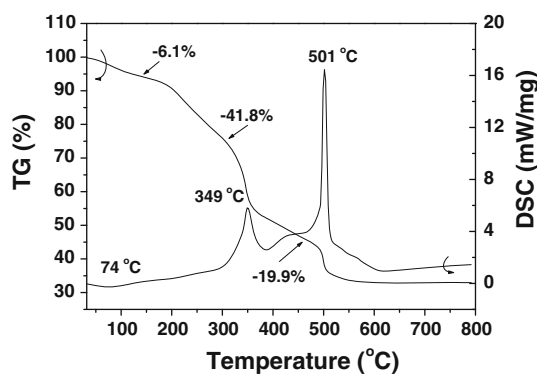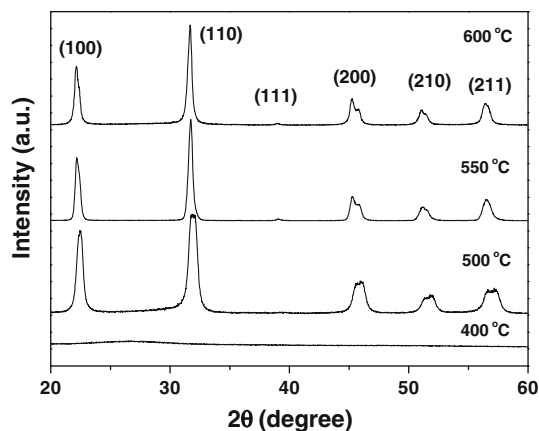

Fig. 1 TG and DSC curves of the NKN-Cu gel

Fig. 2 XRD patterns of NKN-Cu xerogel powders calcined at different temperatures

from the TG curve. Nevertheless, the calcination temperature of NKN-Cu gel powders is approximately 200–300 °C lower than that in a conventional mixed-oxide method because a molecular level mixing in a sol–gel process allows for much shorter migration distance of various ions.

Fig. 3 displays the TEM photographs of the NKN-Cu powder calcined at 500–600 °C for 3 h. It can be seen that the average particle size is about 50 nm as the powder was calcined at 500 °C, but most of the particles are clustered

into agglomerates. This could be caused by some residual organic components between particles at a relatively low calcination temperature. With increasing the calcination temperature up to 550 °C, an increase in particle size and a reduction of agglomeration can be found. The crystalline particles are mostly elongated with an average particle size of ∼100 nm and well dispersed with only a slight degree of soft agglomeration as seen in Fig. 3c. The change in particle size with the calcination temperature could indicate a possible phase transformation as discussed above. The NKN-Cu ceramics were obtained by densifying powder compacts at different sintering temperatures. The grain morphologies of ceramic samples are shown in Fig. 4. All samples have dense microstructures as they were sintered as a low temperature as 1,000 °C. A slight increase of sintering temperatures induces an obvious grain growth. The results indicate that the as-prepared powders have a good sinterability.

