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Investigations on the Synthesis of Bi_3NbTiO_9 Ceramics

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Abstract

The perovskite-layered ceramics of Bi_3NbTiO_9 *(BNT), also known as Aurivillius phase, was obtained. The process of preparation was investigated by X-ray diffraction method. The synthesis of BNT was carried out according to the solid-state reaction from the conventional mixture of oxides (*Bi_2O_3*,* TiO_2*,* Nb_2O_5*) within the temperature range* $T_S = 400–1200°C$*. The influence of addition of NaCl on the process of synthesis was also investigated. It was found that above* $T_S = 900°C$ *the ratio of the* Bi_3NbTiO_9 *phase was almost 90% and the admixture of NaCl decreased the synthesis temperature. Dependence of the amount of the BNT phase in the bulk material versus the temperature of synthesis is given. Evolution of the structural parameters of BNT and NaCl - modified BNT at different synthesis temperatures was shown as well as recording of Raman scattering spectra. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

In the course of a comprehensive investigation of mixed bismuth oxides Aurivillius discovered the existence of a group of metal oxides having bismuth oxide layers alternating with perovskite structure layers.[1–3] He has synthesised a number of mixed bismuth oxides of the formula: $(Bi_2O_2)^{2+}(A_{m\text{-}1}B_mO_{3m+3})^{2-}$. Here A can be mono-, di- or trivalent ions or a mixture of them, B represents Ti^{4+}, Nb^{5+}, Ta^{5+}, Mo^{6+}, W^{6+}, Fe^{3+}, and m is the number of octahedral layers in the perovskite slab (there have been obtained to date layered perovskites with $m = 1$; 1·5; 2; 2·5; 3; 3·5; 4; 5; 8 [4]). Since this discovery more than 50 compounds have been found to adopt this type of structure[4–10] and to show a peak in the temperature dependence of the dielectric constant and/or hysteresis loops, i.e. characteristics of ferroelectricity. Bismuth niobate-titanate, Bi_3NbTiO_9, is an example of such compounds with $m = 2$. The crystal structure of BNT was determined by Aurivillius and is shown in Fig. 1. One can see that the structure of Bi_3NbTiO_9 is thus built up of $Bi_2O_2^{2+}$ layers between which $BiNbTiO_7^{2-}$ layers are inserted. In the $BiNbTiO_7$ units, Nb/Ti ions are enclosed by oxygen octahedra which are linked through corners forming O–Nb/Ti–O linear chains. Bi ions occupy the spaces in the framework of Nb/TiO_6 octahedra. Thus, $BiNbTiO_7$ units possess a remarkable similarity to the perovskite-type structure. The height of the perovskite-type layer sandwiched between Bi_2O_2 layers in Bi_3NbTiO_9 is equal to four O–Nb/Ti–O distances or approximately to $m = 2$ ABO_3 perovskite units.

Bismuth oxide layered perovskites are of substantial interest for different applications. The capacitors based on layered perovskites have negligible polarisation fatigue, long polarisation retention, and ability to maintain good electrical properties even when the layer is < 100 nm thick. This is why they are prospective for integrated circuit memories[11] and high temperature piezoelectric sensors.[12] One can form and/or change electrophysical properties of bismuth oxide layered perovskites because they give great possibilities of changing their chemical constitution[8] (e.g. by ionic substitutions in A and B positions) and crystalline structure[7] (due to displacement of ions from their regular positions, twist of octahedral chains or

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*To whom correspondence should be addressed. Fax: +48-32-291-8243; e-mail: czekaj@us.edu.pl displacement of ions with mutual twist of octahedrons).

It was our goal in the present study to investigate the process of synthesis of Bi_3NbTiO_9 ceramics both pure and modified with 1 wt% NaCl as well as study their structure and optical properties by means of Raman scattering.

2 Experimental

Ceramic discs of Bi_3NbTiO_9 were prepared by conventional mixed oxide method according to the solid-phase synthesis reaction from the mixture of ingredients, viz. Bi_2O_3, TiO_2 and Nb_2O_5. As an active dissolvent NaCl was used in the amount of 1% weight over the BNT stoichiometry. It is known that NaCl is characterised by a low melting point ($T = 801°C$) and in a liquid form it creates high concentration of the surface defects of the particles of the matrix material. Therefore, the activation energy of the sintering process is decreased. According to our estimations 1 wt% of NaCl was enough to form thin cover over the 1 μm-grains of the matrix material.

The crystalline structure was checked by X-ray diffraction method (Θ–2Θ method, CuK_α radiation) at room temperature. Accuracy of calculating of the parameters of the elementary cell was as follows: $\Delta a = \Delta b = \pm 0{\cdot}005 \times 10^{-10}\,m, \Delta c = \pm 0{\cdot}01 \times 10^{-10}\,m$.

