Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 5931–5935

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Synthesis and characterization of single-crystalline (K,Na)NbO_3 nanorods

De-Qing Zhang[a,b,*], Da-Wei Wang[b], Hou-Bin Zhu[a], Xiu-Ying Yang[a], Ran Lu[b], Bo Wen[b], Wen-Qiang Cao[c], Jie Yuan[b], Mao-Sheng Cao[b]

[a]School of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, China
[b]School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
[c]School of EMPS, University College Dublin, Dublin 4, Ireland

Received 28 October 2012; received in revised form 22 November 2012; accepted 22 November 2012
Available online 1 December 2012

Abstract

A modified sol–gel method was used to synthesize single-crystalline lead-free (K,Na)NbO_3 (KNN) nanorods. The effects of calcination temperature and heating rate on the crystal structure and morphology were examined. At low heating rate, it was found that with increasing calcination temperature, the crystallization of KNN gradually completed and the size of the one-dimensional rods increased significantly. On the other hand, increasing heating rate changed the morphology of KNN from one-dimensional rods to cubes. The as-synthesized KNN nanorods calcined at 750 °C with heating rate of 1 °C/min were determined to be orthorhombic single crystals of 100–400 nm wide and 1–2 μm long.

Keywords: (K,Na)NbO3; Sol–gel; Nanorods; Lead free

1. Introduction

For the past 50 years, Pb(Zr,Ti)O_3 (PZT) based piezoelectric ceramics have been widely used in electronic devices, including actuators, sensors, and transducers; the extensive use of these ceramics is due to their good dielectric and piezoelectric properties [1,2]. However, the high lead content of PZT-based ceramics could cause severe environmental issues. Thus, developing environment-friendly lead-free piezoelectric materials to replace PZT is desirable [3,4].

Perovskite (K,Na)NbO_3 (KNN) lead-free piezoelectric ceramics, one of the most important lead-free materials, were first fabricated in the 1950s [5]. Recently, the textured (Li,Ta,Sb)-modified KNN has been reported to exhibit high piezoelectric properties comparable to those of PZT [6]. As a result, numerous studies on the KNN system have been carried out to improve its piezoelectric properties [3–8]. With different additions, such as $LiTaO_3$, $LiNbO_3$, $LiSbO_3$, and $SrTiO_3$, the KNN-based materials were reported to exhibit "soft" piezoelectric behavior analogous to donor-doped PZT materials, indicating that KNN is indeed one of the most promising lead-free piezoelectric materials [9–14].

In the past few years, one-dimensional lead-free ferroelectric perovskites, including nanoneedles, nanowires, nanobars, and nanotubes, have been studied with increasing intensity because of their potential use in non-volatile ferroelectric random access memory, nanoelectromechanical systems, energy-harvesting devices, advanced sensors, and photocatalysis [15–20]. More recently, KNN nanotube arrays with diameters of ~200 nm and wall thickness of ~30 nm to 40 nm were synthesized by Zhou et al. using a sol–gel method with anodic aluminum oxide templates, exhibiting classic ferroelectric behavior [19]. Xu et al. synthesized one-dimensional single-crystalline KNN nanobars through a topochemical method based on molten salt synthesis. The effective piezoelectric coefficient d_{33}^* of 113 pm/V of an individual KNN nanobar was measured

*Corresponding author at: Qiqihar University, School of Materials Science and Engineering, No. 42, Wenhua street, Qiqihaer, Heilongjiang 161006, China. Tel.: +86 18604521203.
E-mail address: zhdqing@163.com (D.-Q. Zhang), caomaosheng@bit.edu.cn (M.-S. Cao).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.11.065