Typical P-E loops were obtained for NKN-Cu samples sintered at various temperatures, as shown in Fig. 5. Similar results were reported in NKN-Cu samples prepared by a conventional mixed oxide method [20, 21]. Cu ions as an acceptor dopant are most likely to occupy Nb^{5+} site, generating oxygen vacancies taking into account the valence compensation. The acceptor-oxygen vacancy defect dipoles can form internal bias field, leading to the formation of double hysteresis like loops. A slight change of loop
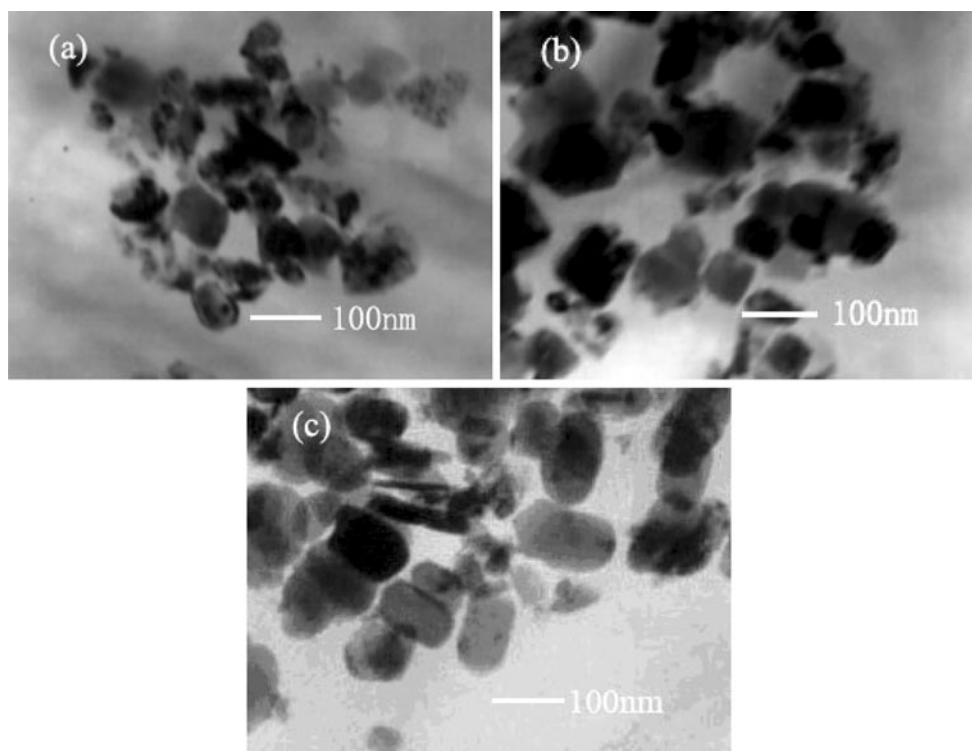
Fig. 3 TEM photographs of NKN-Cu powders calcined at different temperatures for 3 h: **a** 500 °C **b** 550 °C and **c** 600 °C
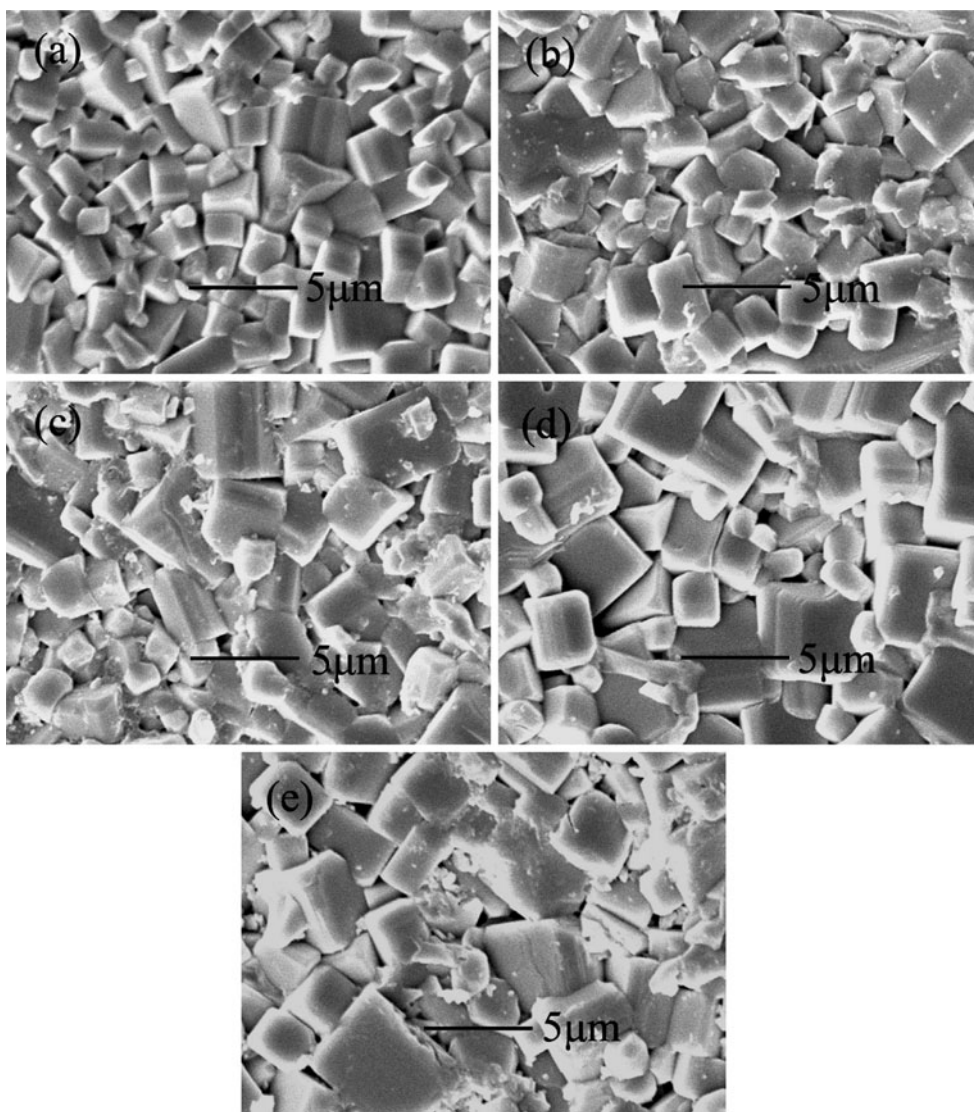
Fig. 4 SEM images of sol–gel derived NKN-Cu ceramics sintered at different temperatures: **a** 1,000 °C **b** 1,040 °C **c** 1,060 °C **d** 1,080 °C and **e** 1,100 °C

