Compositional Inhomogeneity and Segregation in $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ Ceramics

Kepi Chen¹, Jing Tang¹, and Yan Chen²

¹*School of Energy, Power and Mechanical Engineering, North China Electric Power*

University, Beijing 102206, P. R. China

²*Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak*

Ridge, Tennessee, 37831, USA

Abstract

In this report, the effects of the calcination temperature of $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN) powder on the sintering and piezoelectric properties of KNN ceramics have been investigated. KNN powders are synthesized via the solid-state approach. Scanning electron microscopy and X-ray diffraction characterizations indicate that the incomplete reaction at 700 °C and 750 °C calcination results in the compositional inhomogeneity of the K-rich and Na-rich phases while the orthorhombic single phase is obtained after calcination at 900 °C. During the sintering, the presence of the liquid K-rich phase due to the lower melting point has a significant impact on the densification, the abnormal grain growth and the deteriorated piezoelectric properties. From the standpoint of piezoelectric properties, the optimal calcination temperature obtained for KNN ceramics calcined at this temperature is determined to be 800 °C, with piezoelectric constant $d_{33}=128.3$ pC/N, planar electromechanical coupling coefficient $k_p=32.2\%$, mechanical quality factor $Q_m=88$, and dielectric loss $\tan\delta=2.1\%$.

1. Introduction

(K,Na)NbO₃ (KNN)-based lead-free ceramics have attracted considerable attention due to their excellent piezoelectric properties and high Curie temperature [1-6]. However, it is difficult to obtain dense KNN-based ceramics by a conventional sintering process because of the high volatility of alkaline elements, narrow sintering temperature range, and compositional segregation [4, 5]. It is well known that sintering of the ceramic green body can be affected by the characteristics of the powders that depend on the synthesis method and processing [7]. To date, it has been reported that KNN ceramic powders can be synthesized by chemical methods such as solid-state reaction (SSR) [8-12], hydrothermal [13-15], sol-gel [16-18], precipitation [19], and mechanochemical activation [20] et al. Among these synthesis methods, SSR is an accessible and inexpensive approach, and it is thus widely employed for KNN synthesis. Generally, alkaline carbonates, such as K₂CO₃ and Na₂CO₃, have been used as starting materials for the synthesis of KNN ceramic powder by SSR. According to Malic et al., the KNN solid solution forms via the intermediate (K,Na)₂Nb₄O₁₁ phase, with the rate of the diffusion-controlled reaction determined by the diffusion of the slower species [21]. The difference between the K⁺ and Na⁺ diffusion rates likely leads to local inhomogeneity in the KNN solid solution, which can, in principle, be diminished by increasing the calcination temperature [21]. However, the elevated calcination temperature may result in severe evaporation of alkaline elements. To date, most studies report calcination temperatures between 750 °C and 950 °C [8]. To the best of our knowledge, there have been few reports on

1 the effects of the calcination temperature of KNN powders on the sintering and
2
3 piezoelectric properties of KNN ceramics. In this paper, the effects of calcination
4
5 temperature on these properties are systematically investigated in detail.
6
7
8
9

10 **2. Experimental Procedure**

11
12 $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ samples were prepared by the conventional mixed-oxide process
13
14 using K_2CO_3 (>99%), Na_2CO_3 (>99.8%) and Nb_2O_5 (>99.5%) as starting materials.
15
16 Prior to use, the carbonates were dried at 120 °C for 12 h, and then all powders were
17
18 weighed according to the nominal compositions and ball-milled for mixing for 6 h in
19
20 a nylon jar with zirconia balls. The mixed powders were dried and then calcined in an
21
22 alumina crucible at 700 °C~900 °C with a step of 50 °C for 2 h. For convenience of
23
24 description, the calcined powders were labeled as KNN700, KNN750, KNN800,
25
26 KNN850, and KNN900. For the fabrication of ceramics, the calcined powders were
27
28 ball-milled for 6 h and dried. The pellets were prepared by pressing the powders in a
29
30 15 mm diameter die at 100 MPa, then sintering at 1040 °C to 1080 °C for 4 h and
31
32 finally furnace-cooling to room temperature.
33
34
35
36
37
38
39
40
41
42
43
44
45