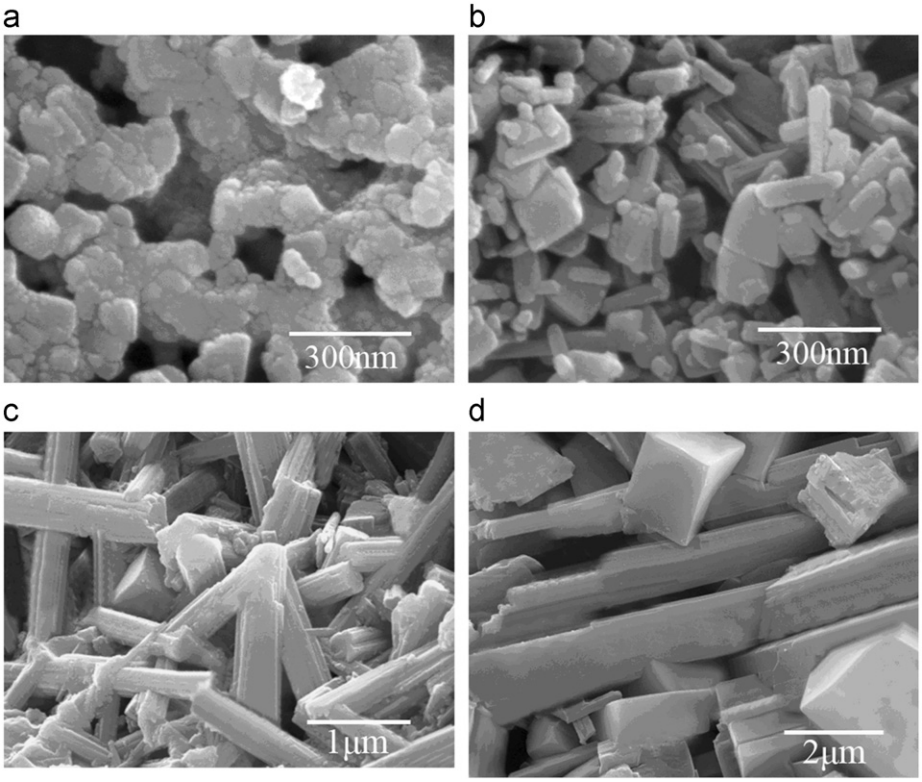

Fig. 1. SEM images of the KNN powders calcined at different temperatures with a heating rate of 1 °C/min: (a) 650 °C, (b) 700 °C, (c) 750 °C and (d) 800 °C.

via scanning probe microscopy. The resulting piezoelectric coefficient was higher than that of bulk ceramics prepared by conventional solid-state reaction [20]. In this work, a one-dimensional rod-like single-crystalline (K,Na)NbO_3 (KNN) was successfully synthesized through a modified sol–gel method. The effects of calcination temperature and heating rate on the crystal structure and morphology of the nanorods were investigated. The probable growth behavior and mechanism were proposed.

2. Experimental procedures

Analytical reagent grade Rochelle salt, oxalic acid, and ethanediol were used as raw materials. $Nb(OH)_5$ was used as a source of Nb, as described elsewhere [21]. First, $Nb(OH)_5$ was dissolved in an oxalic acid solution (with a molar ratio of 1:3) for 30 min. Then, at the molar ratio of $n(Na^+):n(K^+):n(Nb^{5+})=1:1:2$, Rochelle salt was added into the solution and allowed to react for 30 min. Ammonia water was used to adjust the pH value between 2.5 and 3.5. Finally, ethanediol with a molar ratio of n(oxalic acid):n(ethanediol)=1:2 was added into the solution and allowed to react for 2 h to obtain the sol. The as-prepared sol was dried at 120 °C for 24 h to extract the light yellow and subtranslucent xerogel. The xerogel was calcined at 600 °C to 800 °C at different heating rates (1, 2, 3 °C/min) for 3 h to obtain the KNN powder.

The crystalline phases were identified through X-ray diffraction analysis (XRD, Ni-filtered Cu K_α radiation, 40 kV). The microstructures of the samples were observed with a scanning electron microscope (SEM, Hitachi S-4300, Japan) and a transmission electron microscope (TEM, JEOL JEM-2010, Japan).

