Title: Influence of Processing Conditions on Crystal Structure of Bi$_6$Fe$_2$Ti$_3$O$_{18}$ Ceramics

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INFLUENCE OF PROCESSING CONDITIONS ON CRYSTAL STRUCTURE OF Bi6Fe2Ti3O18 CERAMICS

Aim of the present research was to apply a solid state reaction route to fabricate Aurivillius-type ceramics described with the formula Bi₆Fe₂Ti₃O₁₈ (BFTO) and reveal the influence of processing conditions on its crystal structure. Pressureless sintering in ambient air was employed and the sintering temperatures were 850 and 1080 °C. It was found that the fabricated BFTO ceramics were multiphase ones. They consisted of two Bi₆Fe₂₋₃Ti₃O₉₋₃ phases, namely the phase with m=5 (i.e. the stoichiometric phase) and m=4 (i.e. the phase with a reduced number of layers in the slab). Detailed X-ray diffraction patterns analysis showed that both phases adopted the same orthorhombic structure described with Fmm2 (42) space group. The ratio of weight fractions of the constituent phases (m=5): (m=4) was ~30:70.

1. Introduction

One of the very promising approaches to create novel materials is to combine in one material different physical properties to achieve rich functionality. It is commonly known that Aurivillius phases of Bi₆Ti₃O₁₂-BiFeO₃ (BFTO) system, combine ferroelectric, semiconducting and ferromagnetic properties and are potentially attractive for producing high-performance ceramics for information processing and information storage applications [1, 2]. Among the different ferromagnetic compounds of BFTO system Bi₆Fe₂₋₃Ti₃O₉₋₃ was found to be interesting because of the high dielectric transition temperature (Tₘ=805°C) and quadratic magnetoelectric nature [3].

It is worth noting that Bi₆Fe₂Ti₃O₁₈ compound has a layered perovskite-like structure described with the general formula Biₙ₋₁Feₘ₋₃Ti₃O₉₋₃, (m=5). Perovskite-like layered structure consists of the fluorite-like bismuth-oxygen layers of composition [(Bi₂O₂)²⁺∞ which alternate with (001) perovskite-like slabs of composition [(Biₙ₋₁Feₘ₋₃Ti₃O₉₋₃)²⁺∞. The values of m indicates the number of perovskite-like layers per slab and may take integer or fractional values [4, 5].

Although several researches on Bi₆Fe₂₋₃Ti₃O₉ ceramics have already been performed either by us [e.g. 6, 7] or other scientific groups [e.g. 8, 9, 10] however low temperature dielectric behavior of BFTO was not studied yet. Therefore the present research was focused on fabrication of and study of dielectric response of Aurivillius structure multiferroic ceramics.

2. Experimental

The mixed oxide method was employed for the ceramics fabrication. Simple oxide powders Bi₂O₃, TiO₂ and Fe₂O₃ were used for stoichiometric mixture preparation. Parameters of the thermal treatment were determined by simultaneous thermal analysis (DTA/TG/DTG). The measurements were obtained with Netzsch STA409 thermal analyzer. After calcinations process (Tₘ=720°C) the pellets were formed and pressed into disks with the diameter of 10mm and 1mm thickness. Pressureless sintering was used for final densification of ceramic samples. Sintering temperatures were Tₛ=850°C, Tₛ=1080°C, whereas the soaking time was tₛ=2h in both experiment sets.

The crystalline structure of the sintered samples were examined by X-ray diffraction at room temperature (X’Pert – Pro diffractometer, θ – 2θ mode). It should be mentioned that for the sample sintered at Tₛ=850°C the CuKα radiation was used (λCuKα=1.54060 Å; λCuKα=1.54443 Å; ratio αKα=0.5; data angle range 2θ= 8.0042 - 89.9962°; detector scan step Δ2θ=0.008°; scan type continuous; scan step time tₛ=99.7s), whereas for BFTO ceramics sintered at Tₛ=1080 °C the CoKα radiation was utilized (λCoKα=1.78901 Å; λCoKα=1.7929 Å; ratio αKα=0.5; data angle range 2θ=10.0042- 104.9962°; detector scan step Δ2θ=0.008°; scan type continuous; scan step time tₛ=302.9s).