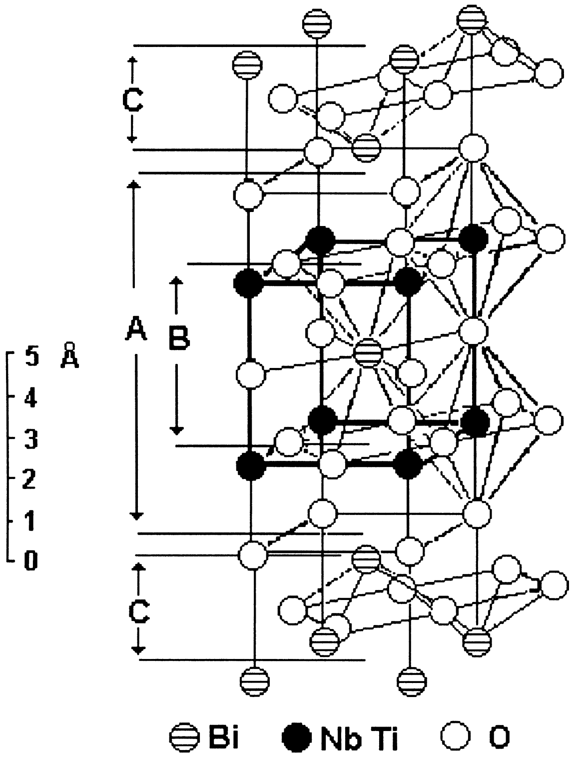

Fig. 1. One half of the pseudo-tetragonal unit cell of Bi_3NbTiO_9 (from $z = 0{\cdot}25$ to $z \approx 0{\cdot}75$). A denotes the perovskitic layer $Bi_3NbTiO_7^{2-}$, C denotes Bi_2O^{2+} layers and B the unit cell of a hypothetical perovskite structure $BiNb_{0.5}Ti_{0.5}O_3$ (after Aurivillius[1]).

The Raman scattering spectra were obtained on a Raman Jobin-Yvon T64000 commercial system with an Olympus BH2-UMA microanalysis system with a CCD detector. The measurements were carried out in a back scattering geometry at room temperature using 514 nm line of an argon laser (Coherent Inova 92 Ar^+) as an excitation source. The peak frequencies are accurate to better than 3 cm^{-1}.

3 Results and Discussion

As the kinetics of the solid-phase synthesis reaction depends on both the temperature of the synthesis T_S and durability of the synthesis t_S one can find initial substances in the sample when T_s and t_s are small enough. Therefore, one has to take into consideration the presence of the diffraction peaks typical for initial oxides or their different modifications on the X-ray diffraction pattern. In the case of our investigations, apart from the diffraction peaks of BNT compound, additional peaks of monoclinic α-Bi_2O_3, pseudorhombic α-Bi_2O_3, cubic δ-Bi_2O_3, tetragonal β-Bi_2O_3, were detected at the particular stages of the experiment.

In the present work the synthesis of Bi_3NbTiO_9 was carried out within the temperature range $T_S = 400$–$1200°C$. It was stated that pure Nb_2O_5 was not present in the prepared samples. Starting from 900°C ratio of BNT present in the calcinated ceramic samples is increasing rapidly from 35 to 83% at 1000°C. Figure 2 shows the dependence of the BNT ratio on temperature of calcination T_S (curve 1) at the constant time of synthesis $t_S = 1$ h. In Table 1 the parameters of the elementary cell of BNT for different T_S are given. One can see from Table 1 that the a_O and b_O orthorhombic elementary

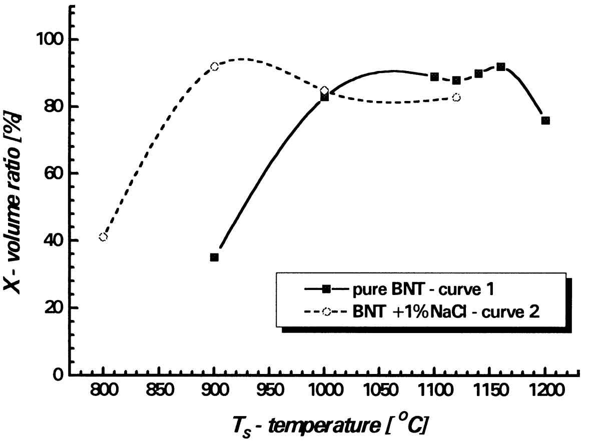

Fig. 2. Dependence of ratio of Bi_3NbTiO_9 (curve 1) and Bi_3NbTiO_9 + 1% NaCl (curve 2) on temperature of synthesis.

cell parameters decrease with increasing in temperature of synthesis while the c_O parameter increases with temperature.

