

Special Issue “Materiais 2015”

Synthesis and structure of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ceramics

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Abstract

The aim of the present research was to fabricate and study crystal structure and phase composition of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ (BTFO) ceramics exhibiting Aurivillius - type structure. By means of simultaneous thermal analysis and X-ray diffraction analysis the process of synthesis of BTFO ceramics has been studied. Mixed oxide method followed by pressureless sintering was used for ceramics preparation. Three endothermic thermal effects have been revealed on heating the stoichiometric mixture of initial powder oxides within the temperature range $\Delta T = 700\text{--}1200^\circ\text{C}$, while only one strong endothermic peak was found on heating the powder after calcination. The weak endothermic peaks were ascribed to the melting points of intermediate surface phases based on Bi_2O_3 -rich phase formed at low temperature. X-ray diffraction studies have shown that BTFO ceramics consisted of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phases in amount of 88.3% and 11.7% (weight fraction), respectively.

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Keywords: Aurivillius compound; $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ceramics; sintering; X-ray diffraction; crystal structure; phase analysis.

1. Introduction

Bismuth layer structured ferroelectrics (BLSFs or Aurivillius phase) are of great technological interest due to their ferroelectric properties and various applications. If modified appropriately, BLSFs may exhibit novel physical properties which enrich their functionality [1].

The motivation of the present research was to develop new high-performance ceramics that promise important practical applications in electrical engineering and especially in mechatronics as sensor-actuator systems. Considerable attention attract multiferroics with rather spectacular properties, in particular, very strong coupling between ferroelectric and magnetic degree of freedom [2].

Materials of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - BiFeO_3 (BTO-BFO) system, combining ferroelectric, semiconducting and

ferromagnetic properties, are potentially attractive for producing advanced materials for information processing and information storage applications [3].

The general formula of BTO-BFO compounds is $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ [4]. These compounds have layered perovskite-like structures, first described by Aurivillius, in which fluorite-like bismuth-oxygen layers of thickness f and composition $\{(\text{Bi}_2\text{O}_2)^{2+}\}_\infty$ alternate with (001) perovskite-like slabs of composition $\{(\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+1})^{2-}\}_\infty$ and thickness $h=pm$. The values of f and h are related to the c cell parameter by $f+h=c/2$, m indicates the number of perovskite-like layers per slab and may take integer or fractional values, and p is the average thickness of perovskite-like layers (Fig. 1). Fractional m value corresponds to mixed-layer structures [5], which contain perovskite slabs of different thicknesses.

Aim of the present research was to utilize the pressureless sintering method to fabricate $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ceramics which is a member of the BTO-BFO system with $m=4$ perovskite-like layers [6]. The evolution of the phase composition and the crystal structure of the

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synthesized compound as well as final ceramics was studied by X-ray diffraction method.

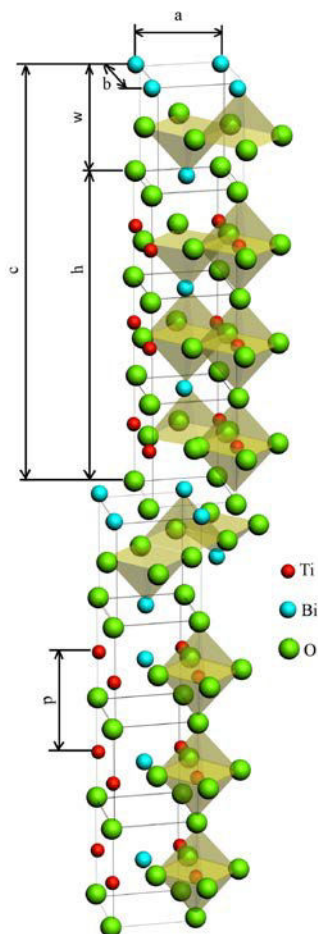
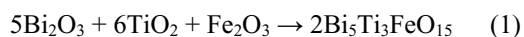


Fig. 1. Elementary cell of Aurivillius structure compound exemplified by $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=3$ perovskite-like layers per slab) [6].