46 The phases in the calcined powders were identified using X-ray powder
47
48 diffraction (XRD, D8 ADVANCE A25, Bruker, Germany). The particle size and
49
50 morphology of the calcined powders and the microstructure of the sintered samples
51
52 were characterized using scanning electron microscopy (SEM, Hitachi S4800, Ibaraki,
53
54 Japan). To measure the electrical properties, silver electrodes were coated on both
55
56 surfaces of each sintered disks by firing at 550 °C for 20 min. The samples were
57
58
59
60
61
62
63
64
65

1 immersed in silicone oil and poled in a 3 kV/ mm field at room temperature or 120 °C
2
3 for 30 min. The piezoelectric constant d_{33} was measured using a quasistatic
4
5 piezoelectric constant testing meter (ZJ-4AN, Institute of Acoustics, Chinese
6
7 Academy of Sciences, Beijing, China). The electromechanical coupling factor k_p and
8
9 mechanical quality factor Q_m were measured using an impedance analyzer (PV 80,
10
11 Beijing, China).
12
13
14
15

16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65

The SEM images of calcined KNN powders are shown in Fig. 1. The calcination temperature has a significant effect on the particle size and morphology of KNN powders. In KNN700 and KNN750, irregular nanosized particles can be observed. When calcination temperature reached 800 °C, cuboid particles appear. Further increase of the calcination temperature leads to a larger population and coarsening of the cuboid particles. The sub-micrometer cuboid particle is observed in KNN900. The formation of cuboid particle is considered to be related to the presence of the liquid phase [11].

The XRD patterns of the powders calcined at various temperatures in the 700 °C-900 °C temperature range are shown in Fig. 2(a). Broad peaks near the expected positions of the desired KNN phase were present in the sample calcined at 700 °C for 2 h. However, as shown in Fig. 2(b), the peaks progressively sharpened and shifted toward lower 2θ values as the calcination temperature was increased,

1 suggesting that the product obtained by calcination at 700-850°C was not a
2
3 chemically homogeneous solid solution phase. As stated previously, this
4
5 compositional inhomogeneity in solid solution resulted from the difference between
6
7 the diffusion rates of sodium and potassium ions. Spatial variations in the Na and K
8
9 fractions due to the incomplete reaction would produce a series of KNN solid
10
11 solution with different K/Na coexisting in the sample. For simplicity, we
12
13 hypothesize that the KNN sample consists of a K-rich phase and a Na-rich KNN
14
15 phase. According to the KNbO_3 - NaNbO_3 phase diagram, the melting temperature is
16
17 elevated in the Na-rich phase and is lowered in the K-rich phase from the 1110 °C
18
19 melting point of the chemically homogeneous $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ [22]. Therefore,
20
21 appropriate compositional segregation that produces more of the K-rich phase at
22
23 low calcination temperature (i.e., 700 °C) should give rise to a lower sintering
24
25 temperature for KNN, as will be verified in the discussion below.
26
27
28
29
30
31
32
33
34
35
36
37
38

39 To study the effect of calcination temperature on the sintering of KNN ceramics,
40
41 the radical shrinkage of KNN discs sintered at 1040-1080 °C was measured with the
42
43 results presented in Fig. 3. It can be seen that the calcination temperature has a
44
45 significant impact on the sintering of KNN ceramics. For KNN ceramics that were
46
47 sintered at a single temperature, lower calcination temperature corresponded to higher
48
49 shrinkage, indicating that lower calcination temperature KNN powders could be
50
51 sintered to high density at lower temperatures. We note that in particular for KNN700
52
53 and KNN750, the highest shrinkage is obtained by 1070 °C sintering, whereas for
54
55
56
57
58
59
60
61
62
63
64
65

1 KNN800, KNN850 and KNN900, maximum shrinkage is observed after sintering at
2
3 1080 °C. Moreover, the maximum shrinkage and density for all the sintered samples
4
5 were observed in the KNN700 sample sintered at 1070 °C, which cannot be explained
6
7 based only on the powder particle size. Microstructure observations discussed below
8
9 indicate that the K-rich phase in KNN700 and KNN800 powders plays a key role in
10
11 microstructure evolution.
12
13
14
15
16
17
18
19