It is worth noting, that when the synthesis was carried out within the range of temperatures $T_S = 900$–1200°C, apart from the main phase of layer perovskite structure the impurities of bismuth titanium oxide $Bi_2Ti_4O_{11}$ as well as bismuth niobium oxide $Bi_5Nb_3O_{15}$ were detected.

To investigate the influence of modifier on the process of synthesis, 1% weight of NaCl over the stoichiometric weight of substrates of the solid-phase reaction was used. The dependence of the BNT + 1% NaCl ratio on temperature of calcination T_S is shown in Fig. 2 (curve 2). Also the parameters of the elementary cell of BNT + 1% NaCl for different temperatures of synthesis are given in Table 2. Comparing the temperature dependence of the elementary cell parameters for pure BNT (Table 1) and the modified one (Table 2) we can see that the a_o parameter for NaCl-modified BNT increases with increasing in synthesis temperature.

One can see in Fig. 2 that addition of NaCl shifts the temperature range of the formation of the bismuth-containing layer, perovskite phase of BNT towards lower temperatures for about 100°C. It means that a small amount of NaCl facilitates the solid phase reaction of formation of Bi_3NbTiO_9.

Complete Raman scattering spectra of BNT and NaCl-modified BNT ceramics taken at room temperature are shown in Fig. 3. One can see that the spectra consist of four broad bands a shoulder near 130 cm^{-1} and two sharp bands, at a very low wave number. The results are in a good agreement with the data reported in Ref. 13. Comparing the two obtained spectra one can see that only the band near 840 cm^{-1} is nearly independent of the chemical compositions. As the admixture of NaCl is added, the peaks at 537 cm^{-1} and 260 cm^{-1} lose intensity and the last one merges into shoulder of the 230 cm^{-1}.

Table 1. Parameters of the elementary cell of Bi_3NbTiO_9 ceramics calcinated at temperature T_S

Calcination temperature T_s *(°C)*	*Parameters of the elementary cell, (m)*			*Ratio of BNT phase* X *(%)*
	$a_o \times 10^{10}$	$b_o \times 10^{10}$	$c_o \times 10^{10}$	
900	5·42	5·48	23·84	35
1000	5·41	5·42	24·96	83
1100	5·41	5·44	25·54	89
1120	5·41	5·43	24·94	88
1140	5·39	5·43	25·01	90
1160	5·41	5·45	25·16	92
1200	5·38	5·42	25·02	76

Table 2. Parameters of the elementary cell of Bi_3NbTiO_9 ceramics modified with 1% NaCl calcinated at temperature T_S

Calcination temperature T_s*(°C)*	*Parameters of the elementary cell (m)*			*Ratio of BNT phase* X *(%)*
	$a_o \times 10^{10}$	$b_o \times 10^{10}$	$c_o \times 10^{10}$	
800	5·36	5·47	24·82	41
900	5·38	5·48	24·13	92
1000	5·41	5·45	25·12	85
1120	5·40	5·43	25·39	83

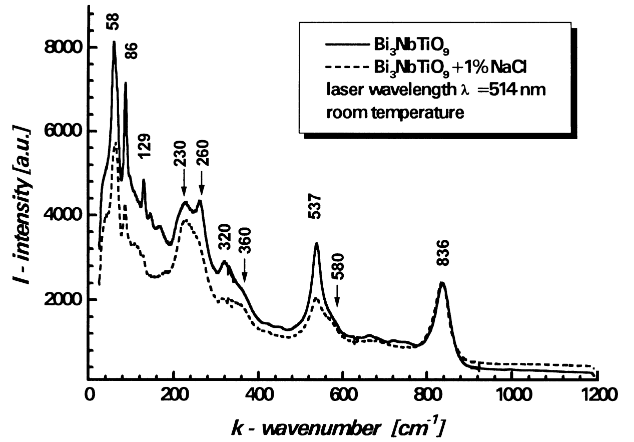

Fig. 3. Raman spectra of Bi_3NbTiO_9 and Bi_3NbTiO_9 + 1% NaCl taken at room temperature

4 Conclusions

With the help of the solid-state reaction from the conventional mixture of oxides: Bi_2O_3, TiO_2, Nb_2O_5 the perovskite-layered ceramics of BNT and BNT modified with NaCl was obtained. The X-ray diffraction method confirmed the compound formation. The structure of the BNT was identified as the orthorhombic one. It was stated that addition of NaCl in the amount of 1% weight facilitated the process of synthesis of the BNT ceramics. The temperature of formation of the bismuth-containing perovskite layered phase was shifted from 1000°C for the pure BNT to 900°C for the NaCl-modified one. The Raman scattering spectra obtained at room temperature are in good agreement with the previous reports.

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