shapes for the sample sintered at different temperatures could be ascribed to the difference of grain size and sample density. The well-saturated P-E loops can be seen for all samples because all of them were well densified.
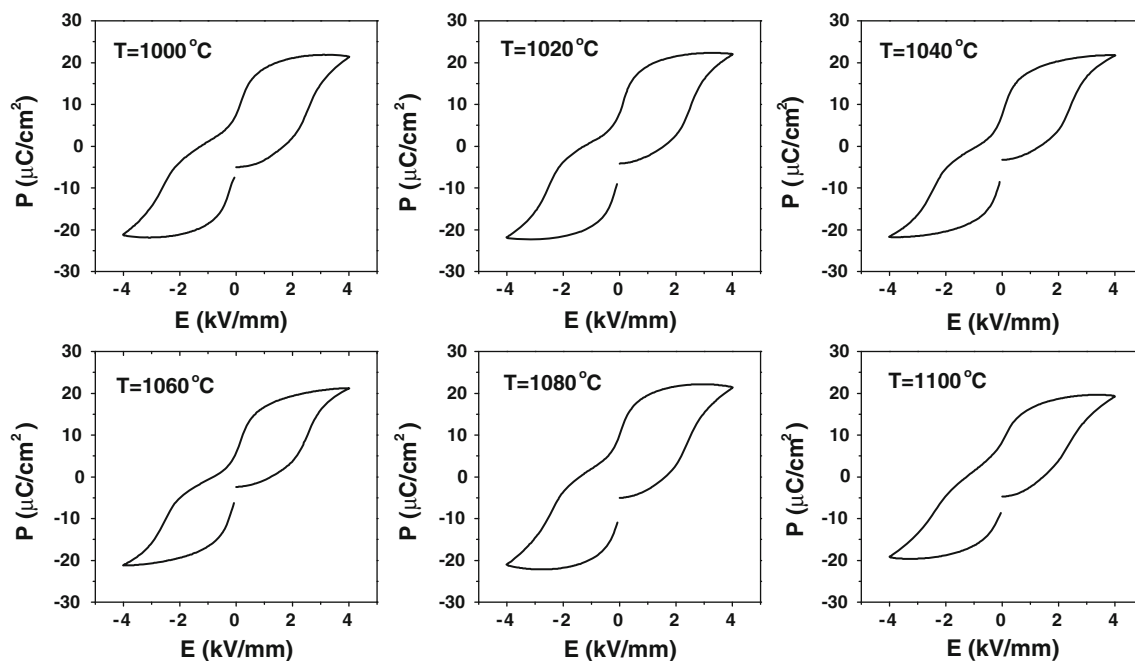
The physical and various electrical properties of NKN and NKN-Cu ceramics prepared by different synthesis methods were compared in Table 1. It can be seen that NKN-Cu ceramics prepared by a citrate sol–gel process show higher density and d_{33} values and lower sintering temperature than those made by a mixed oxide method, which can be attributed to the good sintering activity of as-prepared powders and the dense fine grain microstructure. In addition, apart from the role of sintering aids, the addition of CuO induces the hardening effect of

piezoelectric properties as previously reported [19–21], which was reflected by an obvious increase of Q_m values.

