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Synthesis and dielectric properties of $A_{m-1}Bi_2B_mO_{3m+3}$ ceramic ferroelectrics with $m=1.5$

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Abstract

Bismuth containing ceramic materials of molecular formula $Bi_5TiWNbO_{15}$, $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$, $Bi_5Nb_3O_{15}$ have been synthesised and fabricated. The materials are known as the Aurivillius phases. The Aurivillius phases are a family of oxide ferroelectrics generally formulated as $A_{m-1}Bi_2B_mO_{3m+3}$. The process of preparation was investigated by X-ray diffraction method as well as the simultaneous thermal analysis, in which both thermal (DTA) and mass change effects (TG) were measured on the same sample. The synthesis of the Aurivillius phases was carried out according to the solid state reaction from the conventional mixture of oxides (Nb_2O_5, WO_3, Bi_2O_3, and TiO_2). DTA and TG traces showing the synthesis effects have been recorded. Investigations of the crystalline structure, microstructure and basic dielectric properties were performed.

Keywords: Dielectric properties; Layered bismuth compounds; Perovskites; Sintering; X-ray methods

1. Introduction

Oxides of the Aurivillius[1] family constitute an important class of materials for their ferroelectric properties. They are of substantial interest for integrated circuit memories,[2] high temperature piezoelectric sensors,[3] electrooptic modulators and displays.[4]

Bismuth oxide layered perovskites (BOLP) are generally formulated[5] as $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$. They consist of an intergrowth between $(Bi_2O_2)^{2+}$ sheets and $(A_{m-1}B_mO_{3m+1})^{2-}$ perovskite-like layers, with m being the number of octahedra stacked along the direction perpendicular to the sheets, and A and B are the 12-fold and six-fold coordination sites of the perovskite slab, respectively. More often A is Bi^{3+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Pb^{2+}, K^+ or Na^+; B is Ti^{4+}, Nb^{5+}, Ta^{5+}, Mo^{6+} W^{6+} or Fe^{3+}.[5]

The frequent occurrence of disordered intergrowths—corresponding to different values of m—suggested that ordered intergrowths would be obtained in suitable systems under appropriate thermal treatment.[6] In fact, various ordered intergrowths have been prepared as macroscopic pure phase.[6–8] They always correspond to a regular intergrowth of one half the unit cell of a m member structure and half the unit cell of a $m+1$ member structure. Taking into consideration m *as* the arithmetic average of the number of oxygen octahedra of the intergrowing perovskite like layers the so-called mixed-layer Aurivillius phases are often formulated $A_{2m-2}Bi_4B_{2m}O_{6m+6}$ e.g., $Bi_7Ti_4NbO_{21}$ (intergrowth 2+3, i.e., average $m=2.5$),[9] $M^{II}Bi_8Ti_7O_{27}$ (intergrowth 3+4, i.e., average $m=3.5$).[6]

The aim of the present study is to investigate the process of synthesis of mixed-layer type bismuth compounds[7] by simultaneous thermal analysis (STA), obtain ceramic Aurivillius phases with $m=1.5$ as well as study their structure, microstructure and basic dielectric properties.

2. Experimental

Taking into consideration the crystallochemical requirements favourable for formation of the Aurivillius

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phases[10] the BLOP compounds with the following chemical compositions were prepared: $Bi_5TiWNbO_{15}$, $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$, and $Bi_5Nb_3O_{15}$. Synthesis of BLOP was carried out by conventional mixed-oxide method from the stoichiometric mixture of oxides Nb_2O_5, WO_3, Bi_2O_3, and TiO_2. Ceramic samples were obtained by conventional ceramic sintering method (CCS).

The CCS was carried out in a KS1350-type furnace in an air atmosphere for $t=3$ h. The compacts were first calcinated at temperature T_S^I. The accuracy of the temperature stabilisation was $\Delta T = \pm 2$ °C. The heating and cooling rate was $\nu_T = 300$ °C/h. After cooling the samples to room temperature they were powdered and the compacts were formed and sintered at temperature T_S^{II} (Table 1).

Processing conditions for synthesis and sintering were chosen on the basis of simultaneous thermal analysis (Netzsch STA 409) as well as results published in literature.[11] To confirm the compound formation the crystalline structure was checked by X-ray diffraction method (XRD) (Philips PW1710-type X-ray diffractometer) and the chemical composition investigations were carried out by X-ray fluorescence (XRF). Measurements of the relative permittivity ($\varepsilon/\varepsilon_0$) and dielectric loss tangent (tgδ) were carried out with a bridge technique at frequency$\nu = 1$–20 kHz (Tesla BM 595 RLCG meter). Microstructure was studied in polarized and reflected light (Neofot-21 microscope).

