

# THE SYNTHESIS OF $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ CERAMICS

## SINTEZA KERAMIKE $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$

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$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (NBT) ceramics were solid-state synthesized by reacting materials at 800 °C and 850 °C. After the sintering, minor weight losses and a change of symmetry of the NBT unit cell from cubic-like to rhombohedral were observed. The existence of cubic-like symmetry for the NBT unit cell at room temperature during the preparation of the ceramics has not been reported previously. Using scanning electron microscopy we observed the presence of the  $\text{NaBiTi}_6\text{O}_{14}$  secondary phase in the sintered samples; however, X-ray powder-diffraction analysis was found to be insufficiently sensitive to detect this phase. With prolonged sintering at 1100 °C, or higher, the secondary phase decomposed to form NBT and  $\text{TiO}_2$ . Such a heat treatment resulted in dense NBT ceramics with only traces of the  $\text{TiO}_2$  secondary phase.

Key words:  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ,  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ , synthesis, solid-state reaction, cubic-like symmetry

Sinteza keramike  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (NBT) smo izvedli z reakcijo v trdnem pri 800 °C in 850 °C. Po sintranju smo opazili manjšo izgubo mase vzorca in spremembo simetrije osnovne celice NBT iz kubični podobne v romboedrično. Pri pripravi keramike do sedaj še niso poročali o obstoju kubični podobne simetrije osnovne celice NBT pri sobni temperaturi. Pri analizi sintranjih vzorcev z vrstičnim elektronskim mikroskopom smo opazili sekundarno fazo  $\text{NaBiTi}_6\text{O}_{14}$ , medtem ko se je rentgenska praškovna analiza izkazala kot nezadostna pri njenem detektiranju. Pri podaljšanem sintranju pri 1100 °C ali višje je sekundarna faza razpadla v NBT in  $\text{TiO}_2$ . Po takšnem postopku žganja smo pripravili gosto keramiko NBT, ki je vsebovala le sledove  $\text{TiO}_2$  sekundarne faze.

Ključne besede:  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ,  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ , sinteza, reakcija v trdnem, kubični podobna simetrija

## 1 INTRODUCTION

The most commonly used electric-field tunable devices are phase shifters, tunable filters, tunable capacitors, etc <sup>1</sup>. Such applications demand high values of dielectric tunability, low dielectric losses and a low temperature dependence of permittivity. The relative dielectric tunability is defined as the relative change in the permittivity after applying a DC-bias electric field  $(\epsilon(0) - \epsilon(E_0)) / \epsilon(0)$ . The investigations of tunable materials have been focused mainly on paraelectric modifications near the ferroelectric transition. Among these materials it is mostly the modified incipient ferroelectrics, like  $\text{SrTiO}_3$  and  $\text{KTaO}_3$ , that have been investigated <sup>2</sup>, in particular  $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ -based materials <sup>1</sup>. The paraelectric modifications of these materials can exhibit high values of permittivity, and consequently tunability, due to their high Curie-Weiss constant, low dielectric losses due to the absence of ferroelectric domains and a low temperature dependence of permittivity <sup>3</sup>. However, it was found that the tunability and the dielectric losses are related in such a way that the dielectric losses increase with an increase in the tunability of a particular material <sup>4</sup>. Apart from these materials, the behavior of antiferroelectrics and their paraelectric modifications under a DC-bias field and an assessment of their use in tunable devices have been poorly investigated.

$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (NBT) is a complex perovskite compound. Above 540 °C the symmetry of NBT is cubic;

between 400 °C and 500 °C it is tetragonal; and below 255 °C it is rhombohedral <sup>5</sup>. The maximum in the permittivity occurs at about 320 °C <sup>6</sup>, which is not at the temperature of the phase transition. This is a somewhat unusual behavior for a dielectric property because the maximum of the permittivity normally occurs at the temperature of the ferroelectric transition. In the temperature ranges from 500 °C to 540 °C and from 255 °C to 400 °C the coexistence of the cubic and the tetragonal, and the tetragonal and the rhombohedral phases, respectively, was found <sup>2</sup>. In spite of many recent studies the information about the nature of the phase transitions is still not coherent <sup>7</sup>. However, it has been observed that NBT, when modified with compounds like  $\text{BaTiO}_3$  <sup>8</sup>,  $\text{PbTiO}_3$  <sup>9</sup> and  $\text{SrTiO}_3$  <sup>10</sup>, exhibits regular anti-ferroelectric hysteresis loops at elevated temperatures.

NBT ceramics have already been prepared by solid-state reaction <sup>7</sup>, hydrothermally <sup>11</sup>, mechanochemically <sup>12</sup>, by a sol-gel method <sup>13</sup> and by a citrate-gel method <sup>14</sup>, although the reaction mechanism has been much less investigated and discussed than the phase transitions.