2. Experimental

The ceramic samples of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ chemical composition were synthesized according to solid state reaction route (mixed-oxide method). The appropriate amounts of reagent – grade oxide powders, viz. Bi_2O_3 , TiO_2 and Fe_2O_3 were thoroughly weighted in stoichiometric amounts to provide conditions for formation of the desired composition, given by:



Then the mixture of oxides was ground with an agate mortar and pestle first. After that the planetary ball mill was utilized for wet grinding of the powders. A small amount of ethyl alcohol and zirconia balls as grinding medium were used in the milling-

homogenizing treatment that lasted for $t=24\text{h}$. After milling, the powders were subjected for drying. When dried the mixture of powders was compacted into pellets of 10 mm in diameter by pressing under pressure of $p=30\text{ MPa}$ in a stainless steel die. The green bodies were then placed in an alumina crucible and fired with air at $T=720^\circ\text{C}$ (the heating rate 5°C/min , the soaking time $t=2\text{h}$) to conduct the solid state reaction. After thermal treatment the pellets were crushed in a mortar and the synthesized material was subjected to wet milling and drying again. Before final sintering the compacts were formed in a stainless steel die of 10 mm in diameter. Final sintering was performed by pressureless sintering under ambient air in a furnace at temperature $T=900^\circ\text{C}$ and $T=980^\circ\text{C}$ and soaking time $t=2\text{h}$. Thus fabricated $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ceramics were characterized in terms of phase composition, and crystal structure.

The crystal structure of ceramics were studied by X-ray diffraction method at room temperature (XPert-Pro diffractometer, $\theta - 2\theta$ mode, $\text{CoK}\alpha$ radiation, detector scan step $\Delta 2\theta=0.01^\circ$ and a counting time $t=100\text{s}$). Phase analysis of X-ray diffraction patterns of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ powders was carried out using Match! (Crystal Impact) computer program [7]. As the diffraction data were raw (profile) data, the so-called “raw data processing” had to be carried out. That included: stripping of the α -2-radiation, data smoothing, peak searching, profile fitting, and correction for errors. The goal was to obtain a list of peaks (2θ and intensity values) with highest possible precision. It is extremely important that this step is performed as accurate as possible in order to obtain reasonable results in the search-match process later on. The structural analysis was performed with X'pert HighScore Plus software (PANalytical B.V). The latest available ICSD [8], ICDD [9] and COD [10], databases were utilized. Refinement of the structural parameters of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ceramics was performed with the Rietveld method [11].

3. Results and Discussion

3.1. Thermal behaviour of the powders

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 (viz. Bi_2O_3 , TiO_2 and Fe_2O_3). The measurements were obtained with Netzsch STA409 thermal analyser and results of STA

of the stoichiometric mixture of Bi_2O_3 , TiO_2 and Fe_2O_3 oxides as well as powder of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ compound are given in Fig. 2. Let us mention that uniform process of a mass loss starting at $T=200^\circ\text{C}$ and reaching a value of $\Delta m=-0.76\%$ at $T=900^\circ\text{C}$ took place for stoichiometric mixture of oxides [6].

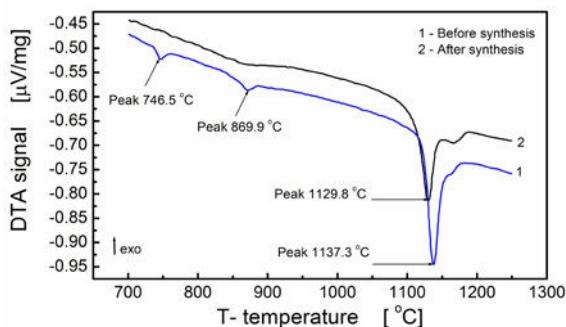


Fig. 2. DTA curves for stoichiometric mixture of oxides (curve 1) and $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ powder after synthesis at $T=720^\circ\text{C}$ (curve 2).

The DTA study revealed three endothermic effects manifested upon heating the samples within the temperature range $\Delta T=700\text{--}1200^\circ\text{C}$ (Fig. 2).

