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Influence of processing conditions on crystal structure of BiNbO₄ ceramics

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Abstract

Bismuth niobate (BiNbO₄) has attracted attention as a low-fired ceramics with promising microwave application potential. It belongs to the bismutocolumbite oxides with similarly to scheelite-like stibiotantalite structure (SbTaO₄) A³⁺B⁵⁺O₄. The aim of the present research was to fabricate BiNbO₄ ceramics by solid state reaction route from the mixture of simple oxides viz. Bi₂O₃, and Nb₂O₅, and study its phase composition as well as crystal structure by X-ray diffraction method. The Rietveld refinement method was utilized for analysis of diffraction patterns. It was found that the mass change effects finished at temperature $T=500^{\circ}\text{C}$ and the total mass change was about $\Delta m=-0.78\%$. It was found that BiNbO₄ ceramics sintered in ambient air exhibited multiphase composition, i.e., apart from the major α -BiNbO₄ phase, the orthorhombic Bi₅Nb₃O₁₅, Bi₃Nb₁₇O₄₇ and cubic Bi₃NbO₇ phases were present. An increase in sintering temperature caused an increase in the amount of major α -BiNbO₄ phase which adopted an orthorhombic symmetry described well by *Pnna*(52) space group.

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1. Introduction

Within a decade a 1000-fold increase in wireless communication traffic volume is expected, requiring increased throughput and data rates [1]. Therefore, an increasing effort has been directed towards achieving even further miniaturization of microwave components and devices by employing passive integration [2]. Passive integration leads to the generation of so-called ceramic multicomponent modules (CMMs). Highest miniaturization at lowest cost is achieved by using multilayer ceramic technology for CMMs. For microwave CMMs, ceramics are required that can be sintered at low

temperatures (<900°C) to enable the use of copper internal conductors.

One possible approach to develop low-temperature-fireable microwave ceramics is to investigate bismuth-based dielectric ceramics. Recently, it was found that bismuth niobate (BiNbO₄) shows promise for high-frequency applications [3]. It was shown that with the addition of small amount of sintering aids, like CuO and V₂O₅, BiNbO₄ ceramics could be sintered at 875-935°C [4].

It is commonly known that sintering of bismuth-based compounds is not a trivial task [5]. Bismuth oxide, Bi₂O₃, has four crystallographic polymorphs, low melting point (~825°C) and the thermal behaviour of Bi₂O₃ is rather complex. One can find information on detection of a single orthorhombic BiNbO₄ phase in scientific reports [6,7]; however, the researches were focused mainly on achieving high density ceramics.

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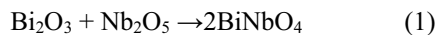
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The Rietveld refinement procedure was not used for justifying the phases' formation during sintering.

The goal of the present research was to study an influence of thermal treatment on phase composition and crystal structure of BiNbO₄ ceramics fabricated by mixed oxide method followed by pressureless sintering at temperature $T < 1000^\circ\text{C}$.

2. Experimental

The ceramic samples of BiNbO₄ chemical composition were synthesized according to mixed-oxide method (solid state reaction route). Details of the preparation method have been reported by us elsewhere [8,9]. Let us only mention that the appropriate amounts of reagent – grade oxide powders, viz. Bi₂O₃, and Nb₂O₅ were thoroughly weighted in stoichiometric amounts to provide conditions for formation of the desired composition, given by:



Simultaneous thermal analysis (STA), in which both thermal analysis (DTA) and mass change effects (TG) are measured concurrently on the same sample, was used to investigate synthesis effects in the stoichiometric mixture of powders. The measurements were obtained with Netzsch STA409 thermal analyser. The crystal structure of the ceramics was studied by X-ray diffraction method at room temperature (X'Pert-Pro diffractometer, θ - 2θ mode, CoK α radiation, data angle range $2\theta = 10.0042 - 104.9962^\circ$, detector scan step $\Delta 2\theta = 0.01^\circ$, a counting time $t = 100\text{s}$). The phase and structural analysis was performed with X'pert HighScore Plus software (PANalytical B.V) and the latest available ICSD [10] database was utilized. Refinement of the structural parameters of bismuth niobium oxide-based phases was performed with the Rietveld method [11].