3. Results and discussion

Thermal behaviours of stoichiometric mixtures of powders i.e., $Bi_5TiWNbO_{15}$, $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$, and $Bi_5Nb_3O_{15}$.precursors are depicted in Fig. 1. From the thermograms in Fig. 1 it can be seen that the weight loss for all the samples becomes significant at 280 °C where it steeply increases to completion achieved at about 600 °C. The experimental weight loss for $Bi_5TiWNbO_{15}$, $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$, and $Bi_5Nb_3O_{15}$.precursors was 1.00, 1.18 and 0.99% respectively. Corresponding DTA curves for the above samples show the strong exothermic lines at 1040 °C, 1120 °C, and 1170 °C which would be assigned to crystallization.[7] Thus, on the base of the thermograms in Fig. 1 the specific temperature ranges corresponding to different rates of the chemical reaction were stated and considered for CCS method of fabrication (Table 1).

Table 1
Processing conditions used in the process of conventional ceramic sintering

Material	Calcination T_S^I (°C)	Sintering T_S^{II} (°C)	Time t_s (h)
$Bi_5TiWNbO_{15}$	800	1050	3
$Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$	800	1075	3
$Bi_5Nb_3O_{15}$	910	1150	3

It results from XRD studies that the structure exhibits tetragonal cell and is thought to consist of $(Bi_2O_2)^{2+}$ layers and mixed perovskite layers. As seen in Fig. 2, the structure of $Bi_5TiWNbO_{15}$ is built up by an intergrowth of one half of the unit cell of Bi_3TiNbO_9—structure ($m=2$) and one half of the unit cell of Bi_2WO_6—structure ($m=1$) along c-axis.

Similarly, $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$ is assumed to form from $Bi_5TiWNbO_{15}$ by decreasing in a number of Ti and W atoms by half and increasing in Nb atoms. Also $Bi_5Nb_3O_{15}$ compound is thought to be obtained from $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$ by multi-ion substitution: $Ti^{4+}W^{6+} \rightarrow 2Nb^{5+}$

Data of X-ray powder diffraction for $Bi_5Nb_3O_{15}$, $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$, $Bi_5TiWNbO_{15}$ are given in Fig. 3. Crystal indices correspond to the tetragonal symmetry for all diffraction patterns.

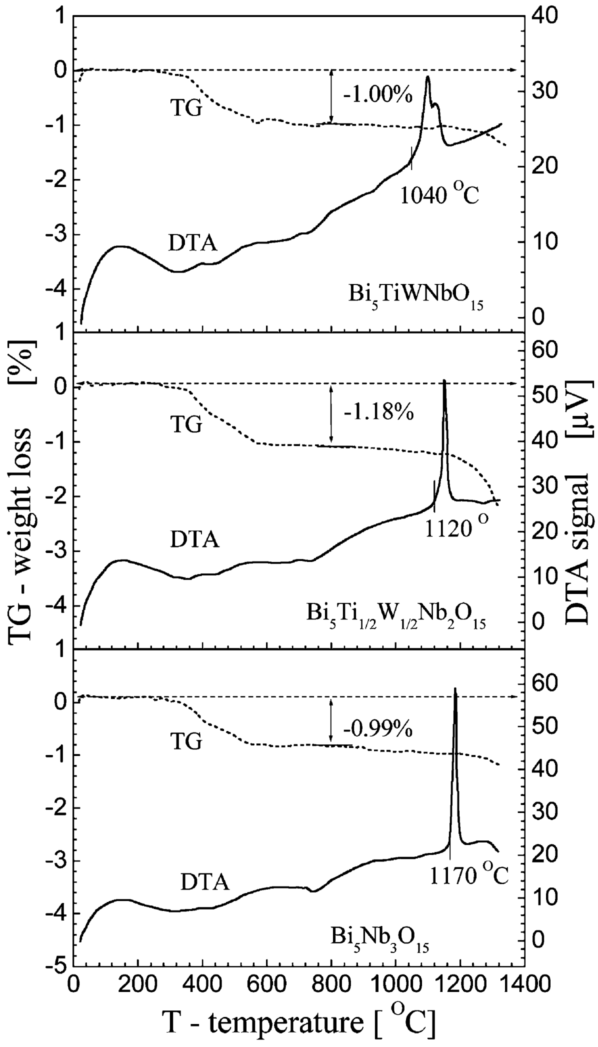

Fig. 1. Simultaneous thermal analysis for stoichiometric mixture of oxides used for preparation of $Bi_5TiWNbO_{15}$, $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$, and $Bi_5Nb_3O_{15}$ layered bismuth compounds.

