



# The influence of different niobium pentoxide precursors on the solid-state synthesis of potassium sodium niobate

Jitka Hreščak<sup>a,b,\*</sup>, Andreja Bencan<sup>a</sup>, Tadej Rojac<sup>a</sup>, Barbara Malič<sup>a,b</sup>

<sup>a</sup> Jožef Stefan Institute, Electronic Ceramics Department, Jamova cesta 39, 1000 Ljubljana, Slovenia

<sup>b</sup> Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia

Received 10 January 2013; received in revised form 4 July 2013; accepted 8 July 2013

Available online 1 August 2013

## Abstract

Two batches of  $K_{0.5}Na_{0.5}NbO_3$  were prepared from the orthorhombic and monoclinic  $Nb_2O_5$  polymorphs and potassium and sodium carbonates. The influence of the different  $Nb_2O_5$  precursors on the solid-state synthesis of  $K_{0.5}Na_{0.5}NbO_3$  was studied. To reduce the particle size, both types of  $Nb_2O_5$  were milled prior to use. XRD and TEM analyses showed that the milled orthorhombic  $Nb_2O_5$  was single phase; however, after milling the monoclinic  $Nb_2O_5$  consisted of large monoclinic particles and orthorhombic nanocrystals. The latter reacted with the carbonates to form  $(K_xNa_{1-x})NbO_3$  solid solutions with varying K/Na molar ratios, while the orthorhombic  $Nb_2O_5$  reacted to form a homogeneous solid solution of  $K_{0.5}Na_{0.5}NbO_3$ . Sintering of the two powder compacts resulted in different densification behavior and microstructure. This study shows the important influence of the  $Nb_2O_5$  precursor phase and the particle size distribution on the homogeneity and further densification of the potassium sodium niobate solid solution.

© 2013 Elsevier Ltd. All rights reserved.

**Keywords:** Potassium sodium niobate; Niobium pentoxide; Solid-state synthesis

## 1. Introduction

Solid solutions of sodium potassium niobate with the composition  $K_{0.5}Na_{0.5}NbO_3$  have been some of the most studied lead-free piezoelectric materials over the past few years.<sup>1,2</sup> A high electromechanical coupling factor and a low dielectric permittivity make potassium sodium niobate ceramics interesting for ultrasonic applications.<sup>1</sup> However, despite there being many reports on the preparation and properties of this material, problems with densification and grain growth control remain. In addition, the reproducibility of the solid-state synthesis is still an issue, based on different authors reporting a variety of properties for the  $K_{0.5}Na_{0.5}NbO_3$  product prepared using the same procedure.<sup>3–5</sup>

Very limited data can be found on the actual reaction mechanism of  $K_{0.5}Na_{0.5}NbO_3$  prepared using the classic solid-state synthesis route. Malič<sup>6</sup> studied the solid-state reaction of  $K_{0.5}Na_{0.5}NbO_3$  from alkaline carbonates and

niobium pentoxide by diffusion couples. They found that at 600 °C,  $K_{0.5}Na_{0.5}NbO_3$  is formed via an intermediate phase that best corresponds to the solid solution  $(K_xNa_{1-x})_2Nb_4O_{11}$ . The reaction proceeds by the diffusion of  $K^+$ ,  $Na^+$  and  $O^{2-}$  ions through the reaction layer of the intermediate phase and  $K_{0.5}Na_{0.5}NbO_3$  toward  $Nb_2O_5$ . The reaction rate is determined by the diffusion of the slower species, i.e.,  $K^+$ .

A similar mechanism was previously reported for a better-known system, i.e.,  $BaTiO_3$ . The solid-state reaction from  $BaCO_3$  and  $TiO_2$  was studied by Templeton et al.<sup>7</sup> They reported that at first, a small amount of  $BaTiO_3$  is formed on the contact of the reagents. The subsequent reaction is diffusion controlled and in addition to the  $BaTiO_3$ ,  $Ba_2TiO_4$  is produced in a prevailing amount until all the  $BaCO_3$  is reacted. Finally,  $BaTiO_3$  is formed at the expense of the  $Ba_2TiO_4$  intermediate product through a reaction with the residual  $TiO_2$ . Later, Buscaglia et al.<sup>8</sup> studied the influence of the particle size distribution (PSD) of  $BaCO_3$  on the solid-state synthesis of the  $BaTiO_3$ . They reported that when nanocrystalline  $TiO_2$  and nanocrystalline  $BaCO_3$  were used as precursors, a single-phase  $BaTiO_3$  was obtained after 10 h of calcination at 800 °C, while in the case of the coarse  $BaCO_3$  annealing for 4 h at 1000 °C was necessary.

