Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Ceramics International 34 (2008) 609–613
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Effects of excess K_2O and processing conditions on the preparation of dense $K(Ta_{1-X}Nb_X)O_3$ ceramics

K. Yoshikawa, T. Asaka, M. Higuchi, Y. Azuma, K. Katayama *

Department of Applied Chemistry, School of Engineering, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

Received 15 June 2006; received in revised form 11 November 2006; accepted 22 December 2006
Available online 30 January 2007

Abstract

Dense ceramics of potassium tantalate niobates ($KTa_{1-X}Nb_XO_3$: $X = 0.4$) with a perovskite-type structure were prepared using powders including excess K_2O and surrounding powder, and by applying vibration to the surrounding powder prior to firing. Excess K_2O was inevitable for increasing density, and the use of surrounding powder reduced density fluctuation to a considerable extent. Furthermore, the powder including 8 mol% excess K_2O fired at 1150 °C led to dense ceramics with relative density higher than 90%. The chemical composition of the resulting dense ceramics prepared here was confirmed to be that of a desired perovskite, $KTa_{0.6}Nb_{0.4}O_3$. The $KTa_{1-X}Nb_XO_3$ ceramics obtained here showed almost the same dielectric properties as those prepared by delicate, costly, and time-consuming methods.

Keywords: A. Sintering; C. Dielectric properties; Potassium tantalate niobate

1. Introduction

Ferroelectric materials such as lead-based PZT ceramics have been widely used for many applications such as electric filters, resonators, sensors, and actuators because of their excellent dielectric, piezoelectric, electromechanical, electro-optical, and pyroelectric properties [1]. However, lead is known to be toxic and to cause headaches, constipation, nausea, anemia, and serious nerve or brain damage [2]. Thus, the replacement of PZTs with lead-free ferroelectric materials has been extensively researched, and a series of alkaline niobates has been found to be among the most promising lead-free ferroelectric materials [3]. In particular, potassium tantalate niobates ($KTa_{1-X}Nb_XO_3$) has received much attention due to its excellent ferroelectric properties and the controllability of the Curie temperature by varying the value of X [4]. However, it has been widely reported that the sinterability of materials containing alkali elements is low and that alkaline niobate ceramics with near-full density are particularly difficult to fabricate [5]. Furthermore, the difficulty in sintering alkaline niobates has been attributed to the volatilization of alkali metals at firing temperatures [6]. In order to overcome the volatilization of alkali metals, pressure-assisted sintering methods such as hot-pressing and plasma-sintering have been employed [7]. Recently, Kakimoto et al. revealed that simultaneous substitution of La and Fe for K for Nb, respectively, is quite effective for producing dense $KNbO_3$ ceramics by sintering in air [8–10]. Xu et al. has found that the addition of Ti enables potassium niobates to be sintered to near-full density because Ti suppresses the vaporization of potassium in potassium niobates [11].

In the present study, the effects of excess K_2O on the sinterability of $K(Ta_{1-X}Nb_X)O_3$ powder were examined, and a new, simple, and effective way of producing dense $K(Ta_{1-X}Nb_X)O_3$ (hereinafter ‘‘KTN’’) ceramics was proposed. The starting composition was selected to be $X = 0.4$, of which the ceramic was expected to show the maximum permittivity just around room temperature [12–14].

2. Experimental

High-purity commercial K_2CO_3, Nb_2O_5 and Ta_2O_5 powders were chosen as starting materials. Preliminary TGA measurements on potassium carbonate revealed that the weight loss caused by the decomposition of carbonate and the concomitant release of carbon dioxide are not observed up to 880 °C [15].

---

* Corresponding author. Tel.: +81 463 58 1211x4181; fax: +81 463 50 2012.
E-mail address: katakei@keyaki.cc.u-tokai.ac.jp (K. Katayama).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.12.006

Thus, only the evaporation of absorbed water was considered while weighing the starting materials. The chemicals were weighed with high precision at the desired proportion, mixed thoroughly in an alumina mortar and pestle using ethanol, and calcined at 850 °C for 4 h. In addition to the stoichiometric composition powder, several powders containing various amounts of excess K_2O were prepared. The calcination conditions employed were the same as those used by DiAntonio and Pilgrim [12]. After calcination, the powders were ball-milled in order to pulverize agglomerates and to reduce the particle size of the powder to 1–2 μm. Calcination/pulverization was repeated at least three times to ensure that the reaction was complete. Ball-milled powders were uniaxially pressed at 100 MPa into pellets, followed by firing in a sealed alumina crucible. In order to suppress volatilization of K_2O, the pellets were surrounded with powders having the same composition as the pellets during firing. In some cases, the crucible containing the pellets and surrounding powder was tapped repeatedly to measure the tap density. Vibration was employed to ensure that the pellets were tightly embedded in the surrounding powder and thus to suppress the sublimation of potassium as much as possible. The vertical moving distance of the crucible was fixed at 1.0×10^{-2} m.