20 The powder calcination temperature influences the microstructure of KNN
21
22 ceramics ,as seen from Fig. 4 that shows the comparison of the ceramics sintered from
23
24 the KNN700 and KNN800 powders. For KNN700 powders, the grain size of the
25
26 ceramic slightly increased as the sintering temperature increased from 1040 °C to
27
28 1060 °C. With sintering at 1070 °C, the grains grow further, and the ceramic density
29
30 reaches the maximum. However, a few cubic-like grains with abnormal growth begin
31
32 to appear. The higher sintering temperature of 1080 °C does not aid to further
33
34 densification. In contrast, the coarse grains form over the sample by completely
35
36 eliminating the fine grains, resulting in large-grained ceramics. The cubic-shaped,
37
38 instead of equiaxed, grains of KNN are unlikely to aid in achieving a high packing
39
40 density. In KNN750, a sintering behavior similar to that in KNN700 was observed. By
41
42 contrast, the KNN800 powders, in which the grains gradually grow as the sintering
43
44 temperature is elevated, do not exhibit abnormal grain growth after sintering at
45
46 temperature up to 1080 °C (Fig. 4(b)). The powders calcined at higher temperatures,
47
48 i.e., KNN850 and KNN900, exhibit sintering behaviors similar to that of KNN800.
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

The abnormal grain growth in KNN has been reported previously, but the mechanism has not been well understood [23-25]. For the results in the present work, the presence of liquid phase likely plays a crucial role on this microstructure evolution. For KNN700 and KNN750 sintered at 1070 °C and 1080 °C, the liquid K-rich phase was formed due to the lower melting point that aids the densification as well as the abnormal grain growth, as shown in Fig. 4(a). For KNN800, KNN850 and KNN900 samples where less of the K-rich phase was formed, the KNN ceramics were densified via a solid state sintering process, and therefore, no abnormal grain growth occurred (Fig. 4(b)). According to the KNbO_3 - NaNbO_3 phase diagram, formation of the liquid phase must result in compositional segregation, leading to a severe deterioration in the electrical properties [22, 26].

The piezoelectric d_{33} constants of KNN ceramics synthesized at various temperatures are plotted as a function of the sintering temperature in Fig. 5. For KNN700 and KNN750 ceramics, the peak d_{33} values were reached at the sintering temperature of 1060 °C, even though maximum density was achieved at 1070 °C (Fig. 3). When the sintering temperature was further increased to 1070 °C and 1080 °C, a sharp decline in d_{33} was observed (Fig. 5). In contrast, for KNN800 and KNN850 ceramics, the peak d_{33} values were obtained after sintering at 1070 °C. The increase of the sintering temperature to 1080 °C only reduced the d_{33} slightly, probably due to the evaporation of alkaline elements at higher temperature.

As shown in Fig. 6, the piezoelectric properties of KNN are optimized by controlling the calcination temperature. The calcination temperature of 800 °C results in optimal piezoelectric properties. Because polarization can also affect the piezoelectric properties of ferroelectric ceramics, it is found that the KNN samples polarized at 120 °C show better dielectric and piezoelectric properties than those poled at RT. The difference is probably due to easier ferroelectric domain switching [27] or stress relief [28] during poled at 120 °C. The KNN ceramics obtained from powders calcined at 800 °C showed the following optimal values: piezoelectric constant d_{33} =128.3 pC/N, planar electromechanical coupling coefficient k_p =32.2%, mechanical quality factor Q_m =88, and dielectric loss $\tan\delta$ =2.1%.

4. Conclusions

(K_{0.5}Na_{0.5})NbO₃ powders were synthesized by the conventional mixed-oxide process using K₂CO₃, Na₂CO₃ and Nb₂O₅ as starting materials. An orthorhombic single-phase product could not be obtained until calcination temperature reached 900 °C. The K-rich phase in KNN powders calcined at 700 °C and 750 °C has a significant impact on the sintering, microstructure evolution, and piezoelectric properties. The presence of the liquid phase due to the melting of the K-rich phase results in densification, abnormal grain growth, compositional segregation, and deteriorated piezoelectric properties. From the standpoint of piezoelectric properties,

the optimal calcination temperature is 800 °C. The optimal values obtained for the KNN ceramics poled at 120 °C were as follows: piezoelectric constant d_{33} =128.3 pC/N, planar electromechanical coupling coefficient k_p =32.2%, mechanical quality factor Q_m =88, and dielectric loss $\tan\delta$ =2.1%.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21371056 and 51372202) and the Fundamental Research Funds for the Central Universities (Grant No. 2015ZZD04). Y. Chen acknowledges the support from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering.