3. Results and Discussion

3.1. Thermal analysis

Results of STA of the stoichiometric mixture of Bi₂O₃ and Nb₂O₅ oxides, as well as powder of BiNbO₄ compound, are given in Figs. 1 and 2. One can see in Fig. 1 that the main mass change effects took place within the temperature range $T = 200\text{--}500^\circ\text{C}$. At temperature $T = 500^\circ\text{C}$ the total mass change was $\Delta m = -0.78\%$. Further increase in temperature was not accompanied with any mass change effects.

DTA analysis (Fig. 2) revealed the existence of an exothermic peak at $T \approx 860^\circ\text{C}$ (formation of α -BiNbO₄) as well as two endothermic peaks that appeared at $T \approx 1067^\circ\text{C}$ (melting of the BiNbO₄ compound), and $T \approx 1186^\circ\text{C}$ (decomposition of the compound).

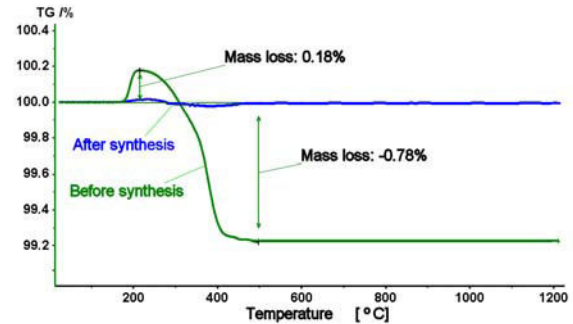


Fig. 1. Results of thermogravimetry (TG) in stoichiometric mixture of oxides Bi₂O₃+Nb₂O₅ (before synthesis) and BiNbO₄ powder (after synthesis).

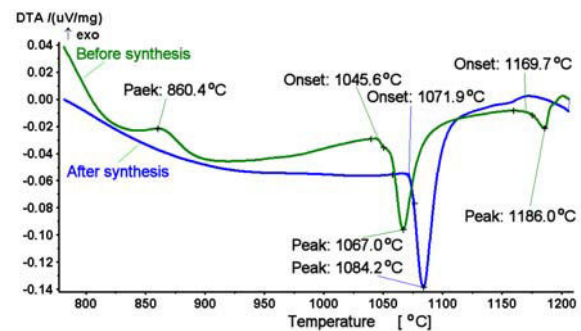


Fig. 2. Results of differential thermal analysis (DTA) for stoichiometric mixture of oxides Bi₂O₃+Nb₂O₅ (before synthesis) and BiNbO₄ powder (after synthesis).

3.2. X-ray phase analysis

Bismuth niobate belongs to the bismutocolumbite oxides with similarly to scheelite-like stibiotantalite structure (SbTaO₄) A³⁺B⁵⁺O₄. Within the temperature range $T < 1020^\circ\text{C}$ it exhibits an orthorhombic crystal structure (Fig. 3).

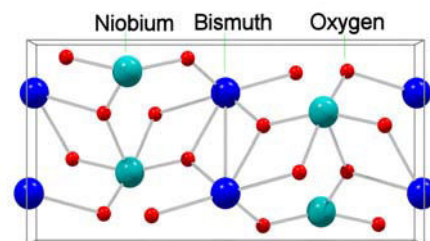


Fig. 3. Model of BiNbO₄ crystal structure for the low-temperature orthorhombic α -phase (axis c in horizontal direction).

Results of the X-ray diffraction measurements for the BiNbO₄ ceramics thermally treated at $T=800^{\circ}\text{C}$, $T=870^{\circ}\text{C}$ and $T=910^{\circ}\text{C}$ are shown in Fig. 4.

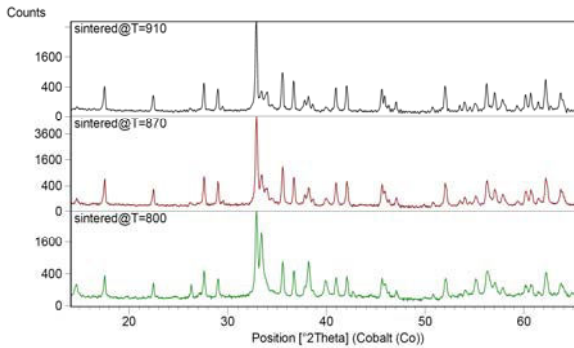


Fig. 4. X-ray diffraction patterns of BiNbO₄ ceramics calcined at $T=800^{\circ}\text{C}$ and sintered at $T=870^{\circ}\text{C}$ and $T=910^{\circ}\text{C}$.