The phases present in the fired samples were identified by X-ray diffractometry (XRD), and the microstructures were observed by scanning electron microscopy (SEM). Sinterability of the powders was evaluated by bulk densities calculated from the weights and dimensions of the sintered specimens. The chemical composition of the resulting ceramics were determined using X-ray fluorescence spectroscopy (XRF), and energy dispersive X-ray spectroscopy (EDX) was conducted for detecting excess K_2O. Lattice parameters were computed with a least-square fit of high-angle diffraction lines, using 5N-purity Si powder as an internal standard. The sintered pellets were polished using #1000 polishing paper, and a silver paste was fired on both surfaces of the polished samples at 500 °C for dielectric measurements.

3. Results and discussion

The crystal structure of KTN ($KTa_{1-X}Nb_XO_3$, where $0 < X < 1.0$) has been reported to vary according to the composition, X [14]. Fig. 1 depicts the XRD diagram of the sample prepared from stoichiometric powder, showing a cubic perovskite rather than tetragonal structure. Increasing firing temperature did not affect the phases or the compositions in the samples. Bursik et al. have demonstrated that the crystal structure of their potassium tantalate niobate films ($KTa_XNb_{1-X}O_3$, where $0 < X < 1.0$) is entirely cubic, probably because of their nano-crystalline nature [16], while Lu and Kuang have demonstrated that the crystal structure of $KTa_{1-X}Nb_XO_3$ thin films depends on the substrate materials [5]. On the other hand, Triebwasser [14] has found that the Curie temperature of KTN ceramics increases linearly with increasing X, and that the Curie point of $KT_{0.6}Nb_{0.4}O_3$ ceramics is around room temperature. The cubic structure of the samples prepared here implied that the Curie temperature of the sample was lower than room temperature. As will be shown later in Fig. 8, the Curie temperature of the sample was found to be just below room temperature, as expected from the phase diagram of KTN [12].

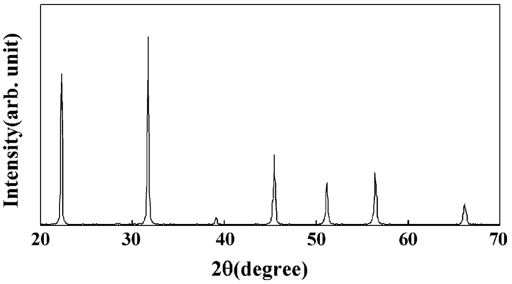

Fig. 1. XRD pattern of KTN ceramics fired at 1000 °C.

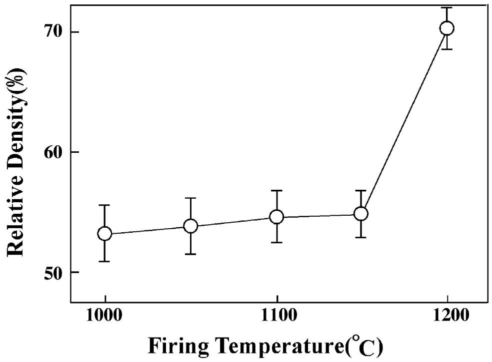

Fig. 2. Density of KTN ceramics fired for 5 h. Bars indicate deviation.