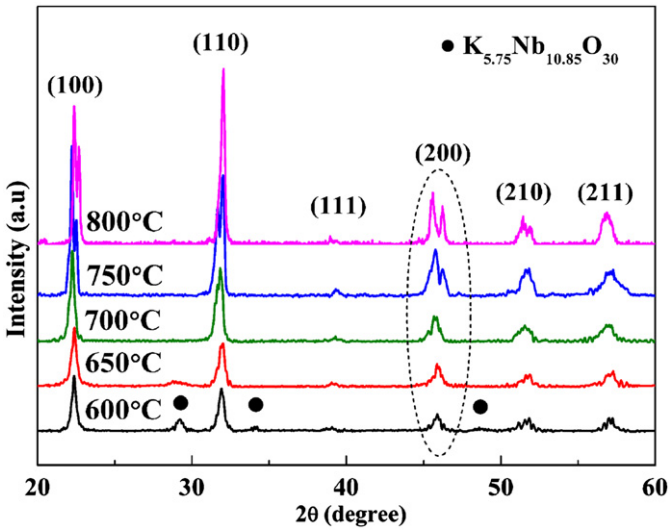

Fig. 2. XRD patterns of the KNN powders calcined at different temperatures (600 °C, 650 °C, 700 °C, 750 °C and 800 °C) with a heating rate of 1 °C/min.

3. Results and discussion

The SEM images of the KNN powders calcined at different temperatures with a heating rate of 1 °C/min are shown in Fig. 1. By increasing the calcination temperature

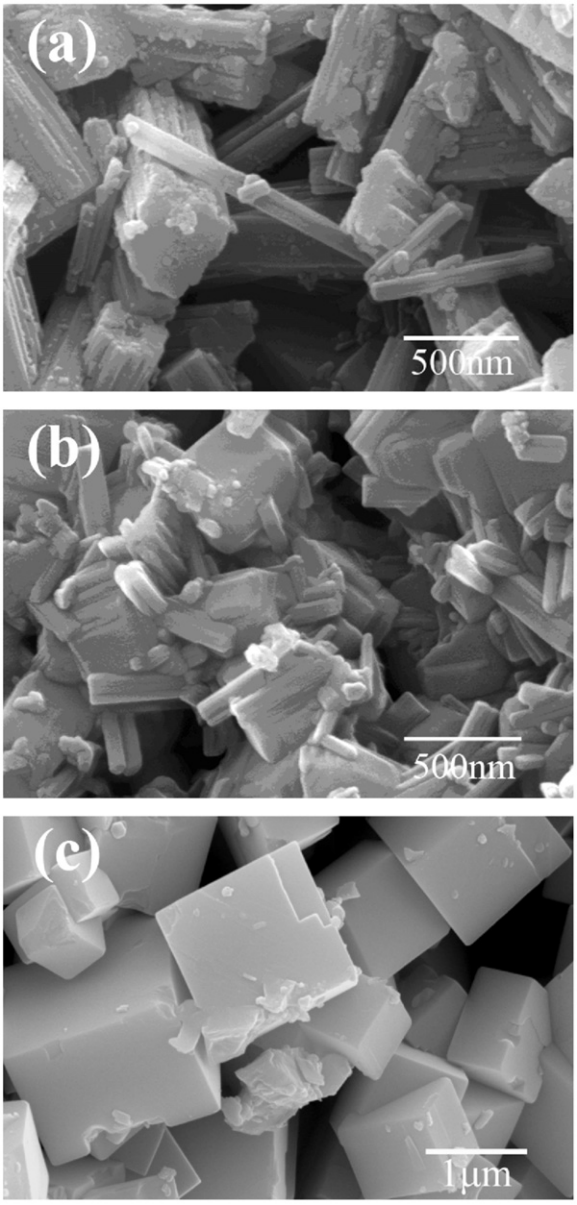

Fig. 3. SEM images of the KNN powders calcined at 750 °C with different heating rates: (a) 1 °C/min, (b) 2 °C/min and (c) 3 °C/min.

from 650 °C to 800 °C, it was found that the morphology of KNN gradually changed from nanopowders to one-dimensional rods, and the size of the one-dimensional rods increased significantly with higher temperature. As shown in Fig. 1(a), the KNN nanopowders with a particle size of 50 nm to 100 nm were obtained at the calcination temperature of 650 °C. With the temperature increasing to 700 °C, the KNN nanorods gradually generated. Short nanorods with a width of 20 nm to 50 nm and a length of 100 nm to 200 nm were observed, as presented in Fig. 1(b). When the calcination temperature was increased to 750 °C, the KNN nanorods became considerably homogeneous with a width of 100 nm to 400 nm and a length of 1 μm to 2 μm as shown in Fig. 1(c). However, when the calcination temperature was increased up to 800 °C, the KNN nanorods changed into a form that was a mixture of microrods and cubes as shown in Fig. 1(d), indicating that an extremely high calcination temperature has negative effects on the growth of KNN nanorods.