According to the suggested scheme for the formation of Aurivillius phases in the $\text{Bi}_2\text{O}_3\text{--TiO}_2\text{--Fe}_2\text{O}_3$ system the formation of $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ compound is considered as a multistage process [12,13]. 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.

Comparison of our results with the published data on phase relationships in the $\text{Bi}_2\text{O}_3\text{--Fe}_2\text{O}_3$ system [14], $\text{Bi}_2\text{O}_3\text{--TiO}_2$ system [15] and $\text{Bi}_2\text{O}_3\text{--TiO}_2\text{--Fe}_2\text{O}_3$ system (i.e., formation of $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$) compounds [3,4,6,12,13] allows us to tentatively attribute the thermal effects manifested in the differential thermogram of the sample (Fig. 2).

It is commonly known [13] that around $T=500^\circ\text{C}$ the $\alpha\text{-Bi}_2\text{O}_3$ reacts with small amounts of TiO_2 and Fe_2O_3 to form intermediate Bi_2O_3 -rich compounds, namely $\text{Bi}_{12}\text{TiO}_{20}$ and a compound close in composition to $\text{Bi}_{25}\text{FeO}_{40}$. These compounds are extremely difficult to distinguish by XRD since both have a structure closely similar to that of the metastable phase $\gamma\text{-Bi}_2\text{O}_3$. As the temperature is increased further the reaction rate grows and reaches its maximum at temperature close to the melting point of the $\gamma\text{-Bi}_2\text{O}_3$ -based surface phase (endothermic peak at $T=746.5^\circ\text{C}$, Fig. 2) and facilitates the formation of BiFeO_3 phase. The second

endothermic peak at $T\approx 870^\circ\text{C}$ can be attributed to the melting point of the $\text{Bi}_{12}\text{TiO}_{20}$ -based surface phase and formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Aurivillius phase [15]. With the further increase in temperature 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 composition $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ is formed. Thermal events within the range $\Delta T=1100\text{--}1200^\circ\text{C}$ refer to the decomposition of the compound.

3.2. X-ray phase analysis

X-ray diffraction patterns of the BFTO powder calcined at $T=720^\circ\text{C}$ and subjected to free sintering at $T=900^\circ\text{C}$ and $T=980^\circ\text{C}$ are shown in Fig. 3.

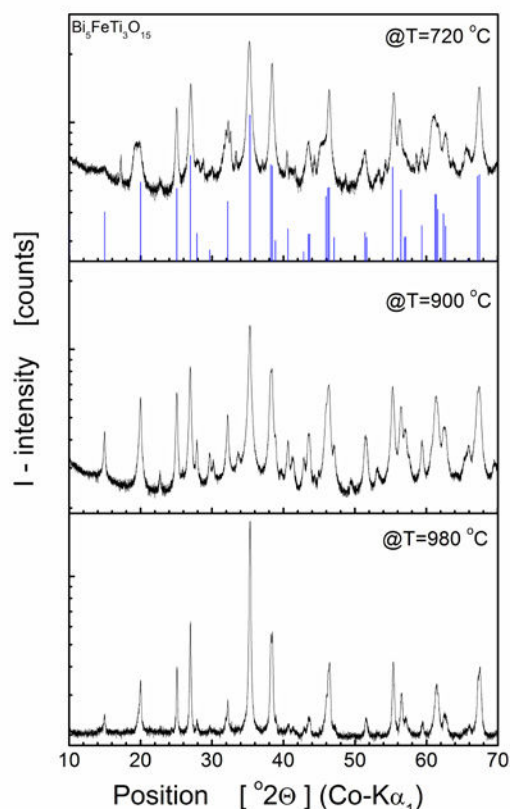


Fig. 3. X-ray diffraction patterns of BFTO powder after synthesis at $T=720^\circ\text{C}$ and sintering at $T=900^\circ\text{C}$ and $T=980^\circ\text{C}$. Positions of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ reference phase with an orthorhombic structure ($A21am$ space group) are also given.

