

## Flash sintering of sodium niobate ceramics

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### ARTICLE INFO

#### Article history:

Received 11 July 2018

Received in revised form 2 September 2018

Accepted 30 September 2018

Available online 1 October 2018

#### Keywords:

Sintering

Sodium niobate

Ceramics

Stoichiometric

Rapid densification

### ABSTRACT

Dense and stoichiometric  $\text{NaNbO}_3$  ceramics were difficult to be prepared by conventional sintering methods because  $\text{Na}_2\text{O}$  easily volatilized at elevated temperature. In this work, the volatility of  $\text{Na}_2\text{O}$  was suppressed by applying an electrical field assisted sintering method. Flash sintering was performed successfully on  $\text{NaNbO}_3$  ceramics under the electrical fields ranging from 400 to 700 V/cm. The Na/Nb ratio of dense ceramic remained similar to that of the green sample. Our work demonstrated that flash sintering was an alternative technique for fabricating dense and high-purity ceramics with highly volatile species.

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## 1. Introduction

Piezoelectric ceramics are important and extensively used materials in many fields. The dominating piezoelectric ceramics are mostly lead-based ceramics. For the sake of the environmental protection and human health, lead-free piezoelectric ceramics need to be developed. Sodium niobate and its alkaline niobates solid solutions are important lead-free family with piezoelectric property [1]. The dense and stoichiometric  $\text{NaNbO}_3$  ceramics are difficult to be fabricated because  $\text{Na}_2\text{O}$  easily evaporates during sintering. Many methods have been presented to enhance densification rate of  $\text{NaNbO}_3$  with minimal deviations from stoichiometry, such as spark plasma sintering, addition of sintering aids, low partial pressure of oxygen sintering and utilization of nanopowders [2–7]. However, these methods are complicated and most of them required high temperature and long time treatment. Other techniques to prepare dense and stoichiometric  $\text{NaNbO}_3$  ceramics are needed to be developed.

Recently, flash sintering has drawn many attentions because of its low sintering temperature and short sintering time [8–10]. Typically, flash sintering occurs at a particular furnace temperature with abrupt increase in the sample conductivity when a DC or AC voltage is applied to a sample during heating, which allows rapid densification. Some mechanisms have been proposed to interpret the flash sintering, including Joule heating [11], nucleation of Frenkel pairs [12], local heating [13], and thermal runaway

[14]. The fundamental mechanism is still not fully understood, and needed to be further studied.

This work aims at exploring the application of flash sintering on the  $\text{NaNbO}_3$  ceramics. It is demonstrated that  $\text{NaNbO}_3$  ceramics can be sintered nearly full dense in 3 s under the electrical fields ranging from 400 to 700 V/cm. Most importantly, the flash-sintered  $\text{NaNbO}_3$  ceramics maintain the stoichiometric ratio (Na/Nb) of starting powders.

## 2. Experimental procedure

$\text{NaNbO}_3$  powder was prepared by a molten salt method (see [Supplementary material](#)). The as-prepared  $\text{NaNbO}_3$  powder was added 5 wt% PVA as a binder, and then uniaxially cold-pressed into a dog bone-shaped bar (a length of 20 mm, a width of 3 mm, and a thickness of 0.9 mm) at 150 MPa. The green sample was kept at 700 °C for 1 h to burn out PVA binder before flash sintering. Subsequently, the green sample was suspended in a tubular furnace by two platinum wires through the holes present at the opposite ends of the sample. The platinum wires were connected to a DC power supply (HPS 0614, Lanyi, China) and to a digital multimeter (DMM 4040, Tektronix, USA). The schematic illustration of experimental setup was shown in [Fig. S1](#). When the furnace temperature (with a heating rate of 10 °C/min) reached to a particular value, the current increased rapidly to a preset peak current of 100 mA, and the voltage control of the power supply switched instantaneously to current control. The sample was kept for 3 s at constant current of 100 mA. Then the power supply and furnace were turned off.

The detailed characterizations are available in [Supplementary material](#).