One can see from Fig. 4 that diffraction patterns exhibited similar profiles but intensities of a few corresponding diffraction lines differ to some extent. To describe the differences in a qualitative way the X-ray diffraction phase analysis was performed. As an example, results obtained during analysis of the X-ray diffraction pattern registered for the BiNbO₄ sample sintered at $T=910^{\circ}\text{C}$ is shown in Fig. 5.

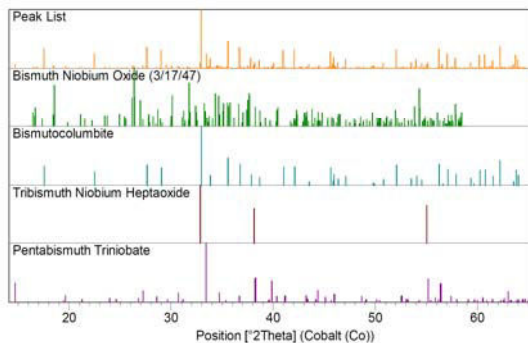


Fig. 5. Positions of the experimental X-ray diffraction peaks (peak list) for ceramics sintered at $T=910^{\circ}\text{C}$ and peaks positions of the reference phases.

According to the search-match analysis, apart the major phase of α -BiNbO₄ (bismutocolumbite; orthorhombic symmetry; ICSD code 74338), three possible minor phases were revealed, namely Bi₅Nb₃O₁₅ (pentabismuth triniobate; orthorhombic symmetry; ICSD code 245707), Bi₃Nb₁₇O₄₇ (bismuth niobium oxide 3/17/47; orthorhombic symmetry; ICSD code 16137), Bi₃NbO₇ (tribismuth niobium heptaoxide; cubic symmetry, ICSD code 81582). One can see in Fig. 5 that the diffraction peaks at the angles

$2\theta \approx 14.7^{\circ}$, 33.4° , 39.9° (Fig. 4) are influenced mainly by the presence of Bi₅Nb₃O₁₅ phase whereas the peaks at $2\theta \approx 26.3^{\circ}$ and 38.2° reflected the presence of Bi₃Nb₁₇O₄₇ and Bi₃NbO₇ phases, respectively.

To calculate the weight fractions, as well as to refine the structural parameters of the constituent phases, the Rietveld refinement method was utilized. Results of the refinement procedure are given in Fig. 6. Global parameters of the Rietveld analysis, in assumption of the multiphase sample, are given in Table 1.

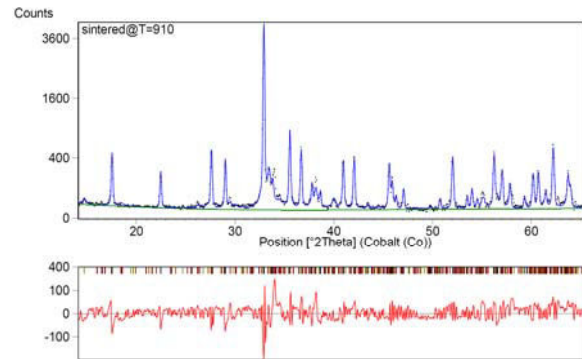


Fig. 6. X-ray diffraction pattern after refinement of the elementary cell parameters for BiNbO₄ ceramics sintered at $T=910^{\circ}\text{C}$; bottom plot shows the difference between the experimental (dots) and refined (solid line) diffraction patterns.

Table 1. Global parameters of the Rietveld analysis.

| Parameter | $T=800^{\circ}\text{C}$ | $T=870^{\circ}\text{C}$ | $T=910^{\circ}\text{C}$ |
|-------------------------|-------------------------|-------------------------|-------------------------|
| Profile function | Pseudo Voigt | | |
| Background | Polynomial | | |
| R (expected), % | 16.44 | 13.93 | 13.84 |
| R (profile), % | 14.16 | 12.51 | 13.52 |
| R (weighted profile), % | 20.24 | 18.48 | 19.73 |
| GOF | 1.52 | 1.76 | 2.03 |
| d-statistic | 0.74 | 0.69 | 0.70 |

One can see from Table 1 that R -parameters of the refinement procedure are less than 20%. The goodness-of-fit parameter (GOF) is about 2. Both R -parameters and GOF parameter exhibit values that prove good quality of experimental data and correctness of the performed analysis.