References

- [1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, *Nature*, 432 (2004) 84-87.
- [2] T.R. Shrout, S.J. Zhang, Lead-free piezoelectric ceramics: Alternatives for PZT?, *J. Electroceram.*, 19 (2007) 113-126.
- [3] P.K. Panda, Review: environmental friendly lead-free piezoelectric materials, *J. Mater. Sci.*, 44 (2009) 5049-5062.
- [4] J. Rodel, W. Jo, K.T.P. Seifert, E.-M. Anton, T. Granzow, D. Damjanovic, Perspective on the Development of Lead-free Piezoceramics, *J. Am. Ceram. Soc.*, 92 (2009) 1153-1177.
- [5] J.-F. Li, K. Wang, F.-Y. Zhu, L.-Q. Cheng, F.-Z. Yao, (K, Na) NbO₃-Based

1 Lead-Free Piezoceramics: Fundamental Aspects, Processing Technologies, and
2
3 Remaining Challenges, J. Am. Ceram. Soc, 96 (2013) 3677-3696.
4

5
6 [6] J.G. Wu, D.Q. Xiao, J.G. Zhu, Potassium-Sodium Niobate Lead-Free Piezoelectric
7
8 Materials: Past, Present, and Future of Phase Boundaries, Chem. Rev., 115 (2015)
9
10 2559-2595.
11

12
13
14 [7] M.N. Rahaman, Ceramic processing and sintering, 2nd Revised ed., Marcel
15
16 Dekker Inc., New York, 2003.
17

18
19
20 [8] B. Malic, A. Bencan, T. Rojac, M. Kosec, Lead-free piezoelectrics based on
21
22 alkaline niobates: synthesis, sintering and microstructure, Acta Chim. Slov., 55 (2008)
23
24 719-726.
25

26
27
28 [9] H. Jiang, T.T. Su, H. Gong, Y.C. Zhai, Direct preparation of $K_{0.5}Na_{0.5}NbO_3$
29
30 powders, Cryst. Res. Technol., 46 (2011) 85-89.
31

32
33
34 [10] M. Senna, J. Pavlic, T. Rojac, B. Malic, M. Kosec, G. Brennecke, Preparation of
35
36 Phase-Pure $K_{0.5}Na_{0.5}NbO_3$ Fine Powders by a Solid-State Reaction at 625°C from a
37
38 Precursor Comprising Nb_2O_5 and K, Na Acetates, J. Am. Ceram. Soc, 97 (2014)
39
40 413-419.
41

42
43
44 [11] P. Bomlai, P. Wichianrat, S. Muensit, S.J. Milne, Effect of calcination conditions
45
46 and excess alkali carbonate on the phase formation and particle morphology of
47
48 $Na_{0.5}K_{0.5}NbO_3$ powders, J. Am. Ceram. Soc, 90 (2007) 1650-1655.
49

50
51
52 [12] J. Acker, H. Kungl, M.J. Hoffmann, Influence of Alkaline and Niobium Excess
53
54 on Sintering and Microstructure of Sodium-Potassium Niobate ($K_{0.5}Na_{0.5}$) NbO_3 , J.
55
56 Am. Ceram. Soc, (2010).
57
58
59
60
61
62
63
64
65