Analysis of the X-ray diffraction patterns was carried out using X’pert HighScore Plus software (PANalytical B.V), Match! (Crystal Impact, Inc.) computer program [11]. The latest available COD [11], ICSD [12] and ICDD [13] databases were utilized.

3. Results and discussion

Thermal analysis. 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. Results of STA of the stoichiometric mixture of the oxides forming Bi₆Fe₂Ti₃O₁₈ compound are given in Fig. 1.

One can see on a thermogravimetric (TG) curve shown in Fig. 1 that the total mass loss during the heat treatment of the stoichiometric mixture of Bi₂O₃, Fe₂O₃, and TiO₂ oxides at T=600 °C reaches a value of about Δm=0.33%. The DTA study revealed thermal effects manifested upon heating the samples. One can see a relatively broad, exothermic peak that appears in the differential thermogram at T≈300 °C. It corresponds to the mass change effects present in the sample.

The experimental data on kinetics of the formation of layered perovskite-like compounds in the BFTO system have shown that detectable amounts of Aurivillius phases appear at 600 °C [14]. This temperature is close to the melting point of the γ-bi₂O₃-based surface phase, \( \gamma_{\text{bi}} \approx 550–630 \) °C at which a sharp increase in the rate of mass transfer activates chemical reactions limited by the rate of transport processes. At still higher temperatures, the percentage of layered perovskite-like compounds rises systematically and reaches a maximum at the melting point of the γ-bi₂O₃-based bulk phase \( \gamma_{\text{bi}} \). Therefore, the broad exothermic effect at the temperature range \( \Delta T=650-700 \) °C (Fig. 1) can be tentatively attributed to formation of BFTO phases.

The weak endothermic peak at about T=1036 °C, one can ascribed to the phase transformations, namely a peritectic decomposition into compounds of the same homologous series with a smaller number of perovskite-like layers in their structure [2], whereas the strong endothermic peak at T=1117 °C - to liquidus temperature [2, 15].

4. X-ray diffraction phase and structural analysis

Results of the qualitative XRD phase analysis for BFTO ceramics produced by solid-phase chemical reactions and sintered at temperatures T=850 and 1080 °C, is given in Fig. 2, Tab. 1 and Fig. 3, Tab. 2, respectively.

![Fig. 2. X-ray diffraction matching parameters for Bi₆Fe₂Ti₃O₁₈ ceramics fabricated via solid state reaction route and pressureless sintering at T=850 °C; (bottom plot – peak positions of the experimental pattern and the main reference phases)]

One can see that the results indicated that the forming Aurivillius phases had an imperfect structure, which may not correspond to the stoichiometric composition owing to

| Weight fraction, % | Formula/Space group/Crystal system | Unit cell parameters | Number of peaks | FoM |
|------------------|----------------------------------|---------------------|----------------|-----|
| 50.8             | Bi₆Fe₂Ti₃O₁₈/ Bn22m/ orthorhombic | \( a=5.4730 \) Å\( b=45.4200 \) Å\( c=5.4500 \) Å | total in range matched | 42 0.8565 |
| 43.2             | Bi₆Fe₂Ti₃O₁₈/ F2mm/ orthorhombic | \( a=5.4950 \) Å\( b=57.5810 \) Å\( c=5.4710 \) Å | total in range matched | 39 0.8036 |
| 2.5              | Bi₁₂FeO₄₀ / I23/ cubic           | \( a=10.1789 \) Å | total in range matched | 41 0.7309 |
| 1.9              | Bi₁₂FeTiO₁₈ / Fmm2/ orthorhombic | \( a=5.4318 \) Å\( b=41.1490 \) Å\( c=5.4691 \) Å | total in range matched | 171 0.8328 |
| 1.6              | Bi₁₂TiO₂₀ / I23/ cubic           | \( a=10.1880 \) Å | total in range matched | 41 0.7137 |

**TABLE 1**
a reduced number of layers ($m=3$, $m=4$, $m=4.5$) in the slab or disordered stacking of the layers.

Fig. 3. X-ray diffraction matching parameters for Bi$_6$Fe$_2$Ti$_3$O$_{18}$ ceramics fabricated via solid state reaction route and pressureless sintering at $T=1080^\circ$C; (bottom plot – peak positions of the experimental pattern and the main reference phases)

According to the suggested scheme for the formation of Aurivillius phases in the Bi$_2$O$_3$–TiO$_2$–Fe$_2$O$_3$ system the formation of Bi$_{m+1}$Fe$_m$–3Ti$_3$O$_{3m+3}$ compound is considered as a multistage process [16]. At early stages compounds with smaller numbers of perovskite-like layers in the structure and BiFeO$_3$ are formed. At the next stage, perovskite-like BiFeO$_3$ is incorporated into a perovskite-like layer of Aurivillius phases to increase the thickness of this layer until an Aurivillius phase of a given composition is formed. In the course of further heat treatment, the number of perovskite layers in the slab approaches that corresponding to the stoichiometric composition, and the proportion of intermediate synthesis products drops.

