

Technical note

Structural and electrical characterization of $(\text{K}_{0.48}\text{Na}_{0.52})_{0.96}\text{Li}_{0.04}\text{Nb}_{0.85}\text{Ta}_{0.15}\text{O}_3$ synthesized by spray drying

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Abstract

The synthesis of lead-free ferroelectric materials with composition $(\text{K}_{0.48}\text{Na}_{0.52})_{0.96}\text{Li}_{0.04}\text{Nb}_{0.85}\text{Ta}_{0.15}\text{O}_3$ has been achieved by spray drying technique. Pure perovskite phase was obtained after calcination of as-prepared powders at 800 °C for 1 h. Crystallized powders have a particle size average of 100 nm. Well sintered samples were obtained at 1120 and 1130 °C for 2 h in air with densities of 4.58 and 4.49 g/cm³, respectively. We attributed this improvement as the result of sintering process and the very small particle size in powders. Sintered samples have promising piezoelectric parameters, k_p 0.40–0.41, d_{31} 50–55 pC/N and dielectric losses around 1%.

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1. Introduction

Ferroelectric materials of the PZT family have a great number of applications due to their outstanding electrical properties. Nowadays, a lot of work has been done over an important number of lead-free materials in order to replace PZT-based piezoelectric ceramics. The main motivation behind these efforts is the environmental protection because of great quantity of disposed electronic products containing PZT. Since the publication of Saito et al.¹ where they reported the synthesis and properties of a lead-free material based on niobium and alkaline cations, the research on bismuth–sodium titanates and potassium–sodium niobates, and their solid solutions with other ions has increased in order to improve their electric and piezoelectric properties. The key issue in alkaline niobates is how to reduce the sintering temperatures, bearing in mind the considerable sublimation of sodium and potassium. This induces an unavoidable variation in the starting stoichiometry and consequently in changes of electrical properties. There are different approaches to achieve this goal. The first way to improve the densification is by adding some

oxides such as, CuO, CdO, ZnO, Sc₂O₃, CeO₂ and WO₃.^{2–4} According to different works it is believed that these compounds form a liquid phase at relatively low temperature improving densification. Another possible solution to the problem is the incorporation of other ions in the A and B sites into ABO₃-like structure of the KNN solid solution. In A site, several cations can be added among them are Li⁺, Ca⁺², Ba⁺², while in B site is possible to introduce Sb⁺⁴, Ti⁺⁴ or Ta⁺⁵. A third strategy to improve densification consists in reducing the particle size of the synthesized powders in order to diminish the activation energy involved in the sintering process. Very few reports follow this approach^{5,6}. The aim of this work is to present a new approach for the synthesis and sintering of KNN compound in solid solution with lithium and tantalum, as well as their morphological and electrical characterization.

2. Experimental

$(\text{K}_{0.48}\text{Na}_{0.52})_{0.96}\text{Li}_{0.04}\text{Nb}_{0.85}\text{Ta}_{0.15}\text{O}_3$ (KNLNT) composition was synthesized, using Nb₂O₅ (99.99%), Ta₂O₅ (99.99%), K₂CO₃ (99.8%), Na₂CO₃ (99.9%), Li₂CO₃ (99.997%) powders as starting materials. For the solution preparation HF (40 vol.%), NH₄OH (30 vol.%) and citric acid monohydrate (C₆H₈O₇·H₂O 99.9%) are used. First, a solution was prepared by dissolving Nb₂O₅ and Ta₂O₅ in HF at 70 °C for 8 h. Then, NH₄OH was