In the literature the most frequently described method for preparing NBT ceramics involves a solid-state reaction, see **Table 1**. In our preliminary investigations we repeated the described procedure. The obtained ceramics were not single phase according to our analysis with a scanning electron microscope. In the literature the NBT ceramics produced in this way are always

described as being single phase, but this information is only based on X-ray powder diffraction.

**Table 1:** Processing parameters for NBT ceramics  
**Tabela 1:** Parametri procesiranja keramike NBT

Synthesis	Reaction temperature and time			Sintering temperature and time	
	1. firing	2. firing			
1*	800 °C, 2 h	/	milling	CIP	1100 °C, 1 h
2	800 °C, 5 h	850 °C, 5h	milling	CIP	1100 °C, 20 min
3				UP	1100 °C, 10 h
4				UP	1150 °C, 20 h

\* = in the literature the most frequently described method for preparing NBT ceramics

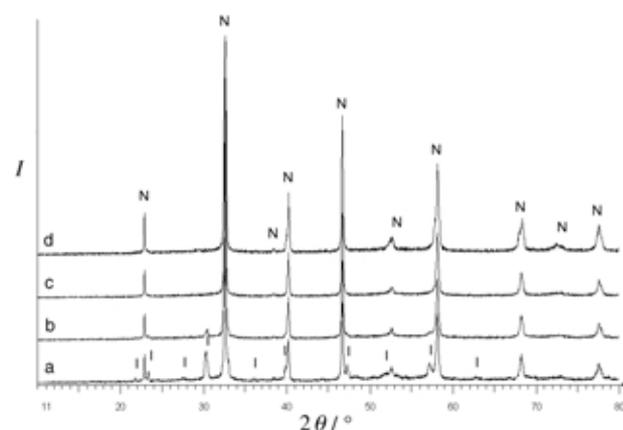
CIP = cold isostatically pressed with 750 MPa

UP = uniaxially pressed with 100 MPa

In this study we investigated the synthesis of NBT ceramics produced by solid-state reaction. The results of this study will further serve for the preparation of, and tunability measurements on, antiferroelectrics and their paraelectric phases.

## 2 EXPERIMENTAL PROCEDURE

The starting materials were  $\text{Bi}_2\text{O}_3$  (Alfa Aesar, 99.975 %),  $\text{TiO}_2$  (Alfa Aesar, 99.8 %) and  $\text{Na}_2\text{CO}_3$  (Alfa Aesar, 99.997 %). A stoichiometric mixture of the starting materials for the preparation of the NBT ceramics was homogenized and treated as indicated in **Table 1**. The procedure, which was carried out under number 1, is the most frequently described in the literature. It consists of 2 h of firing of the stoichiometric



**Figure 1:** XRD patterns of samples after 2 h of firing at 800 °C (a), 5 h of firing at 800 °C (b), 5 h of firing at 850 °C (c) and after 20 min of sintering at 1100 °C (d) (N = NBT, I = intermediate products)

**Slika 1:** Rentgenski difraktogrami vzorcev po 2 h žganju pri 800 °C (a), 5 h žganja pri 800 °C (b), 5 h žganja pri 850 °C (c) in 20 min sintranja pri 1100 °C (d) (N = NBT, I = vmesni produkti)

mixture at 800 °C, milling, cold isostatic pressing and sintering at 1100 °C for 1 h<sup>15</sup>.

The X-ray powder-diffraction (XRD) studies were performed with Bruker AXS D4 Endeavor diffractometer using  $\text{Cu K}\alpha$  radiation. The XRD data were collected from  $10^\circ < 2\theta < 80^\circ$  with a step of  $0.02^\circ$ , a counting time of 2 s, and a variable V12 slit.

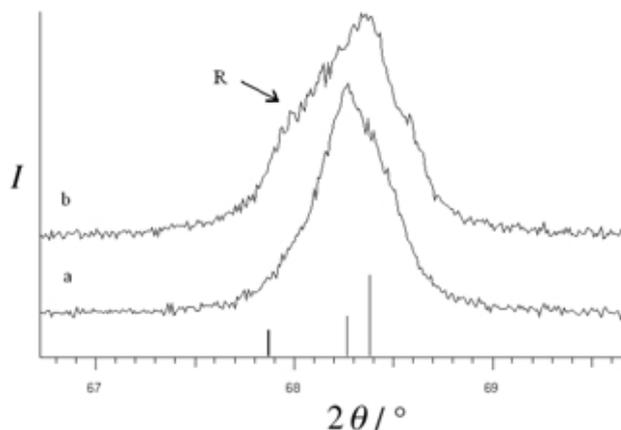
The composition of the sintered samples was also analyzed with a Jeol-5800 scanning electron microscope (SEM), while their porosity was visually inspected with an Olympus B203 optical microscope (OM).