In his connection it should be pointed out that both Bi$_{12}$TiO$_{20}$ and Bi$_{25}$FeO$_{40}$ are intermediate synthesis Bi$_2$O$_3$-reach products that appear around $T=500^\circ$C as the $\alpha$-Bi$_2$O$_3$ reacted with small amounts of TiO$_2$ and Fe$_2$O$_3$. These compounds are extremely difficult to distinguish by XRD, since both are isostructural and have a structure closely similar to that of the metastable phase $\gamma$-Bi$_2$O$_3$ (see Tab. 1) [14]. The amount of these phases in the final ceramic product is quite small – on the level of the resolution of the method (±3%) and can be neglected in the further analysis.

With an increase in the sintering temperature, amount of the intermediate Bi$_2$O$_3$-reach compounds decreased and formation of Aurivillius phases took place. One can see in Fig. 3 and Tab. 2 that phases with a small number of layers $m$ in the slab have been formed, namely $m=3$ - Bi$_4$Ti$_3$O$_{12}$, $m=4$ - Bi$_5$FeTi$_3$O$_{15}$ and $m=4.5$ - Bi$_{11}$Fe$_3$Ti$_6$O$_{33}$.

On the base of the phase analysis one can conclude that Bi$_{m+1}$Fe$_m$–3Ti$_3$O$_{3m+3}$ compounds are difficult to produce because these compounds are formed in several stages and their thermal stability is low.

Detailed structural analysis, together with refinement of the elementary cell parameters (according to the Rietveld method [e.g. 17]) was performed for X-ray diffraction patterns of Bi$_6$Fe$_2$Ti$_3$O$_{18}$ ceramics fabricated via solid state reaction route and pressureless sintering at $T=850$ and $1080^\circ$C. Visual results of the performed analysis are shown in Fig. 4 and Fig. 5. Global parameters of the structural analysis are shown in Tab. 3, whereas structure parameters of the constituent phases are given in Tab. 4.

Fig. 4. X-ray diffraction pattern after refinement of the elementary cell parameters for BFTO ceramics sintered at $T=850^\circ$C in assumption of the multiphase sample; bottom plot shows the difference between the experimental (dots) and refined (solid line) diffraction patterns

**TABLE 2**

| Weight fraction, % | Formula/Space group/Crystal system | Unit cell parameters | Number of peaks | FoM |
|-------------------|-----------------------------------|----------------------|----------------|-----|
| 49.6              | Bi$_4$Ti$_3$O$_{12}$ / Bm2m/ orthorhombic | $a=5.4730$ Å, $b=45.4200$ Å, $c=5.4500$ Å | total 42, in range 41, matched 33 | 0.8206 |
| 30.8              | Bi$_5$FeTi$_3$O$_{15}$ / F2mm/ orthorhombic | $a=5.4950$ Å, $b=57.5810$ Å, $c=5.4710$ Å | total 39, in range 39, matched 29 | 0.7677 |
| 17.2              | Bi$_{11}$Fe$_3$Ti$_6$O$_{33}$ / Fmm2/ orthorhombic | $a=5.4318$ Å, $b=41.1490$ Å, $c=5.4691$ Å | total 144, in range 131, matched 88 | 0.8732 |
| 1.4               | Bi$_{25}$FeO$_{40}$ / I23/ cubic | $a=10.1789$ Å | total 41, in range 38, matched 21 | 0.6931 |
| 1.0               | Bi$_6$Fe$_2$Ti$_3$O$_{18}$ / B2cb/ orthorhombic | $a=5.4451$ Å, $b=5.4101$ Å, $c=32.8565$ Å | total 286, in range 209, matched 69 | 0.7170 |
Fig. 5. X-ray diffraction pattern after refinement of the elementary cell parameters for BFTO ceramics sintered at \( T = 1080 \, ^\circ\text{C} \) in assumption of the multiphase sample; bottom plot shows the difference between the experimental (dots) and refined (solid line) diffraction patterns.