Fig. 2 shows the relative density of ceramics made from a stoichiometric powder. The density varied widely; the deviation from the average is shown in the figure. Firing was performed below 1250 °C because all pressed samples were completely melted when fired at or above 1250 °C. The density increased with firing temperature, first gradually, then sharply at 1200 °C. The trend is probably real, but the validity of the density values is difficult to justify because Fig. 2 shows some scatter. To reduce the scatter, several experimental conditions were varied: the firing time was reduced and the heating/cooling rates were varied, but none of these had any effect. The pressed pellets were then surrounded with a stoichiometric powder before

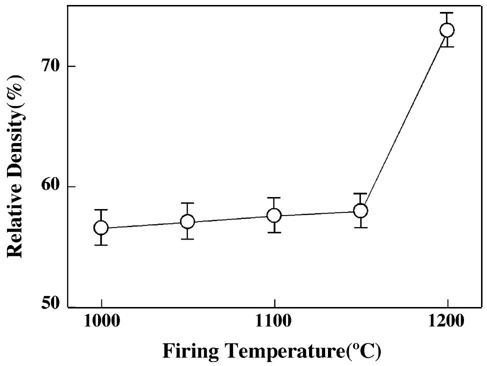

Fig. 3. Density of KTN ceramics prepared using the same powders as shown in Fig. 2. Firing was performed using a stoichiometric surrounding powder. Bars show deviation.

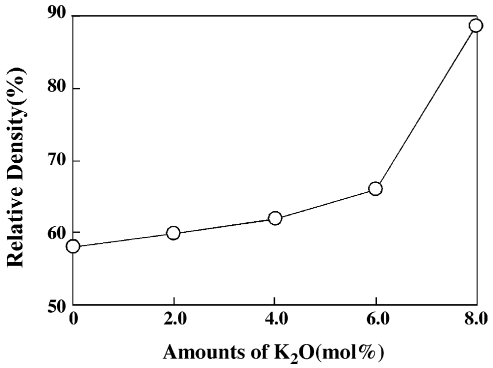

Fig. 4. Density of KTN ceramics fired at 1150 °C for 5 h using surrounding powders of the same composition as the pellets.

firing. The densities of the pellets fired at 1150 °C for 5 h in this manner are shown in Fig. 3. The density scarcely varied, and the fluctuations were greatly reduced. These results indicate that the use of the surrounding powders was effective for reducing density variation. Thus, all subsequent firing runs were performed using surrounding powders; deviation bars are not shown in upcoming figures.

Fig. 4 shows the density of samples fired at 1150 °C for 5 h using surrounding powders of the same composition as the pellets. The density increased with increasing amounts of excess K_2O; the increase was sharp at 8 mol% K_2O. A comparison with Fig. 3 reveals that excess K_2O in the surrounding powder promoted densification. These results indicate that it is preferable to use surrounding powders of the same composition as the sample, and subsequent firing runs were therefore performed using the surrounding powders.

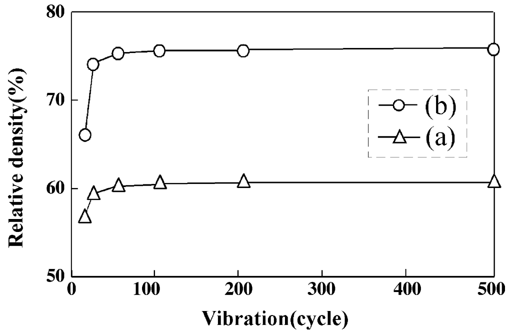

Fig. 5. Effect of the vibration cycle on the density of KTN specimens made from (a) a stoichiometric powder and (b) the powder containing 6 mol% excess K_2O.

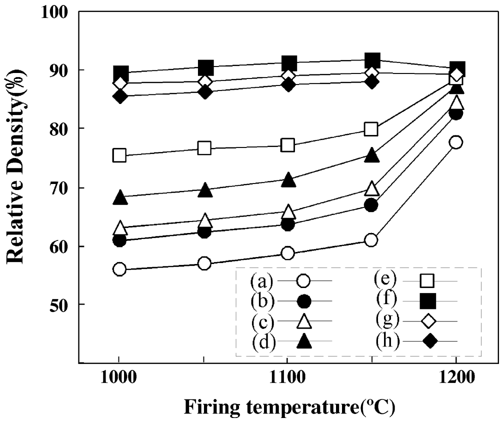

Fig. 6. Effects of the firing temperature and the amount of excess K_2O on the density of KTN ceramics containing (a) 0%, (b) 2%, (c) 4%, (d) 6%, (e) 7%, (f) 8%, (g) 9%, and (h) 10% excess K_2O fired at 1150 °C.