Dependences of the weight fractions of the constituent phases on sintering temperature are given in Fig. 7. One can see from Fig. 7 that, just after calcination at $T=800^{\circ}\text{C}$, the BiNbO₄ powder consists mainly of two phases, namely the desirable orthorhombic α -BiNbO₄ phase and orthorhombic Bi₅Nb₃O₁₅ phase. Subsequent sintering at temperature $T=870^{\circ}\text{C}$ caused an increase in weight fraction of α -BiNbO₄ phase and a decrease in pentabismuth triniobate phase in BiNbO₄ ceramics.

With an increase in sintering temperature a further increase in amount of α -BiNbO₄ took place.

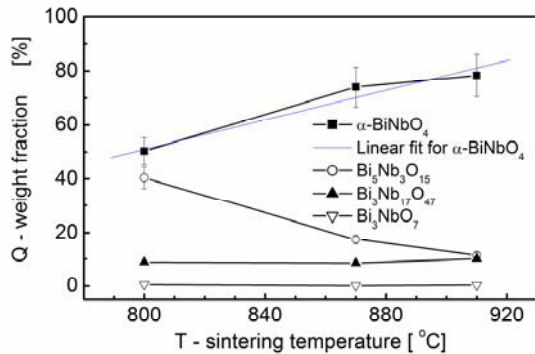


Fig. 7. Phase formation during sintering of BiNbO₄.

3.3. X-ray structural analysis

Structural parameters of the main constituent phase of BiNbO₄ ceramics are given in Table 2.

Table 2. Structural parameters of bismutocolumbite phase

| Relevant parameters of α -BiNbO ₄ phase | T=800°C | T=870°C | T=910°C |
|---|------------------|------------------|------------------|
| Space group (No.) | <i>Pnna</i> (52) | <i>Pnna</i> (52) | <i>Pnna</i> (52) |
| Lattice parameters | | | |
| a (Å) | 5.678 | 5.679 | 5.679 |
| B (Å) | 11.709 | 11.710 | 11.710 |
| C (Å) | 4.982 | 4.982 | 4.982 |
| V (10 ⁶ pm ³) | 331.24 | 331.32 | 331.28 |
| Micro strain (%) | 0.107 | 0.083 | 0.066 |
| Crystallite size (Å) | 916.5 | 826.0 | 1038.3 |

One can see from Table 2 that the main phase of α -BiNbO₄ adopted the orthorhombic symmetry described by the space group *Pnna*(52). An increase in temperature of the thermal treatment caused very small changes in the lattice parameters that in turn caused a change in an elementary cell volume for less than 0.03%. An increase in temperature of the thermal treatment caused a decrease in micro deformations.

4. Conclusions

On the base of thermal analysis of the raw oxides mixture, the temperature regimes for synthesis and consolidation processes of BiNbO₄ ceramics have

been determined. It was found that the mass change effects finished at $T=500^\circ\text{C}$ and the total mass change was about $\Delta m=-0.78\%$. It was established that BiNbO₄ ceramics calcined in ambient air at $T=800^\circ\text{C}$ exhibited multiphase composition, i.e., apart from the major α -BiNbO₄ phase the orthorhombic phases Bi₅Nb₃O₁₅ and Bi₃Nb₁₇O₄₇ as well as cubic Bi₃NbO₇ phases were present. Nevertheless, subsequent sintering at temperature $T=870$ - 910°C caused an increase in amount of α -BiNbO₄ up to 74-78 wt.%. Micro strains less than 0.1% proved high quality of the crystal structure of α -BiNbO₄ phase which can be used as an active phase of the polymer-ceramic composites. It was found however that the amount of the other phases, i.e., Bi₃NbO₇ and Bi₃Nb₁₇O₄₇, was kept constant at the level of about 10%.

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