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added to this solution until complete precipitation of niobium and tantalum hydrated oxides.⁷ The precipitate was filtered and washed three times with de-ionized water. Subsequently, it was dissolved in a 0.35 molar citric acid solution to form the corresponding citrate complex of niobium and tantalum which are more stable and can be handled without any special atmosphere. On the other hand, the alkaline ions solution was prepared by dissolving potassium, sodium and lithium carbonates in citric acid solution. The two solutions containing alkaline ions, niobium and tantalum were mixed. The resulting solution was fed into a spray dryer (YAMATO Mini Spray-Dryer ADL-31). The equipment can operate setting the inlet or outlet air temperature, and then the inlet air temperature and pressure were established at 180 °C and 392 kPa. The flow rate of the sample was fixed at 8.5 cm³/min. Thus precursor powders were obtained and they were subsequently calcined at temperatures between 600 and 900 °C in order to produce the crystalline powders. Finally, powders calcined at 800 °C during 1 h were uniaxially pressed to form disk shaped pellets (13 mm in diameter and 1.5 mm in thickness) and sintered at 1120 and 1130 °C for 2 h in air without special processing or sintering. The powders and sintered samples were characterized by X-ray powder diffraction at room temperature with Cu K α 1 radiation using a Bruker Advanced D-8 diffractometer. Scanning electron microscopy (SEM) images were obtained using a Leica Cambridge Stereoscan 440 microscope at 20 kV. With the aim of determining dielectric and piezoelectric properties, the sintered pellets were polished and silver conductive paste was applied to the parallel faces and annealed at 600 °C for 30 min. Dielectric and piezoelectric measurements were carried out using an Agilent 4294A Precision Impedance Analyzer. For impedance measurements pellets were attached to platinum leads and placed in a furnace whose temperature was controlled to ± 2 °C. Impedance measurements were made over the frequency range 10² to 10⁷ Hz. Runs were taken in 2–5 °C steps in proximity to the transition temperature; otherwise the steps were 10–15 °C. The rms applied voltage was 0.5 V. In order to allow thermal equilibrium, samples were left at the preset temperature for at least 30 min between measurements. Experiments were performed from room temperature up to 500 °C in a normal lab atmosphere.

For piezoelectric characterization the samples were poled at 130 °C in a silicone oil bath under an external dc electric field of strength 50 kV cm⁻¹. The field was kept 30 min and then each sample was slowly cooled to room temperature in the presence of the field in order to “freeze” the status of polarization. The measurement technique for determining the piezoelectric constants consists of inducing the radial resonance at room temperature by electrical stimulation with 0.5 V rms by means of the Impedance Analyzer elsewhere mentioned. Frequency sweeps were carried out covering two intervals in which fundamental and first overtone resonance and anti-resonance appear. The data was processed using an iterative automatic method described in detail elsewhere.⁸ In the acquisition of experimental data, it is very important to be careful with the conditions under which measurements are performed. Thus the samples must be free from external pressure, so the electrical contacts should be by simple friction of a conducting wire with electrode.

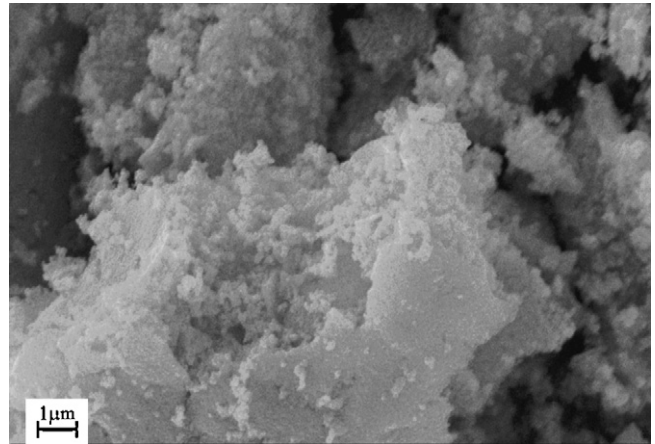


Fig. 1. SEM image of KNLNT powders calcined at 800 °C for 1 h.

3. Results and discussion

A scanning electron microscopy image of KNLNT powder calcined at 800 °C for 1 h is shown in Fig. 1. It is observed that synthesized powders have a particle size average of 100 nm with a standard deviation of 30 nm. This result is not achievable through conventional ceramic technique. It is found that a possible explanation is due to that spray drying eliminates solvent in very short times promoting chemical homogeneity on the precursor powder,^{9,10} besides the fact that the calcination step produces escape of gases resulting in soft agglomerates of fine particles on the calcined powders. On the other hand, it has been reported that the addition of Ta⁺⁵ to KNN reduces considerably the grain growth and can be also one reason of the small size distribution.^{11,12}

The X-rays diffraction patterns for the as-prepared powders and calcined between 600 and 900 °C are shown in Fig. 2. It is possible to observe that the powders obtained by spray drying are completely amorphous. This is due to the rapid solvent elimination and the interaction of the different ions in solution with the citric acid, since citric acid plays the role of complexing and stabilizing niobium, tantalum as well as the