\* Corresponding author.

E-mail address: [jitka.hrescak@ijs.si](mailto:jitka.hrescak@ijs.si) (J. Hreščak).

In analogy with BaTiO<sub>3</sub>, the PSD of the starting powders plays a crucial role in the synthesis of K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>. In principle, the carbonates should have a uniform PSD and a small particle size to obtain good homogeneity of the potassium and sodium carbonates around the particles of niobium pentoxide in the initial mixture. Based on the work of Malič et al.,<sup>6</sup> the PSD of Nb<sub>2</sub>O<sub>5</sub> would determine the rate of the overall diffusion-controlled reaction since at the usual calcination temperature the diffusion of Nb<sup>5+</sup> is negligible and only the diffusion of K<sup>+</sup>, Na<sup>+</sup> and O<sup>2-</sup> takes place.

Nb<sub>2</sub>O<sub>5</sub> is the most commonly used source of Nb in the solid-state synthesis of potassium sodium niobate and is known to exist in different polymorphs. The formation of a polymorph is dependent on the production route and possible contamination.<sup>9</sup> The most common polymorphs are the orthorhombic  $\gamma$ -phase and the high-temperature-stable monoclinic  $\alpha$ -phase. The phase composition is not specified in commercially available Nb<sub>2</sub>O<sub>5</sub>, and neither is it usually reported in the literature when Nb<sub>2</sub>O<sub>5</sub> is used for synthesis. Very limited literature is available on the possible influence of the Nb<sub>2</sub>O<sub>5</sub> phase composition on the solid-state reaction in niobates. For example, Kuznetsova et al.<sup>10</sup> prepared (Na<sub>1-x</sub>Li<sub>x</sub>)NbO<sub>3</sub> ceramics from three different commercial batches of Nb<sub>2</sub>O<sub>5</sub> with different ratios of monoclinic  $\alpha$  and  $\eta$  polymorphs and reported their functional properties.

The aim of this study was to investigate the influence of the polymorphic form of Nb<sub>2</sub>O<sub>5</sub> on the solid-state synthesis of K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>. Two batches of K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> were prepared using identical procedures from two different Nb<sub>2</sub>O<sub>5</sub> polymorphs, i.e., orthorhombic and monoclinic. The reactions of the two homogenized mixtures were studied. The possible reasons for the Nb<sub>2</sub>O<sub>5</sub> polymorphs' different reactivity with the alkaline carbonates during the synthesis of K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> are discussed. The paper clearly shows the importance of different Nb<sub>2</sub>O<sub>5</sub> polymorphs on the course of the solid-state reaction of K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>, which has not been considered so far.

## 2. Experimental procedure

Two batches of K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> were prepared from the following starting powders: K<sub>2</sub>CO<sub>3</sub> (anhydrous, 99.9+ %, ChemPur, Karlsruhe, Germany), Na<sub>2</sub>CO<sub>3</sub> (anhydrous, 99.9+ %, ChemPur, Karlsruhe, Germany) and two types of Nb<sub>2</sub>O<sub>5</sub>. The first Nb<sub>2</sub>O<sub>5</sub> (325 mesh, 99.9%, Sigma-Aldrich, Steinheim, Germany) had an XRD pattern that could be indexed to the orthorhombic unit cell<sup>11</sup> and the second Nb<sub>2</sub>O<sub>5</sub> (99.9985%, Alfa Aesar, Karlsruhe, Germany) could be indexed to the monoclinic unit cell.<sup>12</sup> All the powders were dried for 6 h at 200 °C, ball milled in a planetary mill in acetone for 4 h and dried for 1 h at 105 °C and 2 h at 200 °C. After the milling the K<sub>2</sub>CO<sub>3</sub> had particles with a median diameter ( $d_{50}$ ) 4.52  $\mu$ m, Na<sub>2</sub>CO<sub>3</sub> had  $d_{50}$  = 2.58  $\mu$ m, Nb<sub>2</sub>O<sub>5</sub>-ortho had  $d_{50}$  = 0.33  $\mu$ m and Nb<sub>2</sub>O<sub>5</sub>-mono had  $d_{50}$  = 0.47  $\mu$ m. All the powders were stored in a desiccator.