## 3 RESULTS AND DISCUSSION

The XRD pattern of the sample after 2 h of firing at 800 °C (**Figure 1a**) showed that the sample contained an NBT matrix as well as some other crystalline phases, mainly a compound that is isostructural with  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . The fraction of secondary phases decreased after a prolonged reaction time, i.e., 5 h, at the same temperature (**Figure 1b**).

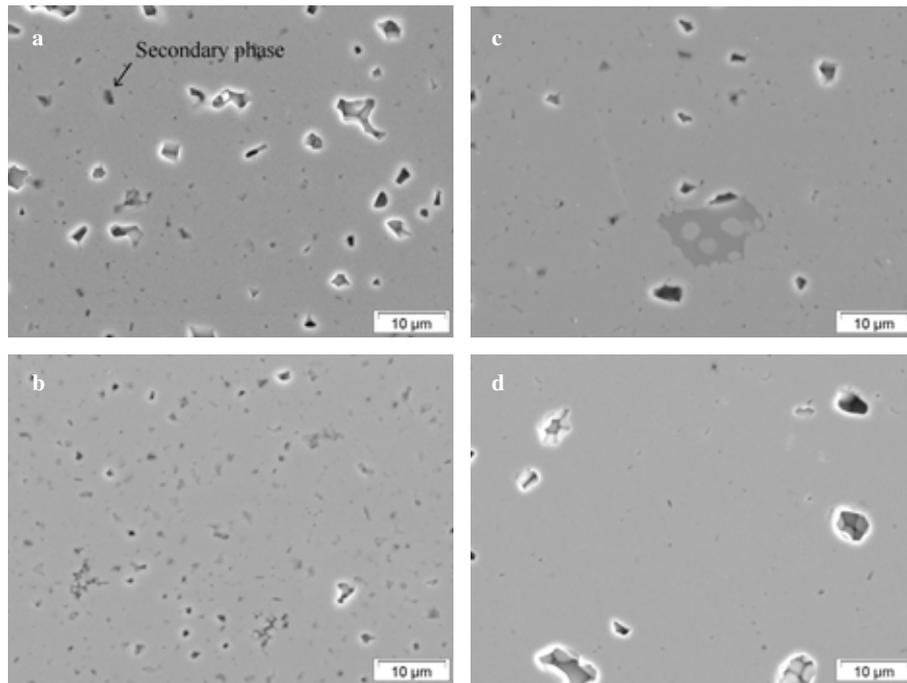
Because the starting mixture for the preparation of the NBT ceramics contained  $\text{Na}_2\text{CO}_3$ , the weight of the mixture should decrease during the reaction due to the evaporation of  $\text{CO}_2$ . After the complete reaction of  $\text{Na}_2\text{CO}_3$  the weight of the mixture should be equal to stoichiometric NBT. Weight-loss measurements during our experiments showed that the weight of the sample after the reaction was higher than that of stoichiometric NBT, which indicated that the  $\text{Na}_2\text{CO}_3$  did not react completely and was therefore still present in the sample.

The XRD pattern of a sample after a subsequent 5 h of firing at 850 °C (**Figure 1c**) showed the presence of only the NBT phase. Similarly, XRD patterns of all the sintered samples did not show the presence of any additional phase (**Figure 1d**). However, a detailed examination of all the patterns revealed that during the



**Figure 2:** XRD diffraction lines at  $2\theta \approx 68^\circ$  of samples after 5 h of firing at 800 °C (a) and after 10 h of sintering at 1100 °C (b) (R: rhombohedral split)

**Slika 2:** Rentgenske uklonske linije pri  $2\theta \approx 68^\circ$  vzorcev po 5 h žganja pri 850 °C (a) in po 10 h sintranja pri 1100 °C (b) (R: romboedrična cepitev)



**Figure 3:** SEM images of samples sintered at 1100 °C for 1 h (a), at 1100 °C for 20 min (b), at 1100 °C for 10 h (c) and at 1150 °C for 20 h (d)  
**Slika 3:** SEM posnetki vzorcev, sintranih 1 h pri 1100 °C (a), 20 min pri 1100 °C (b), 10 h pri 1100 °C (c) in 20 h pri 1150 °C (d)