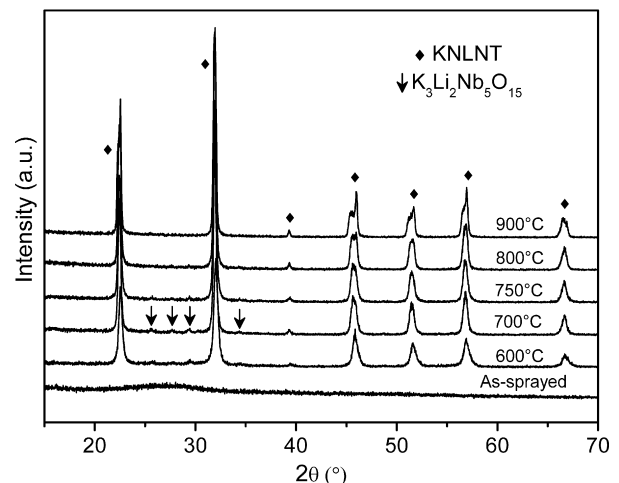


Fig. 2. XRD evolution analysis of KNLNT precursor powders.

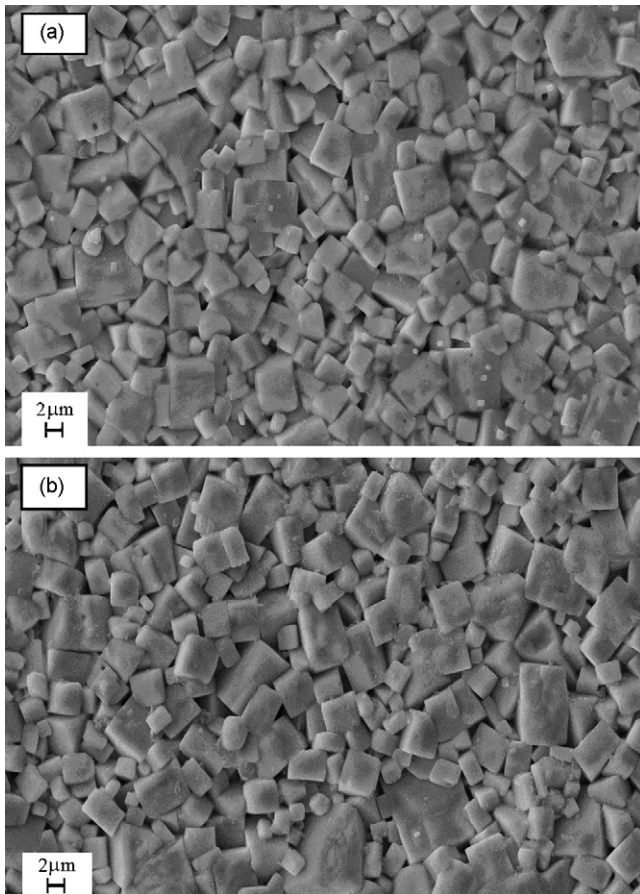


Fig. 3. SEM images of KNLNT sintered pellets: (a) 1120 °C and (b) 1130 °C.

alkaline ions. Thus making possible their homogeneous distribution along the solution.¹³ Then, the dried powders are the mixture of different alkaline ions, niobium, tantalum and citric acid. Once they were thermally treated at 600 °C several Bragg reflections, corresponding to the tetragonal secondary phase $K_3Li_2Nb_5O_{15}$ (JCPDS-ICDD 52-0157) (marked with arrows) and those expected for the KNLNT phase were observed. The secondary phase reflections diminish considerably for the sample calcined at 750 and 800 °C only reflections of the KNLNT phase can be observed. The synthesis of the KNLNT crystalline phase with heat treatment as short as 1 h at 800 °C is possible due to the homogeneous atomic distribution into precursor solution as well as in dried powders.

Compared with the conventional ceramic method, the heat treatment time of powders synthesized by spray drying is reduced, which allows to reduce considerably the deviation of the initial stoichiometry. In addition, the decrease in the powder grain size is expected to improve the sinterability.

Scanning electron microscopy images of samples sintered at 1120 and 1130 °C for 2 h in air are shown in Fig. 3. It is observed that the grains have a pseudo-cubic shape, which is characteristic of KNN-related compounds. Furthermore, depending on the amount and kind of dopant (Li and Ta), orthorhombic–tetragonal structures coexist near room temperature making possible the presence of morphotropic phase boundary (MPB). The Li^+ replaces K^+/Na^+ at the perovskite A site, while the Ta^{+5} enters