The milled and dried precursors were weighed in the exact stoichiometric ratio to prepare K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> from two different Nb<sub>2</sub>O<sub>5</sub> in a dry box and the two mixtures were homogenized in a planetary mill for 4 h in acetone. The

homogenized mixtures were dried, compacted into pellets and calcined two times at 800 °C for 4 h with intermediate and final planetary milling for 4 h in acetone.

For the sintering study, the powders were compacted by uniaxial press into cylindrical samples, cold isostatically pressed with 200 MPa and sintered at the selected sintering temperature for 2 h, with the heating and cooling rate of 5 K/min, in the tube furnace. The density of the sintered ceramics was determined by the geometric or Archimedes method in deionized water at room temperature and is reported as the average of 3 measurements. For the XRD analysis, the sintered pellets were crushed into powders.

Granulometric analyses of the starting powders were performed with a Microtrac S3500 laser granulometer. Thermogravimetry (TG) and differential thermal analysis (DTA) were conducted on a Netzsch STA 409 C/CD. Approximately 50 mg of the homogenized mixtures for the TG/DTA were placed in Pt/Rh crucibles and the homogenized mixtures were recorded at a heating rate of 10 K/min up to 750 °C. The powders were kept at 200 °C for 3 h before the actual TG/DTA measurements.

The dimensional changes of the pellets of the homogenized, calcined and milled mixtures during heating were recorded with a Leitz heating-stage microscope, Version 1A, at a heating rate of 10 K/min. The phase composition and structure of the precursors and the ceramic powders were determined by X-ray diffraction (XRD) analyses performed on a PANalytical X'Pert PRO diffractometer with a Cu K $\alpha$  radiation source and a Ge monochromator. The data were collected in the 2 $\theta$  range from 10° to 90° with a step of 0.016°/100 s. A Rietveld refinement was performed to estimate the phase ratio of the Nb<sub>2</sub>O<sub>5</sub>-mono after milling. The refinement was carried out using the Topas program refining the unit cell parameters and the scale factor. The background was modeled using the Legendre polynomial in the interval 23° to 90° 2 $\theta$ . The peak profile was refined using the Pseudo-Voigt function. Orthorhombic (ICSD 1840) and monoclinic (ICSD 16605) Nb<sub>2</sub>O<sub>5</sub> were used as model structures for the refinement. The specific surface area was analyzed using the N<sub>2</sub> adsorption BET method on a NOVA 2200E, Quantachrome Instruments. The morphology of the precursors and the ceramic powders was analyzed using a Jeol JSM-7600F field-emission scanning electron microscope (SEM) and a Jeol JEM-2100 transmission electron microscope (TEM). For the SEM analysis of the ceramics, the samples were cut with a diamond wire saw, mounted in epoxy and polished using standard metallographic techniques to a 0.25  $\mu$ m finish. Thermal etching of the ceramics was done at 1020 °C, 40 min. Prior to the analysis, the samples were coated with 4-nm-thick carbon layer in a Gatan PECS 682.

The annealing of the samples up to 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, and 950 °C for a subsequent XRD investigation, as well as the additional annealing of the calcined powder at 950 °C for 4 h were made in a chamber furnace with a heating rate of 5 K/min.

In the subsequent text the monoclinic Nb<sub>2</sub>O<sub>5</sub> and the potassium sodium niobate prepared from the monoclinic Nb<sub>2</sub>O<sub>5</sub> are denoted as Nb<sub>2</sub>O<sub>5</sub>-mono and KNN-mono, respectively, and the orthorhombic Nb<sub>2</sub>O<sub>5</sub> and the potassium sodium niobate

Download English Version:

<https://daneshyari.com/en/article/7899077>

Download Persian Version:

<https://daneshyari.com/article/7899077>

[Daneshyari.com](https://daneshyari.com)