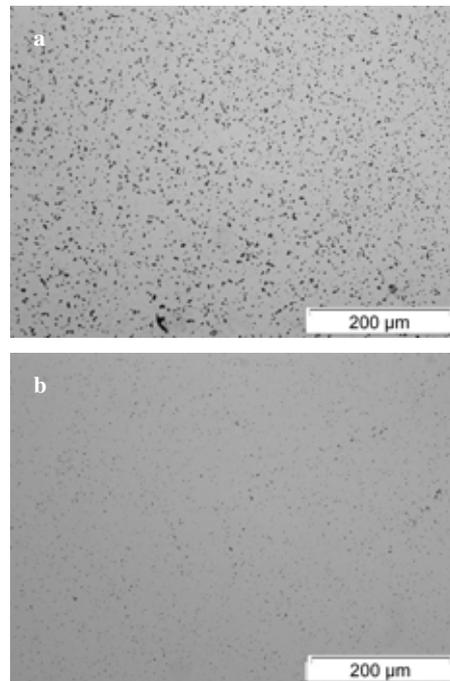
sintering process the symmetry of all the diffraction peaks changed from cubic-like to rhombohedral (**Figure 2**). The latter is identical with the rhombohedral symmetry described in the literature <sup>2</sup>. The existence of a cubic-like symmetry for NBT at room temperature has been reported once, for an NBT single crystal produced by the Czochralski method <sup>16</sup>. Although NBT single crystals have been produced by this method many times, they have always been found to be rhombohedral, except for this one example.

SEM images of all the sintered samples are shown in **Figure 3**. Except for the case of prolonged sintering at 1150 °C, all the images revealed the presence of the same secondary phase, even though it could not be seen from the XRD patterns. The composition of the secondary phase was determined with EDS analysis to be  $\text{NaBiTi}_6\text{O}_{14}$ .

During the sintering of all the samples we detected weight losses of less than 1 wt. %. With regard to the presence of the  $\text{NaBiTi}_6\text{O}_{14}$  secondary phase in the sintered samples and the stoichiometric NBT, the weight losses could be associated with the evaporation of sodium- and bismuth-rich compounds.

In cases 2, 3 and 4 the samples after the second firing were sintered under different conditions (**Table 1**). According to the SEM analyses of these sintered samples the fraction of  $\text{NaBiTi}_6\text{O}_{14}$  secondary phase decreased with increasing sintering time and temperature (**Figures 3b, 3c and 3d**). This is in agreement with the literature data that indicates that the  $\text{NaBiTi}_6\text{O}_{14}$  decomposes to form NBT and  $\text{TiO}_2$  at 1100 °C <sup>17</sup>. We observed that it

completely decomposed when the sample was exposed to 1150 °C for 20 h. In this sample we found that no  $\text{NaBiTi}_6\text{O}_{14}$  phase was present; however, we observed traces of a secondary phase, which is most likely  $\text{TiO}_2$ .



**Figure 4:** OM images of samples sintered at 1100 °C for 1 h (a) and at 1100 °C for 20 min (b)

**Slika 4:** OM posnetka vzorcev, sintranih 1 h pri 1100 °C (a) in 20 min pri 1100 °C (b)

An exact EDS analysis was not performed due to the small volumes of this phase.

In case 1 we sintered a sample at 1100 °C for 1 h after only one firing, when the sample still contained intermediate products as well as some initial Na<sub>2</sub>CO<sub>3</sub>. According to the SEM analysis of a sintered sample the fraction of NaBiTi<sub>6</sub>O<sub>14</sub> secondary phase was lower than in case 2, when the sample was sintered at 1100 °C for 20 min after double firing (**Figures 3a** and **3b**). From this it appears that when the synthesis of the NBT was completed during the sintering, less secondary phase was formed. However, this is not an appropriate procedure for the development of the microstructure because of the evaporation of CO<sub>2</sub>. The porosity of the sintered sample is shown in **Figure 4a**, and it is much higher than in case 2 (**Figure 4b**).

#### 4 CONCLUSIONS

We found that the synthesis of NBT ceramics follows a different reaction mechanism than described in the literature. Single-phase NBT ceramics have not been well documented, even though the properties of NBT ceramics have been extensively discussed. From our study we believe that this can be due to low XRD sensitivity when it comes to detecting the NaBiTi<sub>6</sub>O<sub>14</sub> secondary phase.

We observed that during the preparation of NBT ceramics the symmetry of the unit cell changed from cubic-like to rhombohedral. This change can be associated with a different stoichiometry of the unit cell, which would, on the basis of the existing phase relations in the Bi<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-TiO<sub>2</sub> system, result in weight losses and the formation of the NaBiTi<sub>6</sub>O<sub>14</sub> phase. However, with optimization of the heat-treatment conditions we

managed to prepare dense NBT ceramics with only traces of TiO<sub>2</sub> secondary phase.

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