Fig. 2 shows the XRD patterns of the KNN powders calcined at different temperatures. When the calcination temperature was lower than 700 °C, a second phase of $K_{5.75}Nb_{10.85}O_{30}$ (PDF#38–0297) was clearly observed aside from the main perovskite phase, as indicated in Fig. 2. By increasing the calcination temperature to 750 °C, the crystallization of KNN gradually completed, and a pure orthorhombic phase with the lattice parameters of $a=5.5808$ Å, $b=5.5906$ Å, and $c=3.8977$ Å was obtained. Notably, when the calcination temperature was increased, the diffraction peaks (200) for KNN gradually split as circled in Fig. 2, attributed to a grain-sized induced structural phase transition [12,13].

The effects of the heating rate on the phase structure and morphology of the KNN powders calcined at 750 °C are shown in Figs. 3 and 4. By increasing the heating rate from 1 °C/min to 3 °C/min, the one-dimensional rod-like KNN nanorods gradually evolved into cubes with 1 μm to 2 μm in length as shown in Fig. 3, indicating that the KNN nanorods could only develop at a low heating rate. When the heating rate was as low as 1 °C/min, complete KNN nanorods with a width of 200 nm–400 nm and a length of 1 μm–2 μm were obtained as shown in Fig. 3(a). By increasing the heating rate to 2 °C/min, the KNN nanorods gradually grew close together, and a mixture of nanorods and cubes was observed in Fig. 3(b). When the heating rate was increased to 3 °C/min, only KNN cubes with 1 μm–2 μm in length were found, as presented in Fig. 3(c). On the other hand, the increase in heating rate had limited effects on the crystal structure of KNN. As shown in Fig. 4, the studied KNN samples with different heating rates were found to be the orthorhombic phase.

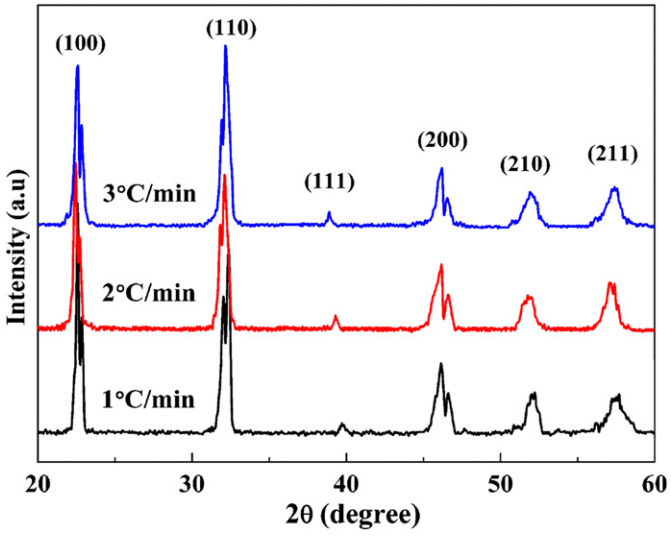

Fig. 4. XRD patterns of the KNN powders calcined at 750 °C with different heating rates (1 °C/min, 2 °C/min and 3 °C/min).