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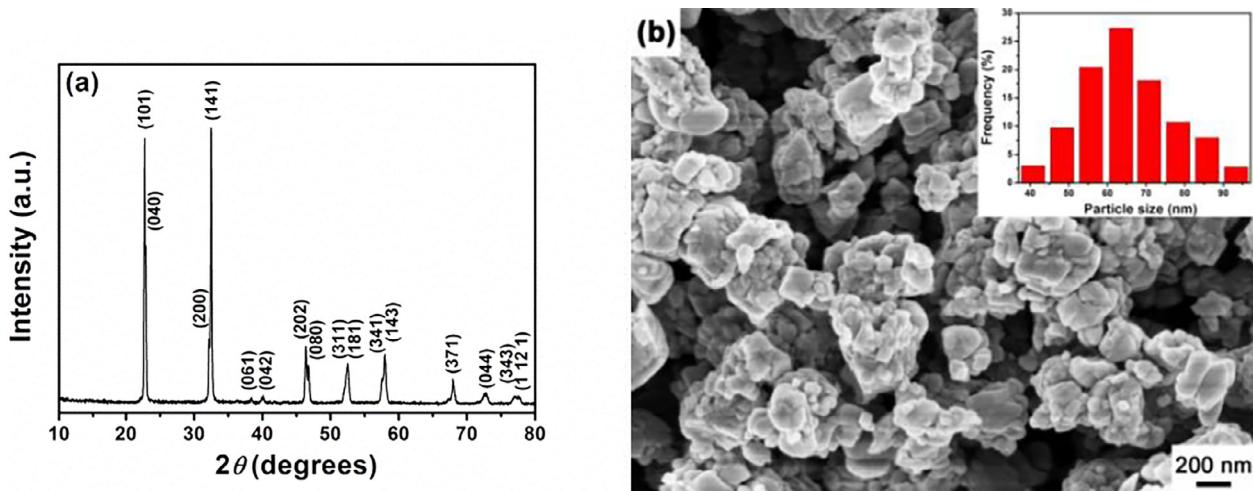


Fig. 1. XRD pattern (a), and SEM image, inset: particle size distribution (b) of NaNbO<sub>3</sub> powder prepared by the molten salt method.

### 3. Results and discussion

The XRD pattern of the powder prepared by molten salt method is shown in Fig. 1(a). All of the diffraction peaks are assigned to the orthorhombic phase of NaNbO<sub>3</sub> (PCPDF No. 33-1270) without any impurity phase. The average particle size is ~65 nm, as shown in Fig. 1(b) and insert. The chemical composition is measured by EDS and given in Table S1. The Na/Nb atom ratio of NaNbO<sub>3</sub> powder is close to 1, which follows stoichiometric ratio well.

The current density vs. furnace temperature curve for the sintering of NaNbO<sub>3</sub> under various electrical fields is plotted in Fig. 2(a). The current density of sample rises rapidly to a maximum value of ~3.70 A/cm<sup>2</sup>, which signals onset of flash sintering [8]. The flash sintering can be seen at 1010, 976, 916, and 862 °C at the electrical field of 400, 500, 600 and 700 V/cm, respectively. The onset temperature of flash sintering is dependent on the electrical field. The flash sintering occurs at a lower temperature as the electrical field increases, as indicated in Fig. S2.

Fig. 2(b) shows the Arrhenius plots of power dissipation for flash sintering of NaNbO<sub>3</sub> under a range of electrical fields. A specific power dissipation of 30 mW/mm<sup>3</sup> corresponds to the onset of flash sintering [15,16]. It is widely known that only when power dissipation exceeds a critical value, the densification during flash sintering can take place. According to the data plotted in the Fig. 2(b), it can be concluded that a power dissipation of 30 mW/

mm<sup>3</sup> is required for the flash sintering of NaNbO<sub>3</sub> ceramics, which is in accordance with reported works [8].

The microstructures of the samples flash-sintered at electrical fields of 400, 500, 600 and 700 V/cm are shown in Fig. 3. All of the samples show a densified structure with low porosity. The relative densities of samples are given in Table S2. The average grain size is measured to be 4.37, 4.03, 3.18, and 2.23 μm, respectively. Obviously, the electrical field has an influence on the average grain size. The larger electrical field leads to the smaller average grain size, as shown in Fig. 4.