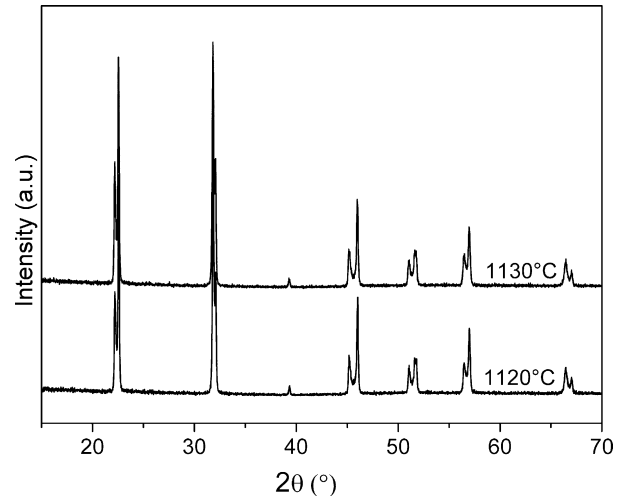


Fig. 4. X-ray diffraction analysis of $(K_{0.48}Na_{0.52})_{0.96}Li_{0.04}Nb_{0.85}Ta_{0.15}O_3$ sintered samples at 1120 and 1130 °C for 2 h.

into the perovskite B site in the ABO_3 perovskite-like structure. The grain size distribution is homogeneous with almost a bimodal grain growth having mean values of 2 and 5 μm . In the synthesis of KNN materials there is an opposite effect between Li^+ and Ta^{+5} , Li^+ promotes grain growth and develops inhomogeneous grain size distribution; on the other hand tantalum inhibits growth and gives materials with narrow grain size distribution.^{11,12,14}

The X-rays diffraction patterns of sintered samples at 1120 and 1130 °C for 2 h are shown in Fig. 4. Apparently, both samples have perovskite-like structure without the evidence of secondary phases. Some studies claim that orthorhombic–tetragonal crystalline structures coexist near room temperature at the MPB, which enhances considerably the dielectric and piezoelectric properties.^{15–17} Based on this supposition it is expected that high values of these properties will be obtained at the MPB.

Variation of dielectric constant with temperature for samples sintered at 1120 °C (5a) and 1130 °C (5b) are plotted in Fig. 5. For the sample sintered at 1120 °C it is noticeable that there is no appreciable dispersion of dielectric constant even when

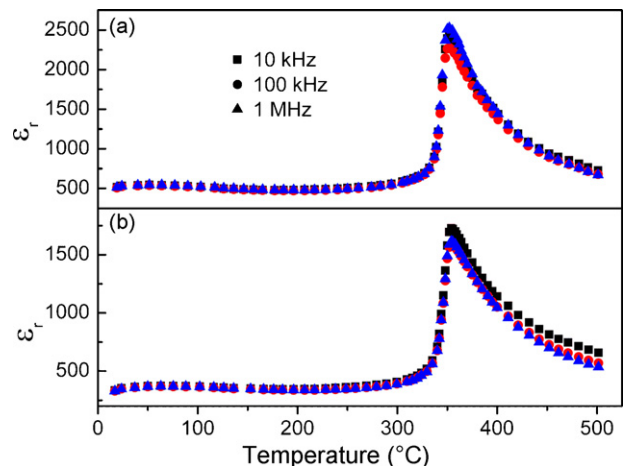


Fig. 5. Variation of dielectric constant with temperature for: (a) sample 1120 °C and (b) sample 1130 °C.

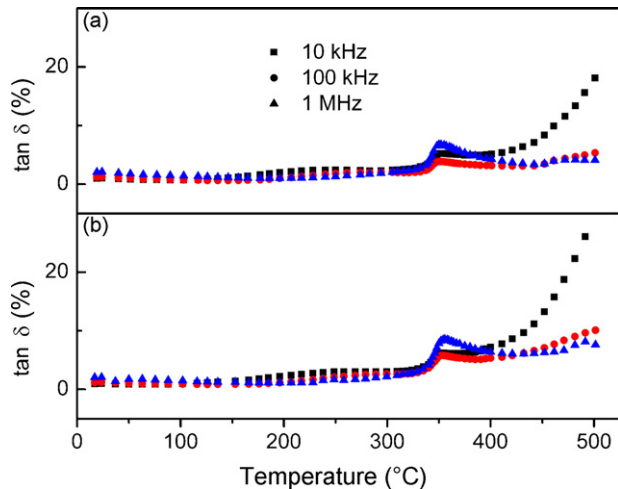


Fig. 6. Dielectric losses of KNLNT samples: (a) 1120 °C and (b) 1130 °C.