Positions of the X-ray diffraction lines of the main phases likely to exist in the BFTO powder under investigation are shown in Fig. 4.

It was found that BFTO powder calcined at $T=720^\circ\text{C}$ consisted of the phase $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$, and the end-members of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - BiFeO_3 system.

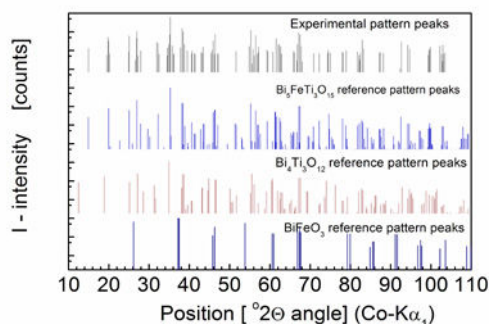


Fig. 4. Reference pattern peaks' positions of the main BFTO constituent phases. As an example experimental pattern peaks found for BFTO powder sintered at $T=980^{\circ}\text{C}$ are shown.

Amount of the intermediate phases, namely $\text{Bi}_{25}\text{FeO}_{40}$ and $\text{Bi}_{12}\text{TiO}_{20}$, was about 9 wt.%. Results of the semi-quantitative analysis of the phase composition are given in Table 1.

Table 1. Matched phases for BFTO powder after synthesis ($T=720^{\circ}\text{C}$).

Amount, %	Formula / Space group / crystal system	(FoM)
50.8	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ / $B2cb$ / orthorhombic	0.822
27.7	$\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ / $A21am$ / orthorhombic	0.809
12.6	BiFeO_3 / $R-3m$ / rhombohedral	0.429
5.2	$\text{Bi}_{25}\text{FeO}_{40}$ / $I23$ / cubic	0.730
3.8	$\text{Bi}_{12}\text{TiO}_{20}$ / $Fm-3m$ / cubic	0.458

The phase composition of BFTO ceramics after sintering at $T=900^{\circ}\text{C}$ was found to change. Amount of the desired $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ phase has increased from about 28% to 63%. Sintering at $T=900^{\circ}\text{C}$ made it possible to fabricate BFTO ceramics that also exhibited orthorhombic symmetry with $A21am$ space group and a figure-of-merit (FoM) reaching a value of $FoM=0.893$. Results of the semi-quantitative analysis of the X-ray diffraction pattern are given in Table 2.

Table 2. Matched phases for BFTO powder after sintering at $T=900^{\circ}\text{C}$.

Amount, %	Formula / Space group / crystal system	(FoM)
63.1	$\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ / $A21am$ / orthorhombic	0.893
19.3	BiFeO_3 / $R-3m$ / rhombohedral	0.445
8.7	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ / $B2cb$ / orthorhombic	0.731
7.4	$\text{Bi}_{12}\text{TiO}_{20}$ / $Fm-3m$ / cubic	0.657
1.5	$\text{Bi}_{25}\text{FeO}_{40}$ / $I23$ / cubic	0.672

An increase in the sintering temperature to $T=980^{\circ}\text{C}$ caused formation of the BFTO phase that exhibited orthorhombic symmetry described well with the $Fmm2$ space group ($FoM=0.892$). Results of the search-and-match analysis of BFTO ceramics sintered at $T=980^{\circ}\text{C}$ are given in Table 3.

Table 3. Matched phases for BFTO powder after sintering at $T=980^{\circ}\text{C}$.

Amount, %	Formula / Space group / crystal system	(FoM)
85.2	$\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ / $Fmm2$ / orthorhombic	0.892
9.7	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ / Fmm / orthorhombic	0.748
5.1	BiFeO_3 / $R3c$ / trigonal	0.305

3.3. X-ray structural analysis

Detailed structural analysis, together with refinement of the elementary cell parameters (according to the Rietveld method) was performed for X-ray diffraction pattern of BFTO ceramics sintered at $T=980^{\circ}\text{C}$. Global parameters of the analysis are shown in Table 4.