The EDS results of the flash-sintered samples are given in Table S1. The chemical compositions of NaNbO<sub>3</sub> ceramics flash-sintered at 700 and 600 V/cm are similar to those of NaNbO<sub>3</sub> powder. The Na/Nb ratios of samples flash-sintered at 500 and 400 V/cm are slightly decreased, but still close to 1. The retention of Na/Nb ratio implies the suppression of the Na<sub>2</sub>O volatilization. It is suggested that flash sintering can allow the rapid densification at low temperature, thus reduces the evaporation of Na<sub>2</sub>O, and maintains the stoichiometry ratio of the green sample. Undoubtedly, flash sintering can address the challenge of the producing dense and stoichiometric NaNbO<sub>3</sub> ceramics.

The piezoelectric coefficient *d*<sub>33</sub> values of flash-sintered NaNbO<sub>3</sub> ceramics under the electrical fields of 400, 500, 600 and 700 V/cm are 32, 30, 33, 36 pC/N, respectively. These values are slightly higher than those prepared by traditional sintering [4].

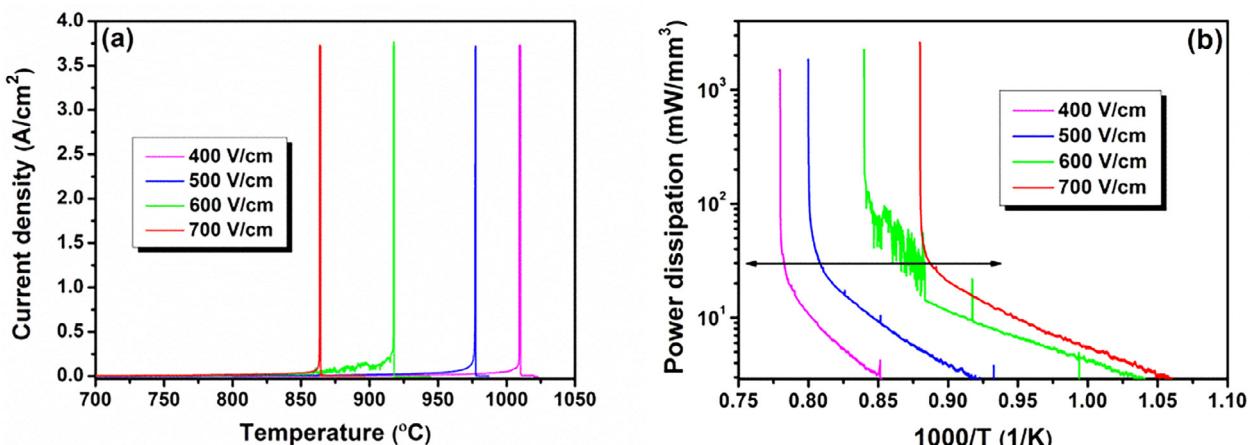
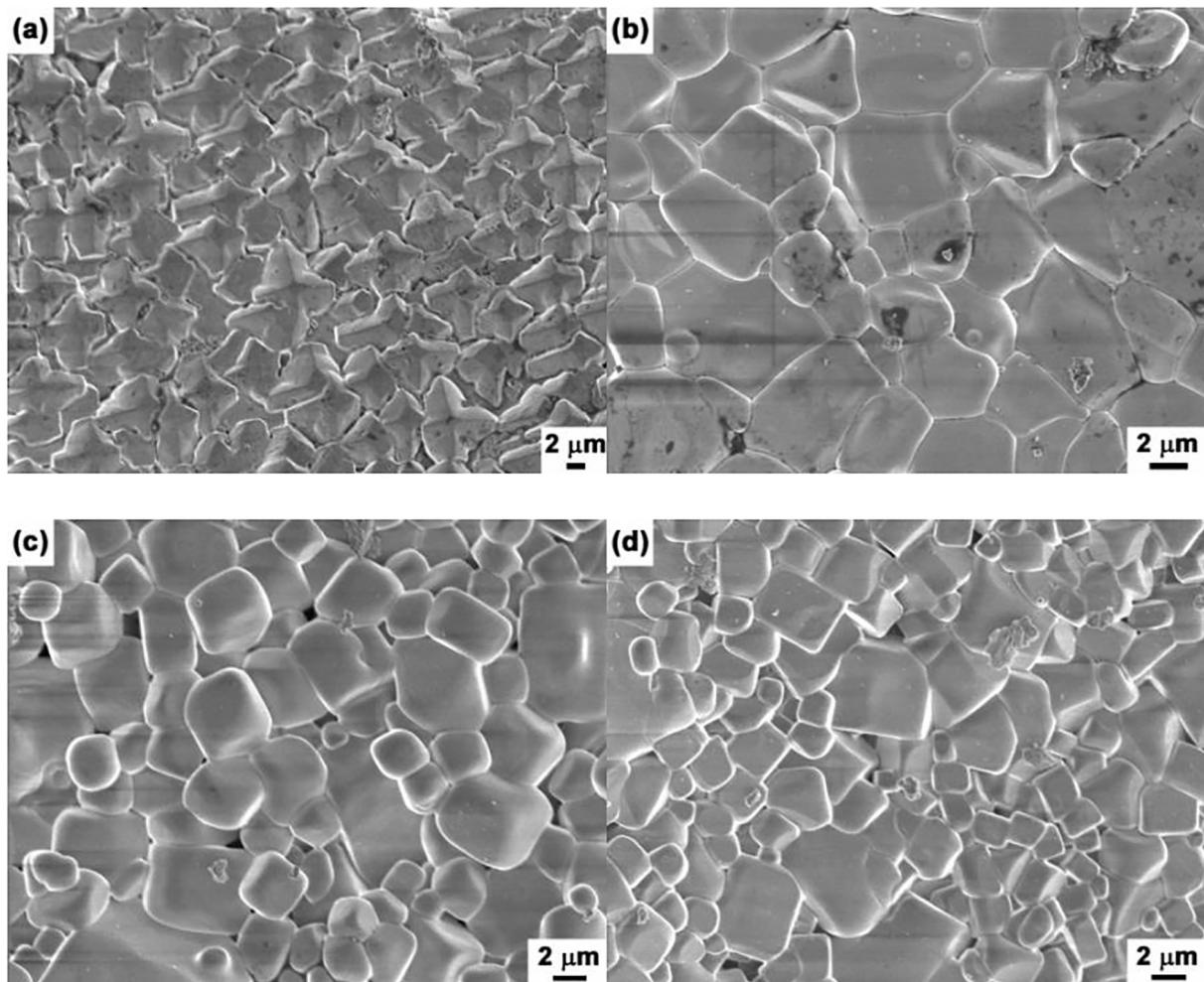
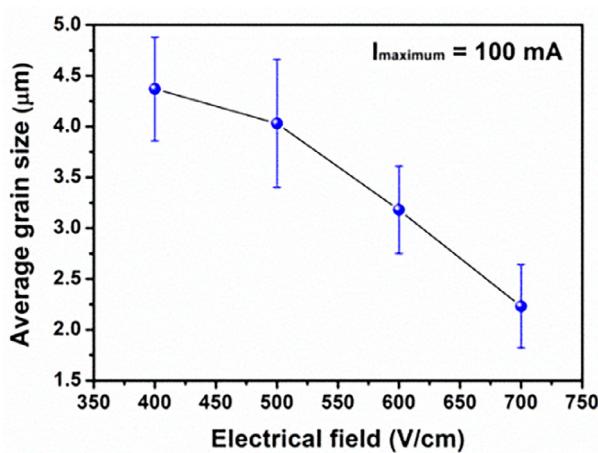


Fig. 2. Measured current density vs. furnace temperature curves for sintering of NaNbO<sub>3</sub> under various electrical fields (a), and specific power dissipation vs. furnace temperature curves (b).