$T > T_C$ at 10 kHz, 100 kHz and 1 MHz. For this composition T_C is about 354 °C a comparable value for data reported for samples synthesized through conventional ceramic process. A similar behavior was observed for the sample sintered at 1130 °C, but lower values of ε_r at any temperature and higher dispersion of ε_r when $T > 400$ °C for 10 kHz than sample sintered at 1120 °C were measured.

The values of $\tan \delta$ (%) is presented in Fig. 6 for both samples sintered at 1120 °C (6a) and at 1130 °C (6b). Dielectric losses in both samples are considerably low at room temperature and even near Curie temperature (T_C). At room temperature (25 °C) the value of $\tan \delta$ (%) in both samples at 10 kHz, 100 kHz and 1 MHz are 1.0, 1.2, 2.1 and 1.0, 1.2, 2.0, respectively. Very near the transition ($T = 340$ °C) the values are 3.1, 2.3, 3.2 and 4.2, 3.6, 4.2, respectively. As it can be observed at low frequency $\tan \delta$ increases faster than at higher frequencies, nevertheless this increment is small and only when $T > T_C$ it increases rapidly for 10 kHz. For the other frequencies it increases in a slower manner, this is a sign that samples have good thermal stability due to a well sintering.

In Table 1 the values of k_p , d_{31} , and $\tan \delta$ are presented for both samples. k_p for the sample sintered at 1120 °C has a value of 0.41 while for the sample sintered at 1130 °C is 0.40. Li et al.¹⁸ reported a k_p of 0.40 for the same composition using cold-isostatic pressing (CIP) while Rubio et al.¹⁹ obtained a k_p of 0.37 for $(K_{0.38}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_{2.97}$ com-

position also with CIP. Zhao et al.²⁰ found a k_p of 0.394 for $[(Na_{0.535}K_{0.480})_{0.942}Li_{0.058}](Nb_{0.92}Ta_{0.08})O_3$ composition with normal sintering. Regarding d_{31} , values are of 55 and 50 pC/N, respectively, for samples sintered at 1120 and 1130 °C. Rubio et al. reported a value of 62.1 pC/N in their study while Ringgaard and Wurlitzer found 45 pC/N for the $K_{0.5}Na_{0.5}NbO_3$ compound.^{19,21} As it is well known is difficult to sinter these compounds with stoichiometric composition due to the volatilization of sodium, potassium and lithium. The variation in composition promotes the apparition of secondary phases with a decrease in piezoelectric properties.¹⁷ On the other hand, the optimum sintering temperature for KNN ceramics has very narrow window of around 50 °C for making materials with small variation in their properties.

4. Conclusions

It was possible to synthesize KNLNT powders at relatively low temperature and short calcination time (800 °C at 1 h). The synthesized powders have a particle size average of 100 nm that demonstrated the effectiveness of Spray drying method in the synthesis of KNN-doped piezoceramics and could be an alternative to the conventional oxide method. The synthesized powders were uniaxially pressed and successfully sintered at 1120–1130 °C for 2 h in air with very high densities and without CIP. The piezoelectric properties of sample sintered at 1120 °C were k_p 0.41, d_{31} 55.7 pC/N and $\tan \delta$ (%) 1.0. It was found that sintered samples have a pure perovskite-like structure. The presence of a MPB near room temperature could be the reason of the improved piezoelectric properties, although currently structural analysis are being conducted in our laboratory in order to get a better understanding of the crystalline structure of our compounds. The results presented here show that lead-free piezoceramics based on KNN solid solution are very promising candidates for substituting PZT in some applications.

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References

- Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, et al. Lead-free piezoceramics. *Nature* 2004;**432**:84–7.
- Park H, Choi J, Choi M, Cho K, Nahm S, Lee H, et al. Effect of CuO on the sintering temperature and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$ lead-free piezoelectric ceramics. *J Am Ceram Soc* 2008;**91**:2374–7.
- Zuo R, Rödel J, Chen R, Li L. Sintering and electrical properties of lead-free $Na_{0.5}K_{0.5}NbO_3$. *J Am Ceram Soc* 2006;**89**:2010–5.
- Zuo R, Ye C, Fang X, Yue Z, Li L. Processing and piezoelectric properties of $(Na_{0.5}K_{0.5})_{0.96}Li_{0.04}(Ta_{0.1}Nb_{0.9})_{1-x}Cu_xO_{3-3x/2}$ lead-free ceramics. *J Am Ceram Soc* 2008;**91**:914–7.
- Shiratori Y, Magrez A, Pithan C. Particle size effect on the crystal structure symmetry of $K_{0.5}Na_{0.5}NbO_3$. *J Eur Ceram Soc* 2005;**25**:2075–9.