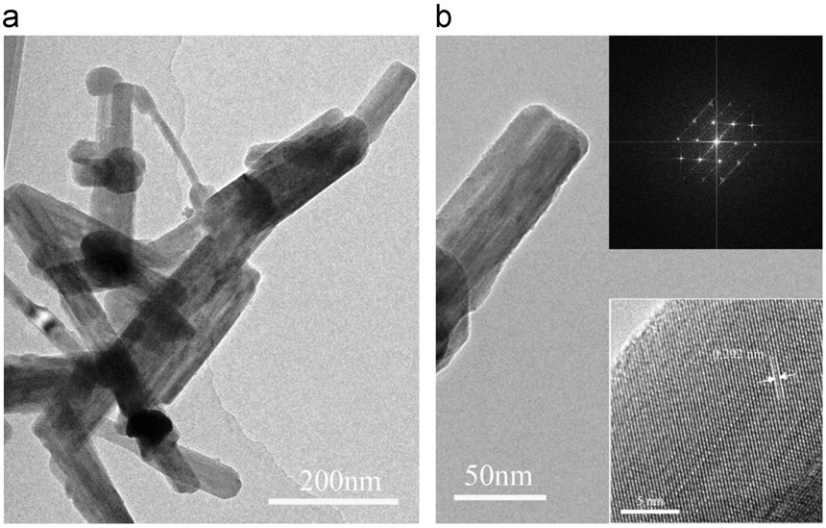

Fig. 5. (a) TEM image of KNN nanorods and (b) TEM image of a single KNN nanorod; insets are the corresponding SAED pattern and HRTEM image of the edge of the nanorod.

In light of the above discussion, the calcination temperature of 750 °C and the heating rate of 1 °C/min were determined to be the optimum processing condition for synthesizing KNN nanorods. Fig. 5(a) shows the TEM image of as-synthesized KNN products consisting of uniform nanorods. An individual nanorod is shown in Fig. 5(b). The corresponding selected area electron diffraction (SAED) pattern and lattice fringes are given in the insets of Fig. 5(b), confirming the single-crystalline nature of the products.

It was proposed that the use of oxalic acid and ethanediol during preparation could promote the growth of KNN nanorods [22]. The carboxyl in oxalic acid would form a complex of K^+, Na^+, and Nb^{5+} ions, leading to the formation of gel with the assistance of ethanediol. By increasing the calcination temperature and time, the gel particles gradually evolved into one-dimensional rods along the direction with the fastest growth velocity [23]. As a consequence, a low heating rate could provide sufficient time for crystallization and play a critical role in the formation of KNN nanorods. The more in-depth investigation of the growth behavior and mechanism of KNN nanorods is underway.

4. Conclusions

Single-crystalline lead-free KNN nanorods were successfully synthesized through a modified sol–gel method. Calcination temperature and heating rate had significant influence on the structure and morphology of the KNN nanorods. By increasing the calcination temperature, the crystallization of KNN gradually completed, and the morphology of the resulting products changed from nanopowders to one-dimensional rods. At higher temperature, the size of the KNN nanorods was found to increase significantly. In addition, the morphology of KNN nanorods gradually changed from one-dimensional rods to cubes by increasing the heating rate. The as-synthesized KNN nanorods, calcined at the optimum processing condition (750 °C, 1 °C/min), were proven to be single crystals of 100–400 nm wide and 1–2 μm long.

Acknowledgments

This work was supported by the National Natural Science Foundation of China under Grant nos. 51132002 and 51272110, the Key Laboratory Foundation of Sonar Technology of China under Grant no. 9140C24KF0901, the Scientific Project of Heilongjiang Province under Grant no. E201101 and the Scientific Research Project of Education Bureau of Heilongjiang Province under Grant no. 12521592.

References

[1] G.H. Haertling, Ferroelectric ceramics: history and technology, Journal of the American Ceramic Society 82 (1999) 797–818.
[2] D.W. Wang, M.S. Cao, S.J. Zhang, Piezoelectric properties of $PbHfO_3$–$PbTiO_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$ ternary ceramics, Physica Status Solidi RRL 6 (2012) 135–137.
[3] J. Rodel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, D. Damjanovic, Journal of the American Ceramic Society 92 (2009) 1153–1177.
[4] T.R. Shrout, S.J. Zhang, Lead-free piezoelectric ceramics: alternatives for PZT., Journal of Electroceramics 19 (2007) 113–126.
[5] L. Egerton, D.M. Dillon, Piezoelectric and dielectric properties of ceramics in the system potassium sodium niobate, Journal of the American Ceramic Society 42 (1959) 438–442.
[6] Y. Saito, H. Takao, T. Tami, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, Nature 432 (2004) 84–87.
[7] A. Safari, M. Abazari, Lead free piezoelectric ceramics and thin films, IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control 57 (2010) 2165–2176.
[8] D.Q. Xiao, J.G. Wu, L. Wu, J.G. Zhu, P. Yu, D.M. Lin, Y.W. Liao, Y. Sun, Investigation on the composition design and properties study