Table 4. Global parameters of the Rietveld analysis (X-ray diffraction pattern of BFTO powder sintered at $T=980^{\circ}\text{C}$).

Parameter	Value
Profile function	Pseudo Voigt
Background	Polynomial
R (expected), %	14.25
R (profile), %	13.51
R (weighted profile), %	15.33
GOF	1.16

As far as global parameters are concerned it should be noted that the refinement procedure was performed after subtracting the background. One can see that numerical parameters of quality of the refinement analysis (R -parameters, Table 4) exhibit acceptable values.

According to the results of the semi-quantitative phase analysis (Table 3), three phases, i.e., pentabismuth trititanium iron(III) oxide ($\text{Bi}_5\text{FeTi}_3\text{O}_{15}$), tetrabismuth trititanium dodecaoxide ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) and bismuth iron(III) oxide (BiFeO_3) were expected to constitute BFTO ceramics. However, results of the Rietveld refinement method have shown that the sample is two-phase and consisted of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in amount of 88.3% and 11.7%, respectively. The presence of bismuth ferrate was excluded in the course of calculations. Results of the analysis are demonstrated in Fig. 5. Structural parameters of the phases that constituted BFTO ceramics are given in Table 5.

4. Conclusions

In the course of the present studies mixed oxide method followed by pressureless sintering was utilized for fabrication of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ceramics. Simultaneous

thermal analysis revealed three endothermic thermal effects on heating within the temperature range $\Delta T=700\text{--}1200^\circ\text{C}$, while only one strong endothermic peak was found on heating the powder after calcination. The weak endothermic peaks were attributed to the melting points of intermediate surface phases based on Bi_2O_3 -rich phase formed at low temperature, namely $\text{Bi}_{12}\text{TiO}_{20}$ and/or $\text{Bi}_{25}\text{FeO}_{40}$. The strong peak at the temperature range $\Delta T=1100\text{--}1200^\circ\text{C}$ was ascribed to the decomposition of the compound. X-ray diffraction studies have shown that BFTO ceramics sintered at various temperatures exhibited multiphase composition. It was found that, with an increase in sintering temperature, the intermediate Bi_2O_3 -rich compounds transform and the weight fraction of the desired $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ phase increased. Calculations based on the Rietveld refinement method showed that BFTO ceramics sintered at $T=980^\circ\text{C}$ was also multiphase and apart from the main $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ phase of orthorhombic symmetry with $Fmm2(42)$ space group it included 11.7 wt.% of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase (orthorhombic symmetry, $Aba2(41)$ space group).

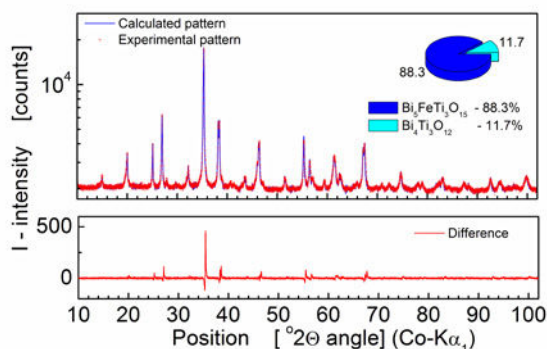


Fig. 5. Results of the Rietveld analysis for BFTO ceramics sintered at $T=980^\circ\text{C}$ in assumption of the multiphase sample. Bottom curve shows the difference between the observed and calculated patterns.

Table 5. Structure parameters of the constituent phases.

Relevant parameters	$\text{Bi}_5\text{FeTi}_3\text{O}_{15}$	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$
Weight fraction (%)	88.3	11.7
Space group (No.)	$Fmm2(42)$	$Aba2(41)$
Lattice parameters		
a (Å)	5.434	32.31
b (Å)	41.21	5.429
c (Å)	5.462	5.473
V (10^6 pm^3)	1223.43	960.08

Acknowledgements

The present research was supported by University of Silesia in Katowice, Poland from the funds for science – research potential (NO 1S-0800-001-1-05-01).

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