It results from Fig. 4(a) that microstructure of Bi$_5$TiWNbO$_{15}$ ceramics consisted of chaotically oriented grains with prismatic walls. The grains exhibited plate or needle habits ($l < 20$ µm). No distinct grain form was revealed by the chemical etching. Voids with flat isometric walls and dimensions of 10–12 µm constituted 8% of the ceramics volume.

Bi$_5$Ti$_{1/2}$W$_{1/2}$Nb$_2$O$_{15}$ ceramic exhibited grains with the elongated form and dimensions within the range from (0.2–0.4) µm to (4.0–8.0) µm (Fig. 4b). Voids were heterogeneous from the point of view of both size and form.

Bi$_5$Nb$_3$O$_{15}$ ceramics exhibited relatively close mosaic packing of grains with elongated form and chaotic orientation of the crystallographic axes (Fig. 4c). The average size of the plane figures of grain cross-sections was about 3.2 µm long and 2.0 µm wide. The grains were of a prism-shape with the ratio of sides ~2:2:1. It was found by stereological analysis of microstructure[12] that the average radius of the sphere equal in volume to the prismatic grain was $\bar{r} = 1.85$ µm. The average chord of the plane figure of cross-section was $\bar{h} = 2.2$ µm.

4. Dielectric properties

Dependence of relative permittivity $\varepsilon/\varepsilon_0(T)$ and loss tangent tg$\delta(T)$ for Bi$_5$TiWNbO$_{15}$ ceramics is given in Fig. 5 One can see a local maximum of tg$\delta(T)$ at $T = 350$ °C. The occurrence of such a maximum below the Curie point ($T_m = 475$ °C, T_m—temperature of maximum of relative permittivity) indicate loses connected to the switching process i.e., dielectric hysteresis. Maximum of tg$\delta(T)$ at $T < T_m$ one can explain by an increase in spontaneous polarisation P_S and coercive

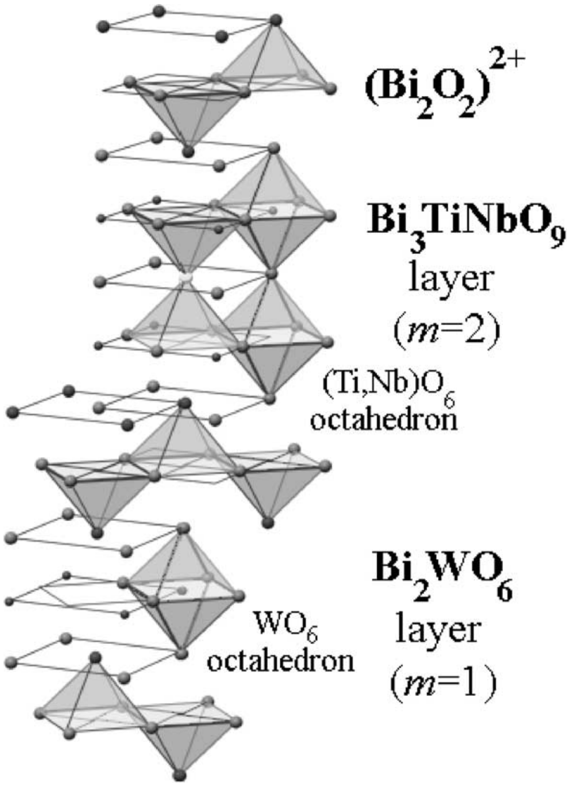

Fig. 2. Prototype structure of Bi$_5$TiWNbO$_{15}$ (one half of the pseudo-tetragonal unit cell).