Table 1
Piezoelectric properties of KNLNT ceramics.

	Sintering temperature (°C)	
	1120	1130
k_p (%)	41	40
ε_r	465	418
d_{31} (pC/N)	55.73	50.55
T_C (°C)	354	354
$\tan \delta$ (%)	1.0 ^(10 kHz)	1.0 ^(10 kHz)
ρ (g/cm ³)	4.58	4.49

6. Rojac T, Benčan A, Uršič H, Malič B, Kosec M. Synthesis of a Li- and Ta-modified (K,Na)NbO₃ solid solution by mechanochemical activation. *J Am Ceram Soc* 2008;**91**:3789–91.
7. Nowak I, Ziolk M. Niobium compounds: preparation characterization, and application in heterogeneous catalysis. *Chem Rev* 1999;**99**:3603–24.
8. Algueró M, Alemany C, Pardo L, González AM. Method for obtaining the full set of linear electric mechanical, and electromechanical coefficients and all related losses of a piezoelectric ceramic. *J Am Ceram Soc* 2004;**87**:209–15.
9. López R, Zárate J, Aguilar EA, Muñoz-Saldaña J. Preparation of neodymium-doped yttrium aluminum garnet powders and fibers. *J Rare Earths* 2008;**26**:670–3.
10. Bezzi F, Costa AL, Piazza D, Ruffini A, Albonetti S, Galassi C. PZT prepared by spray drying: from powder synthesis to electromechanical properties. *J Eur Ceram Soc* 2005;**25**:3323–34.
11. Saito Y, Takao H. High performance lead-free piezoelectric ceramics in the (K,Na)NbO₃–LiTaO₃ solid solution system. *Ferroelectrics* 2006;**338**:17–32.
12. Chang Y, Yang Z, Wei L. Microstructure, density, and dielectric properties of lead-free (K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.96–x}Ta_xSb_{0.04})O₃ piezoelectric ceramics. *J Am Ceram Soc* 2007;**90**:1656–8.
13. Camargo ER, Popa M, Kakihana M. Sodium niobate (NaNbO₃) powders synthesized by a wet-chemical method using a water-soluble malic acid complex. *Chem Mater* 2002;**14**:2365–8.
14. Song HC, Cho KH, Park HY, Ahn CW, Nahm S, Uchino K, et al. Microstructure and piezoelectric properties of (1–x)(Na_{0.5}K_{0.5})NbO₃–xLiNbO₃ ceramics. *J Am Ceram Soc* 2007;**90**:1812–6.
15. Guo Y, Kakimoto K, Ohsato H. (Na_{0.5}K_{0.5})NbO₃–LiTaO₃ lead-free piezoelectric ceramics. *Mater Lett* 2005;**59**:241–4.
16. Du H, Tang F, Liu D, Zhu D, Zhou W, Qu S. The microstructure and ferroelectric properties of (K_{0.5}Na_{0.5})NbO₃–LiNbO₃ lead-free piezoelectric ceramics. *Mater Sci Eng B* 2007;**136**:165–9.
17. Yang Z, Chang Y, Liu B, Wei L. Effects of composition on phase structure, microstructure and electrical properties of (K_{0.5}Na_{0.5})NbO₃–LiSbO₃ ceramics. *Mater Sci Eng A* 2006;**432**:292–8.
18. Li J, Zhen Y, Zhang B, Zhang L, Wang K. Normal sintering of (K,Na)NbO₃-based lead-free piezoelectric ceramics. *Ceram Int* 2008;**34**:783–6.
19. Rubio-Marcos F, Ochoa P, Fernandez JF. Sintering and properties of lead-free (K,Na,Li)(Nb,Ta,Sb)O₃ ceramics. *J Eur Ceram Soc* 2007;**27**:4125–9.
20. Zhao P, Tu R, Goto T, Zhang B, Yang S. Effect of Ta content on phase structure and electrical properties of piezoelectric lead-free [(Na_{0.535}K_{0.480})_{0.942}Li_{0.058}](Nb_{1–x}Ta_x)O₃ ceramics. *J Am Ceram Soc* 2008;**91**:3440–3.
21. Ringgaard E, Wurlitzer T. Lead-free piezoceramics based on alkali niobates. *J Eur Ceram Soc* 2005;**25**:2701–0706.