In tap density measurements, the vibration applied ensures that the smaller powders work their way into the spaces between the large powders. Thus, it is expected that a vibration similar to that used in tap density measurements can pack the surrounding powders as densely as possible and suppress the vaporization of K_2O during heat treatment. Fig. 5 shows the density of ceramics prepared from a stoichiometric powder and a powder containing 6 mol% excess K_2O. All specimens were fired after a vibration cycle. Density increased with increasing numbers of vibration cycles and stayed nearly constant after 50 cycles, irrespective of the amount of excess K_2O. On the basis of these results, 50 vibration cycles were employed before each firing run.

Fig. 6 shows the effects of the amount of excess K_2O and firing temperature on the density. The density increased with increasing amounts of excess K_2O up to 8 mol%, as well as with increasing firing temperature. The duration of firing was fixed at 5 h because the density did not increase on further heating. Bulk densities higher than 90% of the theoretical density were obtained using powders containing 8 mol% of excess K_2O.

The microstructures of the sintered samples varied with the quantity of excess K_2O. Fig. 7 shows the fractured surfaces of samples containing 0, 4, 8, or 10 mol% K_2O fired at 1150 °C for 5 h. In the sample free of excess K_2O, the grain size did not increase, indicating that sintering scarcely proceeded, irrespective of firing temperature as shown in Fig. 7(a). By contrast, cubic particles along with irregular-shaped fine (submicron) particles were clearly visible in samples containing excess K_2O, and the particle size of the cubes increased with increasing amounts of excess K_2O (Fig. 7(b) and (c)). EDX measurement revealed that the fine particles were composed primarily of potassium, and all fired samples containing 10 mol% excess K_2O completely fragmented soon after contact with air (Fig. 7(d)). These results indicate that small particles composed primarily of K_2O were transformed into KOH or K_2CO_3, causing total fragmentation of the fired samples [17].

Fig. 8 shows the dielectric constants of samples containing various amounts of excess K_2O. Dielectric properties were measured on the cooling portion of the temperature cycle. The temperature at which the dielectric constant attained its maximum value decreased with increasing amounts of excess K_2O, and the maximum dielectric constant of 3500 was observed for the sample containing 8 mol% excess K_2O [18]. The dielectric constant is thought to reach its maximum value at the Curie temperature, which for the KTN ceramics prepared here is confirmed to be just below the room temperature. This finding leads to the assumption that the KTN ceramics here have nearly the expected mol fractions of Ta and Nb, which is almost the same composition as the starting material. Moreover, X-ray fluorescence spectroscopy demonstrated that the above assumption was reasonable.

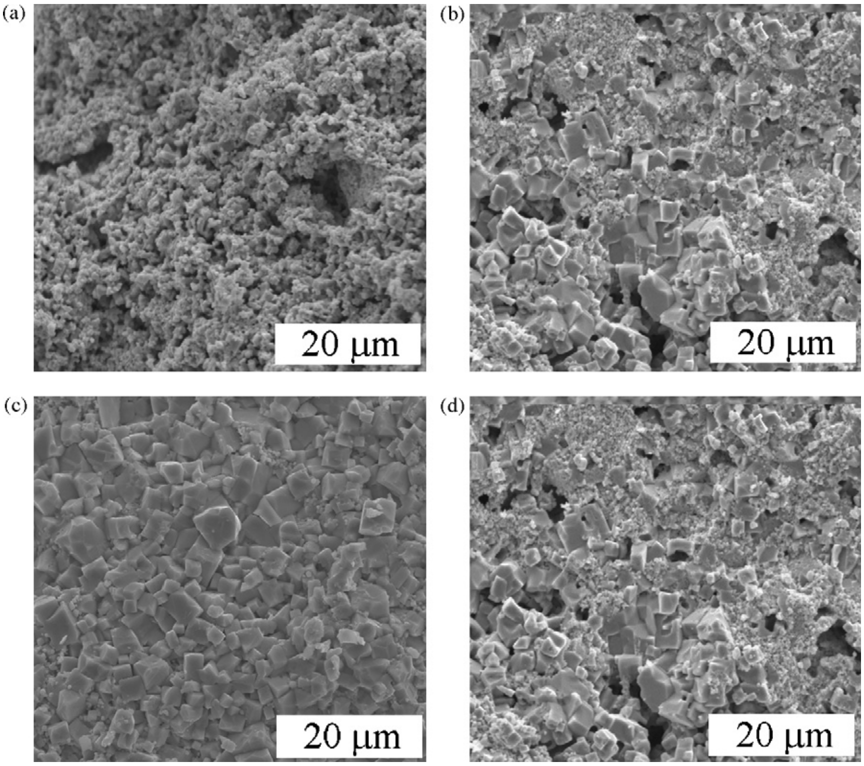

Fig. 7. Microstructures of KTN specimens containing (a) 0%, (b) 4%, (c) 8%, and (d) 10% excess K_2O fired at 1150 °C.