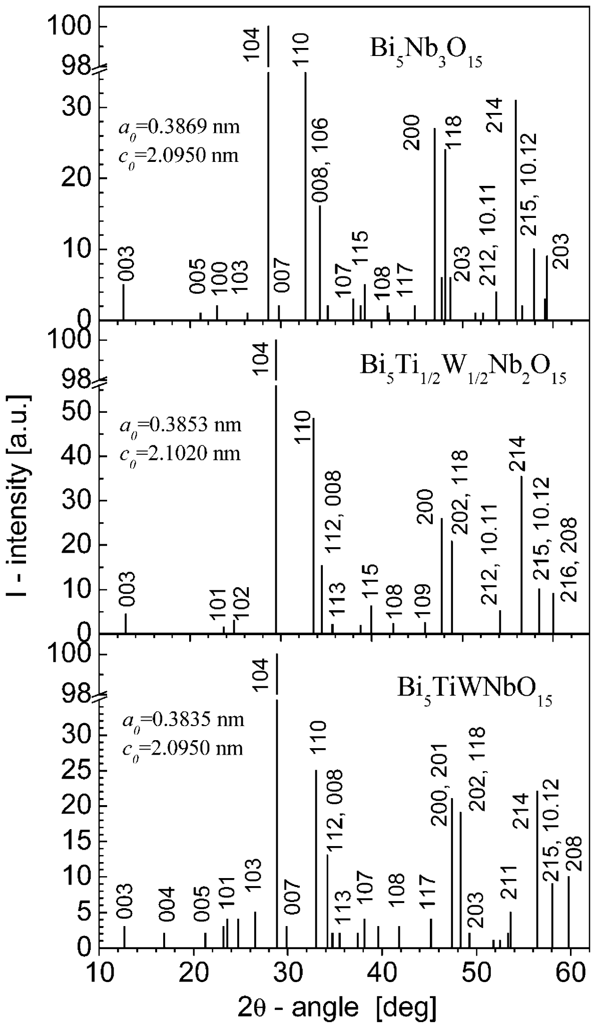

Fig. 3. Positions of X-ray diffraction lines for Bi$_5$TiWNbO$_{15}$, Bi$_5$Ti$_{1/2}$W$_{1/2}$Nb$_2$O$_{15}$, and Bi$_5$Nb$_3$O$_{15}$ ceramics.

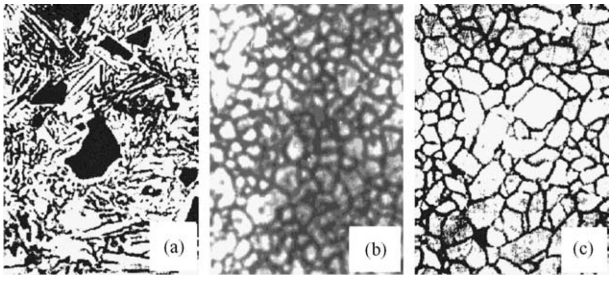

Fig. 4. Binary pictures of investigated microstructures used for stereological processing: (a) Bi$_5$TiWNbO$_{15}$–$T_S^I = 800$ °C, $T_S^{II} = 1050$ °C, $t_s = 3$ h; (b) Bi$_5$Ti$_{1/2}$W$_{1/2}$Nb$_2$O$_{15}$- $T_S^I = 800$ °C, $T_S^{II} = 1075$ °C, $t_s = 3$h; (c) Bi$_5$NbO$_{15}$–$T_S^I = 910$ °C, $T_S^{II} = 1150$ °C, $t_s = 3$ h. CCS method of fabrication; chemical etching; non-polarized light, magnification ×2200.

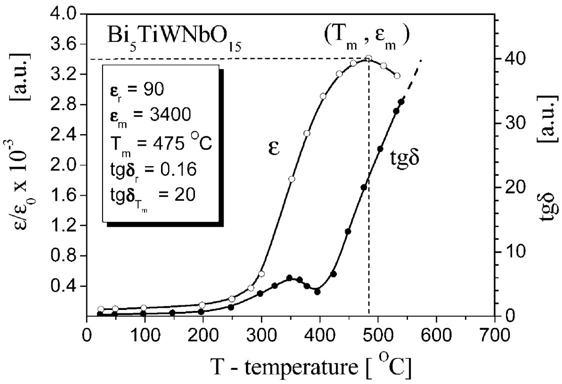

Fig. 5. Dependence of dielectric permittivity ($\varepsilon/\varepsilon_0$) and tangent of dielectric loss (tgδ) on temperature for $Bi_5TiWNbO_{15}$ ceramics obtained by CCS method ($T_S^I = 800$ °C, $T_S^{II} = 1050$ °C, $t_s = 3$ h).

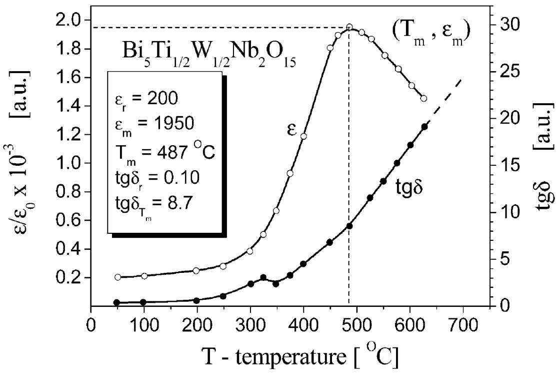

Fig. 6. Dependence of dielectric permittivity ($\varepsilon/\varepsilon_0$) and tangent of dielectric loss (tgδ) on temperature for $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$ ceramics obtained by CCS method ($T_S^I = 800$ °C, $T_S^{II} = 1075$ °C, $t_s = 3$ h).