**Fig. 3.** SEM images of flash-sintered samples under electrical fields of 400 (a), 500 (b), 600 (c), and 700 V/cm (d).



**Fig. 4.** Average grain size of flash-sintered sample as a function of electrical field.

#### 4. Conclusions

The dense and stoichiometric  $\text{NaNbO}_3$  ceramics are prepared by flash sintering technique. A specific power dissipation of  $30 \text{ mW}/\text{mm}^3$  is found to be required for the flash sintering of  $\text{NaNbO}_3$ . The  $d_{33}$  values are slightly higher than those prepared by

traditional sintering. The evaporation of  $\text{Na}_2\text{O}$  under the flash sintering is well suppressed, which sheds a new light for the fabrication of dense and stoichiometric ceramics with highly volatile species.

#### Acknowledgements

This work was financially supported by the Natural Science Basic Research Plan in Shaanxi Province of China (No. 2018JM5170), the International Project on Scientific and Technological Cooperation in Shaanxi Province of China (Grant No. 2018KW-052), the China Postdoctoral Science Foundation (No. 2015M582584), the Postdoctoral Research Project of Shaanxi Province (No. 2016BSHEDZZ06), and the Fundamental Research Funds for the Central Universities of China (Nos. 310831171011 and 300102318402).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2018.09.167>.

#### References

- [1] J.-F. Li, K. Wang, F.-Y. Zhu, L.-Q. Cheng, F.-Z. Yao, D.J. Green, *J. Am. Ceram. Soc.* 96 (2013) 3677–3696.
- [2] T. Wada, K. Tsuji, T. Saito, Y. Matsuo, *Jpn. J. Appl. Phys.* 42 (2003) 6110–6114.
- [3] H. Shimizu, K. Kobayashi, Y. Mizuno, C.A. Randall, *J. Am. Ceram. Soc.* 97 (2014) 1791–1796.

- [4] H. Ge, Y. Hou, C. Xia, M. Zhu, H. Wang, H. Yan, D. Lupascu, *J. Am. Ceram. Soc.* 94 (2011) 4329–4334.
- [5] Q. Gu, Q. Sun, K. Zhu, J. Liu, J. Qiu, *Ceram. Int.* 43 (2017) 1135–1144.
- [6] X. Lu, B. Fang, S. Zhang, N. Yuan, J. Ding, X. Zhao, F. Wang, Y. Tang, W. Shi, H. Xu, H. Luo, *Funct. Mater. Lett.* 10 (2017) 1750046–1750049.
- [7] K. Bian, Q. Gu, K. Zhu, R. Zhu, J. Wang, J. Liu, J. Qiu, *J. Mater. Sci: Mater. Electron.* 27 (2016) 8573–8579.
- [8] M. Yu, S. Grasso, R. Mckinnon, T. Saunders, M.J. Reece, *Adv. Appl. Ceram.* 116 (2017) 24–60.
- [9] X. Su, G. Bai, J. Zhang, J. Zhou, Y. Jia, *Appl. Surf. Sci.* 442 (2018) 12–19.
- [10] J. Xu, C. Fu, J. Xie, X. Zhao, T. Zhu, *Funct. Mater. Lett.* 6 (2013) 1340006–1340009.
- [11] R. Raj, *J. Eur. Ceram. Soc.* 32 (2012) 2293–2301.
- [12] R. Raj, M. Cologna, J.S.C. Francis, *J. Am. Ceram. Soc.* 94 (2011) 1941–1965.
- [13] M. Cologna, B. Rashkova, R. Raj, *J. Am. Ceram. Soc.* 93 (2010) 3556–3559.
- [14] R.I. Todd, E. Zapata-Solvas, R.S. Bonilla, T. Sneddon, P.R. Wilshaw, *J. Eur. Ceram. Soc.* 35 (2015) 1865–1877.
- [15] R. Raj, *J. Am. Ceram. Soc.* 99 (2016) 3226–3232.
- [16] X. Su, G. Bai, Y. Jia, Z. Wang, W. Wu, X. Yan, T. Ai, P. Zhao, L. Zhou, *J. Eur. Ceram. Soc.* 38 (2018) 3489–3497.