4 Conclusion

Nano-scaled NKN-Cu powders were synthesized using Nb_2O_5 as Nb source by a polymerized complex method using the citrate precursor. The crystalline powders with a single perovskite structure could be obtained after the gel was calcined at 500–600 °C. The ceramics have dense fine grain microstructure and good electrical properties when sintered at a relatively low temperature compared with those prepared by a mixed oxide method. The results

Fig. 5 P-E loops of sol–gel derived NKN-Cu ceramics sintered at different temperatures as indicated

Table 1 Physical and various electrical properties of NKN and NKN-Cu ceramics prepared by different synthesis methods

Processing	Sintering temperature (°C)	Relative density	Grain size (μm)	d_{33} (pC/N)	k_p	Q_m
NKN mixed oxide method [1, 5]	1,100–1,110	94–95%	1–2	80–110	0.36–0.39	2 25 130
NKN-Cu mixed oxide method [19–21]	1,090	96%	5–12	82–95	0.30–0.39	405–2,500
NKN-Cu sol–gel method [this study]	1,060	97%	2–3	117	0.38	725

indicate that this low-cost citrate sol–gel route could be extended to the preparation of NKN based lead-free ceramics with more complex compositions.

References

1. L. Egerton, D.M. Dillon, J. Am. Ceram. Soc. **42**, 438 (1959)
2. G. Shirane, R. Newnham, R. Pepinsky, Phys. Rev. **96**, 581 (1954)
3. R.Z. Zuo, J. Rodel, R.Z. Chen, L.T. Li, J. Am.Ceram. Soc. **89**, 2010 (2006)
4. S.H. Park, C.W. Ahn, S. Nahm, J.S. Song, Jpn. J. Appl. Phys. **43**, L1072 (2004)
5. H. Birol, D. Damjanovic, N. Setter, J. Eur. Ceram. Soc. **26**, 861 (2006)
6. R.E. Jaeger, L. Egerton, J. Am. Ceram. Soc. **45**, 209 (1962)
7. L. Egerton, C.A. Bieling, Ceram. Bull. **47**, 1151 (1968)
8. R. Wang, R. Xie, T. Sekiya, Y. Shimojo, Mater. Res. Bull. **39**, 1709 (2004)
9. M. Kosec, V. Bobnar, M. Hrovat, J. Bernard, B. Malic, J. Holc, J. Mater. Res. **19**, 1849 (2004)
10. Y.P. Guo, K. Kakimoto, H. Ohsato, Appl. Phys. Lett. **85**, 4121 (2004)
11. E. Hollemstein, M. Davis, D. Damjanovic, N. Setter, Appl. Phys. Lett. **87**, 18295 (2005)
12. R.Z. Zuo, X.S. Fang, C. Ye, Appl Phys Lett **90**, 092904 (2007)
13. D.J. Liu, H.L. Du, F.S. Tang, F. Luo, D.M. Zhu, W.C. Zhou, J. Electroceram. **20**, 107 (2008)
14. S. Tashiro, K. Nagata, Jpn. J. Appl. Phys. **43**, 6711 (2004)
15. R. Lopez, F. Gonzalez, M.E. Villafuerte-Castrejon, J. Eur. Ceram. Soc. **30**, 1549 (2010)
16. S.C. Navale, V. Samuel, V. Ravi, Mater. Lett. **59**, 2476 (2005)
17. K. Bhattacharyya, A.K. Tyagi, J. Alloys Compd. **470**, 580 (2009)
18. C. Wang, Y.D. Hou, H.Y. Ge, M.K. Zhu, H. Yan, J. Eur. Ceram. Soc. **29**, 2589 (2009)
19. E. Li, H. Kakemoto, S. Wada, T. Tsurumi, J. Am. Ceram. Soc. **90**, 1787 (2007)
20. H.Y. Park, J.Y. Choi, M.K. Choi, K.H. Cho, S. Nahm, J. Am. Ceram. Soc. **91**, 2374 (2008)
21. D.M. Lin, K.W. Kwok, H.L.W. Chan, J. Am. Ceram. Soc. **92**, 1362 (2009)
22. A. Chowdhury, J. Bould, Y.F. Zhang, C. James, S.J. Milne, J. Nanopart. Res. doi: 10.1007/s11051-009-9595-0