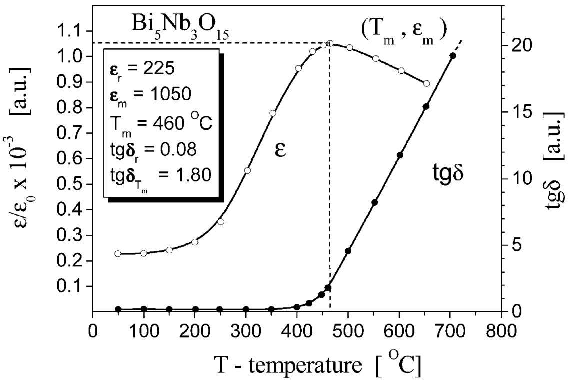

Fig. 7. Dependence of dielectric permittivity ($\varepsilon/\varepsilon_0$) and tangent of dielectric loss (tgδ) on temperature for $Bi_5Nb_3O_{15}$ ceramics obtained by CCS method ($T_S^I = 910$ °C, $T_S^{II} = 1150$ °C, $t_s = 3$ h).

Table 2
Comparison of dielectric parameters for mixed-layer type bismuth ceramics

Material	ε_r	tgδ_r	T_m (°C)	ε_m	tgδ_{T_m}
$Bi_5TiWNbO_{15}$	90	0.16	475	3400	20.0
$Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$	200	0.10	487	1950	8.7
$Bi_5Nb_3O_{15}$	225	0.08	500	1050	1.8

field E_C during the sample cooling. Both of these factors cause an increase in losses for hysteresis. Measurements were impossible with the bridge technique for $T > 525$ °C due to high dielectric losses. For the same reason (i.e., high dielectric losses) it was impossible to pole the samples and observe piezoelectric activity. Even though high electric field strength was employed in Sawyer-Tower method the hysteresis loop was not observed. Thus no non-linear properties typical for ferroelectrics were revealed at room temperature T_R or $T > T_R$. This is testimony to very high ferroelectric hardness of $Bi_5TiWNbO_{15}$.

Figs. 6 and 7 show similar dependencies for $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$ and $Bi_5Nb_3O_{15}$ respectively. One can see that the tg$\delta(T)$ curve exhibits a local maximum at $T = 325$ °C (tg$\delta = 3.1$) for $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$ (Fig. 6). No local maximum below T_m was recorded on the tg$\delta(T)$ curve for $Bi_5Nb_3O_{15}$ ceramics (Fig. 7). As in case of $Bi_5TiWNbO_{15}$ no hysteresis loop or piezoelectric activity was revealed.

Table 2 shows characteristic dielectric parameters for BOLP with $m = 1.5$. It results from Table 2 that an increase in Nb content is followed by an increase in both relative permittivity at room temperature $\varepsilon_r = \varepsilon/\varepsilon_0(T_R)$ and T_m and by a decrease in ε_m, tgδ_r and tgδ_{T_m}. Local maximum on tg$\delta(T)$ curve at $T < T_m$ gradually decreases.

5. Conclusions

Mixed-layer type bismuth compounds $Bi_5TiWNbO_{15}$, $Bi_5Ti_{1/2}W_{1/2}Nb_2O_{15}$, and $Bi_5Nb_3O_{15}$ generally formulated as $A_{2m-2}Bi_4B_{2m}O_{6m+6}$ (with $m = 1.5$) were synthesised and fabricated. It was found that at room temperature the compounds exhibited tetragonal structure.

Temperature run of relative permittivity $\varepsilon/\varepsilon_0(T)$ and dielectric loss tg$\delta(T)$ proves ferroelectric properties of the compounds under investigation. It was stated that with an increase in Nb content dielectric permittivity at room temperature ε_r and temperature T_m at which ε reaches its maximum increase, whereas ε_r, tgδ_{T_r} and tgδ_{T_m}decrease.

No one of the compounds exhibited non-linear properties (i.e., dielectric hysteresis loop) or was successfully poled, despite different methods and poling conditions were applied. Lack of such experimental evidences of ferroelectric state like the hysteresis loop and piezoelectric activity may be connected with relatively high dielectric losses.

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