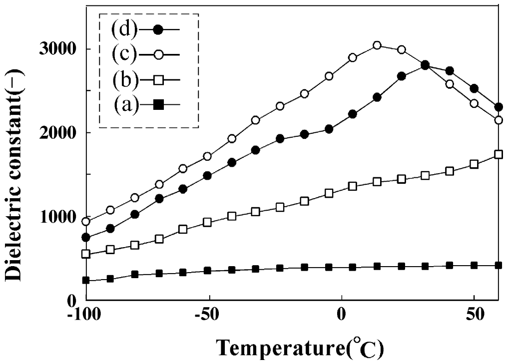

Fig. 8. Dielectric constants of KTN specimens containing (a) 0%, (b) 4%, (c) 8%, and (d) 10% excess K_2O fired at 1150 °C.

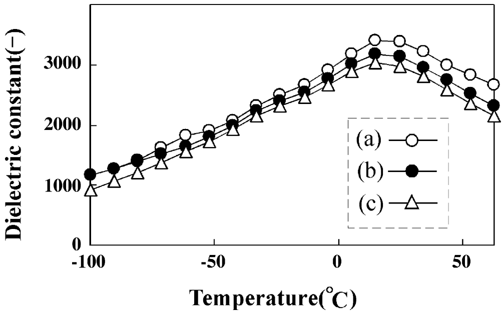

Fig. 9. Dielectric constants of KTN specimens containing 8% K_2O fired at 1150 °C measured at frequencies of (a) 1 kHz, (b) 10 kHz, and (c) 100 kHz.

Fig. 9 shows the frequency dependence of the dielectric constant for the sample containing 8 mol% of excess K_2O. As expected, the dielectric constant decreased with frequency. The chemical composition of the specimens was analyzed by X-ray fluorescence spectrometry, which confirmed that the specimens fabricated from powder containing 8 mol% excess K_2O were almost stoichiometric. Furthermore, specimens made from the powder containing 4 mol% excess K_2O were depleted in potassium, while that made from powder containing 10 mol% K_2O had excess potassium. These results suggest that the other peak in the dielectric constant of the sample containing 10 mol% K_2O in Fig. 8 depends on the existence of a small amount of impurity phase and the compositional fluctuation of B-site ions in the perovskite phase. Finally, the loss tangents of the sample in Fig. 9 are shown in Fig. 10. The values are relatively low, scarcely varying between −100 and 50 °C. The results are almost identical to those reported by Lanfredi et al. [19].

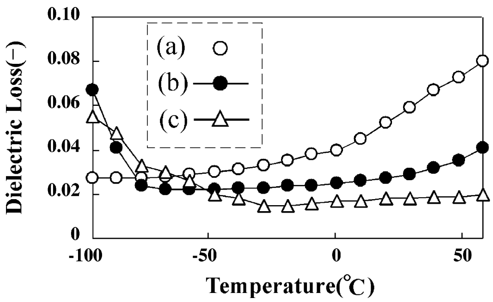

Fig. 10. Dielectric losses of KTN specimens containing 8% K_2O fired at 1150 °C measured at the same frequencies as shown in Fig. 9.

4. Conclusions

Dense KTN ceramics were prepared using powders containing excess K_2O and surrounding powder, and by applying vibration to the surrounding powder prior to firing. The use of powder containing excess K_2O was indispensable to obtaining KTN ceramics because the content of potassium decreased during firing. The surrounding powder greatly reduced density fluctuation, while the vibration proved rather effective in increasing the packing density of the powder bed and thereby suppressing the volatilization of potassium. Furthermore, the dielectric properties of the dense ceramics prepared here were identical to results reported earlier.

References

[1] S. Seifert, D. Sporn, T. Hauke, G. Muller, H. Beige, Dielectric and electromechanical properties of sol–gel prepared PZT thin films on metallic substrates, J. Eur. Ceram. Soc. 24 (9) (2004) 2553–2566.