One can see from Tab. 3 that Rietveld refinement of the crystal structure of fabricated BFTO ceramics was performed with good quality so the data obtained are correct and reasonable. It was found that the samples were multiphase ones. They consisted of two BFTO Aurivillius phases with consecutive, integer number of layers \( m \) in the slab, namely \( m = 4 \) and \( m = 5 \). The dominant phase in the BFTO ceramics was the one with \( m = 4 \). The weight fraction of a BFTO phase with a reduced number of layers (\( m \)) in the slab increased from 69\% to 72\% with an increase in the sintering temperature.

It should be noted, however, that both phases were described with the same orthorhombic symmetry, the same space group \((Fmm2)\) and it is likely that they exhibited the same axis setting. Taking into consideration the above mentioned and the fact that ratio of weight fractions of the constituent phases \((m=5):(m=4)\) in fabricated BFTO ceramics is almost independent on sintering temperature one can postulate that the resultant phase can be an Aurivillius mixed phase [e.g. 18, 19] described with a fractional number \( m = (4.3 \pm 0.02) \). However, The Authors realize that the above mentioned hypothesis needs further investigations on synthesis of BFTO ceramics.

5. Conclusions

Single-phase samples of \( \text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18} \) compounds are difficult to produce by solid-phase chemical reactions because these compounds are formed in several stages and their thermal stability is low. Results of the XRD analysis indicated that the forming Aurivillius phases had an imperfect structure. They corresponded to the mixture of \( \text{Bi}_{5n+1}\text{Fe}_{n-3}\text{Ti}_3\text{O}_{3m+3} \) compositions with both stoichiometric \((m = 5)\) and reduced \((m = 4)\) number of perovskite-like layers \((m)\) in the slab. The ratio of weight fractions of the constituent phases \((m = 5):(m = 4)\) was found to be \( \sim 30:70 \).

It was found that the influence of sintering temperature, within the chosen range, on crystal structure and phase composition of BFTO ceramics was rather minor. However, a small increase in the amount of BFTO phase with \( m = 4 \) was observed.

### TABLE 3

| Parameter                  | Value BFTO @ \( T = 850 \, ^\circ\text{C} \) | Value BFTO @ \( T = 1080 \, ^\circ\text{C} \) |
|---------------------------|---------------------------------------------|---------------------------------------------|
| Profile function:         | Pseudo Voigt                                | Pseudo Voigt                                |
| Background:               | Polynomial                                  | Polynomial                                  |
| \( R \) (expected)/ %:    | 5.07159                                     | 8.17205                                     |
| \( R \) (profile)/ %:     | 7.01839                                     | 14.12068                                    |
| \( R \) (weighted profile)/ %: | 8.75605                                | 13.59406                                    |
| GOF:                      | 2.98076                                     | 2.76718                                     |

### TABLE 4

| Relevant parameters | BFTO @ \( T = 850 \, ^\circ\text{C} \) | BFTO @ \( T = 1080 \, ^\circ\text{C} \) |
|---------------------|----------------------------------------|----------------------------------------|
| Formula sum         | \( \text{O}_6\text{Fe}_2\text{Ti}_3\text{Bi}_{24} \) | \( \text{O}_6\text{Fe}_2\text{Ti}_3\text{Bi}_{20} \) |
| Formula mass/ g/mol  | 7189.062                                | 5937.76                                |
| Density calculated   | 8.0683                                  | 8.0901                                 |
| Weight fraction/ %:  | 31(1)                                   | 69(1)                                  |
| Space group (No.):   | F m m 2 (42)                            | F m m 2 (42)                            |
| Lattice parameters:  |                                         |                                         |
| \( a/ \text{Å} \)    | 5.467(9)                                 | 5.459(2)                                |
| \( b/ \text{Å} \)    | 49.485(5)                                | 40.851(6)                               |
| \( c/ \text{Å} \)    | 5.468(9)                                 | 5.465(1)                                |
| \( V/ 10^6 \text{pm}^3 \) | 1479.37                               | 1218.579                               |
| \( R \) (Bragg)/ %:  | 6.21572                                  | 6.22126                                 |

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