of perovskite lead free piezoelectric ceramics, Journal of Materials Science 19 (2009) 5408–5419.
[9] S.J. Zhang, R. Xia, T.R. Shrout, Modified KNN based lead free piezoelectrics with broad temperature usage range, Applied Physics Letters 91 (2007) 132913.
[10] S.J. Zhang, R. Xia, T.R. Shrout, G.Z. Zang, J.F. Wang, Piezoelectric properties in perovskite 0.948KNN-0.052LS lead free ceramics, Journal of Applied Physics 100 (2006) 104108.
[11] P. Zhao, B.P. Zhang, J.F. Li, Enhancing piezoelectric d33 coefficient in Li/Ta-codoped lead-free (Na,K)NbO3 ceramics by compensating Na and K at a fixed ratio, Applied Physics Letters 91 (2007) 172901.
[12] H.Q. Wang, R.Z. Zuo, L. Wang, J. Fang, X.H. Wang, L.T. Li, Preparation and piezoelectric properties of CuO-doped (Na0.5K0.5)NbO3 ceramics by the citrate precursor method, Journal of Materials Science—Materials in Electronics 22 (2011) 458–462.
[13] A. Chowdhury, J. Bould, Y.F. Zhang, C. James, S.J. Milne, Effect of the temperature on the synthesis of (K,Na)NbO_3-modified nanoparticles by a solid state reaction route, Journal of Nanoparticle Research 12 (2010) 2495–2502.
[14] Y.F. Chang, Z.P. Yang, L.L. Wei, Microstructure, density, and dielectric properties of lead-free (K0.44Na0.52Li0.04)(Nb0.96-xTaxSb0.04)O_3 piezoelectric ceramics, Journal of the American Ceramic Society 90 (2007) 1656–1658.
[15] I. Pribosic, D. Makovec, M. Drofenik, Formation of nanoneedles and nanoplatelets of KNbO3 perovskite during templated crystallization of the precursor gel, Chemistry of Materials: a Publication of the American Chemical Society 17 (2005) 2953–2958.
[16] T.Y. Ke, H.A. Chen, H.S. Sheu, J.W. Yeh, H.N. Lin, C.Y. Lee, H.T. Chiu, Sodium niobate nanowire and its piezoelectricity, Journal of Physical Chemistry C 112 (2008) 8827–8831.
[17] Z. Wang, H.S. Gu, Y.M. Hu, K. Yang, M.Z. Hu, D. Zhou, J.G. Guan, Synthesis, growth mechanism and optical properties of (K,Na)NbO3 nanostructures, Crystal Engineering Communication 12 (2010) 3157–3162.
[18] P.M. Rørvik, T. Grande, M.A. Einarsrud, One-dimensional nanostructures of ferroelectric perovskites, Advanced Materials 23 (2011) 4007–4034.
[19] D. Zhou, H.S. Gu, Y.M. Hu, H.Y. Tian, Z. Wang, Z.L. Qian, Y. Wang, Synthesis, characterization and ferroelectric properties of lead-free K0.5Na0.5NbO3 nanotube arrays, Journal of Applied Physics 109 (2011) 114104.
[20] S.Y. Xu, J.F. Li, Synthesis and piezoelectricity of single-crystalline (K,Na)NbO3 nanobars, Journal of the American Ceramic Society 94 (2011) 3812–3818.
[21] 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, Journal of Sol–Gel Science and Technology 57 (2011) 31–35.
[22] H.B. Yang, Y. Lin, F. Wang, Low-temperature synthesis of NaNbO3 ultrafine powder and morphology control, Journal of Wuhan University of Technology 29 (2007) 58–61.
[23] C.R. Cho, A. Grishin, Background oxygen effects on pulsed laser deposited Na0.5K0.5NbO3 films: from superparaelectric state to ferroelectricity, Journal of Applied Physics 87 (2000) 4439–4448.