[2] E. Ringgaard, T. Wurlitzer, Lead-free piezoceramics based on alkali niobates, J. Eur. Ceram. Soc. 25 (12) (2005) 2701–2706.

[3] S.-Y. Chu, W. Water, Y.-D. Juang, J.-T. Liaw, S.B. Dai, Piezoelectric and dielectric characterics of lithium potassium niobate ceramic system, Ferroelectrics 297 (1) (2003) 11–17.

[4] B. Malic, J. Bernard, J. Holc, D. Jenko, M. Kosec, Alkaline-earth doping in $(K,Na)NbO_3$ based piezoceramics, J. Eur. Ceram. Soc. 25 (12) (2005) 2707–2711.

[5] C.J. Lu, A.X. Kuang, Preparation of potassium tantalate niobate through sol-gel processing, J. Mater. Sci. 32 (16) (1997) 4421–4427.

[6] T. Wada, K. Toyoike, Y. Imanaka, Y. Matsuo, Dielectric and piezoelectric properties of $(A_{0.5}Bi_{0.5})TiO_3$-$ANbO_3$(A = Na, K) system, Jpn. J. Appl. Phys. 40 (9B) (2001) 5703–5705.

[7] R. Wang, R. Xie, T. Sekiya, Y. Shimojo, Fabrication and characterization of potassium–sodium niobate piezoelectric ceramics by spark-plasma-sintering method, Mater. Res. Bull. 39 (11) (2004) 1709–1715.

[8] K. Kakimoto, I. Matsuda, H. Ohsato, Jpn. ferroelectric and piezoelectric properties of $KNbO_3$ ceramics containing small amounts of $LaFeO_3$, J. Appl. Phys. 42 (9B) (2003) 6102–6105.

[9] I. Masuda, K. Kakimoto, H. Ohsato, Ferroelectric property and crystal structure of $KNbO_3$ based ceramics, J. Electroceram. 13 (1–3) (2004) 555–559.

[10] K. Kakimoto, I. Masuda, H. Ohsato, Lead-free $KNbO_3$ piezoceramics synthesized by pressure-less sintering, J. Eur. Chem. Soc. 25 (12) (2005) 2719–2722.

[11] S.-L. Xu, J.-H. Lee, J.-J. Kim, H.Y. Lee, S.-H. Cho, Effect of Nb_2O_5 content on dielectric characteristics of tungsten–bronze-structured KLN ceramics, Mater. Sci. Eng. B 99 (1–3) (2003) 483–486.

[12] C.B. DiAntonio, S.M. Pilgrim, Processing, characterization, and dielectric studies on $K(Ta_{1-X}Nb_X)O_3$ for use at cryogenic temperatures, J. Am. Ceram. Soc. 84 (11) (2001) 2547–2552.

[13] H. Khemakhem, J. Ravez, A. Daoud, Effect of dc and ac bias fields on the dielectric and ferroelectric propertiew of a KTN ceramics, Phys. Stat. Sol. 161 (2) (1997) 557–564.

[14] S. Triebwasser, Study of ferroelectric transitions of solid-solution single crystals of $KNbO_3$–$KTaO_3$, Phys. Rev. 114 (1) (1959) 63–70.

[15] R.L. Lehman, J.S. Gentry, N.G. Glumac, Thermal stability of potassium carbonate near its melting point, Thermochim. Acta 316 (1) (1998) 1–9.

[16] J. Bursik, V. Zelezny, P. Vanek, Preparation of potassium tantalate niobate thin films by chemical solution deposition and their characterization, J. Eur. Ceram. Soc. 25 (12) (2005) 2151–2154.

[17] S. Lanfredi, L. Dessemond, A.C. Martins Rodrigues, Dense ceramics of $NaNbO_3$ produced from powders prepared by a new chemical route, J. Eur. Ceram. Soc. 20 (7) (2000) 983–990.

[18] H.-G. Wul, S.-M. Wang, Z.-X. Xu, J. Fu, Fabrication and electrical properties of KTN multilayer thin films, Mater. Lett. 57 (18) (2003) 2742–2745.

[19] S. Lanfredi, A.C. Martins Rodrigues, L. Dessemond, Effect of porosity on the electrical properties of polycrystalline sodium niobate. II. Dielectric behavior, J. Am. Ceram. Soc. 86 (12) (2003) 2103–2110.