- [13] D. Zhang, F. Shi, J. Cheng, Z. Cheng, X. Yang, G. Zheng, M. Cao, Modified hydrothermal synthesis and structural characterization of monoclinic $(K_xNa_{1-x})NbO_3$ ($0.05 \leq x \leq 0.15$) rods, *Ceram. Int.*, 41 (2015) 8837-8842.
- [14] H. Gu, K. Zhu, X. Pang, B. Shao, J. Qiu, H. Ji, Synthesis of (K, Na) (Nb, Ta)O₃ lead-free piezoelectric ceramic powders by high temperature mixing method under hydrothermal conditions, *Ceram. Int.*, 38 (2012) 1807-1813.
- [15] R. López-Juárez, R. Castañeda-Guzmán, M.E. Villafuerte-Castrejón, Fast synthesis of NaNbO₃ and K_{0.5}Na_{0.5}NbO₃ by microwave hydrothermal method, *Ceram. Int.*, 40 (2014) 14757-14764.
- [16] D.-Q. Zhang, Z.-C. Qin, X.-Y. Yang, H.-B. Zhu, M.-S. Cao, Study on synthesis and evolution of sodium potassium niobate ceramic powders by an oxalic acid-based sol-gel method, *J. Sol-Gel Sci. Technol.*, 57 (2010) 31-35.
- [17] Y. Cao, K. Zhu, H. Zheng, J. Qiu, H. Gu, Synthesis of potassium sodium niobate powders using an EDTA/citrate complexing sol-gel method, *Particuology*, 10 (2012) 777-782.
- [18] G.H. Khorrami, A. Kompany, A. Khorsand Zak, A facile sol-gel approach to synthesize KNN nanoparticles at low temperature, *Mater. Lett.*, 110 (2013) 172-175.
- [19] P. Kumar, M. Pattanaik, Sonia, Synthesis and characterizations of KNN ferroelectric ceramics near 50/50 MPB, *Ceram. Int.*, 39 (2013) 65-69.
- [20] R. Singh, P.K. Patro, A.R. Kulkarni, C.S. Harendranath, Synthesis of nano-crystalline potassium sodium niobate ceramic using mechanochemical activation, *Ceram. Int.*, 40 (2014) 10641-10647.

- [21] B. Malic, D. Jenko, J. Holc, M. Hrovat, M. Kosec, Synthesis of sodium potassium niobate: A diffusion couples study, *J. Am. Ceram. Soc.*, 91 (2008) 1916-1922.
- [22] J. Fang, X. Wang, R. Zuo, Z. Tian, C. Zhong, L. Li, Narrow sintering temperature window for (K, Na)NbO₃-based lead-free piezoceramics caused by compositional segregation, *Phys. Status Solidi A*, 208 (2011) 791-794.
- [23] Y. Zhen, J.-F. Li, Abnormal grain growth and new core shell structure in (K, Na)NbO₃-based lead-free piezoelectric ceramics, *J. Am. Ceram. Soc.*, 89 (2007) 3496-502.
- [24] J. G. Fisher, S.-J. Kang, Microstructural changes in (K_{0.5}Na_{0.5})NbO₃ ceramics sintered in various atmospheres, *J. Eur. Ceram. Soc.*, 38 (2009) 227-49.
- [25] C.-W. Ahn, C.-S. Park, C.-H. Chang, S. Nahm, M.-J. Yoo, H.-G. Lee, S. Priya, Sintering behavior of lead free (K,Na)NbO₃-based piezoelectric ceramics, *J. Am. Ceram. Soc.*, 92 (2009) 2033-2038.
- [26] S. Zhang, H.J. Lee, C. Ma, X. Tan, A. Fetiera, Sintering Effect on Microstructure and Properties of (K,Na)NbO₃ Ceramics, *J. Am. Ceram. Soc.*, 94 (2011) 3659-3665.
- [27] H.-l. Du, F.-s. Tang, Z.-m. Li, W.-c. Zhou, S.-b. Qu, Z.-b. Pei, Effect of poling condition on piezoelectric properties of (K_{0.5}Na_{0.5})NbO₃ ceramics, *Trans. Nonferrous Metal Soc. Ch.*, 16 (2006) s462-s465.
- [28] F. Rubio-Marcos, J.J. Romero, D.A. Ochoa, J.E. García, R. Perez, J.F. Fernandez, Effects of Poling Process on KNN-Modified Piezoceramic Properties, *J. Am. Ceram. Soc.*, 93 (2010) 318-321.

List of figure captions

Fig. 1 SEM images of KNN powders calcined at (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C, and (e) 900 °C for 2 hours.

Fig. 2 X-ray diffraction patterns of (a) the calcined KNN powders and (b) a magnified view of the patterns at $2\theta=44.2^\circ \sim 48^\circ$.

Fig. 3 Contour plot of radical sintering shrinkage variation with calcination temperature and sintering temperature for KNN ceramics.

Fig. 4 SEM images of KNN ceramics obtained from powders calcined at (a) 700 °C and (b) 800 °C.

Fig. 5 Piezoelectric constant d_{33} of KNN ceramics obtained from powders calcined at various temperatures.

Fig. 6 Optimization of piezoelectric properties of KNN samples poled at room temperature and 120 °C.

Figure1

FIGURES

Figure2

Figure3

Figure4

Figure5

Figure6