CORRELATION BETWEEN STRUCTURE, MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF Bi7Fe3Ti3O21 CERAMICS OBTAINED IN DIFFERENT CONDITIONS

Multiferroic six-layer Aurivillius type Bi7Fe3Ti3O21 ceramics was obtained by conventional mixed oxides method. The final sintering process was taken in several different sintering times, which determined changes in properties of discussed ceramic material. The structure and dielectric properties of the material are reported. In order to examine the technological conditions on the crystal structure, XRD analysis was carried out. The microstructure, as well as the quantitative and qualitative analysis of the chemical composition were investigated by scanning electron microscope with an energy dispersion spectrometer. The main purpose of the paper is to present the effect of sintering time on the microstructure, crystallographic structure and dielectric properties of Bi7Fe3Ti3O21 ceramics.

Keywords: multiferroic materials, Aurivillius phases, Bi7Fe3Ti3O21, dielectric properties

1. Introduction

Nowadays, where scientists aim at device’s miniaturization, it causes the increase of interests in finding new, functional materials. Multiferroic materials are their representative. The properties of it change very strongly under the impact of external influences. They combine ferroelectric, (ferro)magnetic and/or ferroelastic properties simultaneously [1-3]. An interesting group of the multiferroic materials is perovskite-like layered structures called Aurivillius phases. Due to their properties, these materials can be used for example in optical devices, ferroelectric memories, actuators, transducers or humidity sensors [4-8]. The general formula of compounds with Aurivillius-type structure is \((\text{Bi}_2\text{O}_2)^2+(\text{Am}_1\text{Bm}_m\text{O}_{3m+1})^2\) for the first time described by Aurivillius in 1949 [9]. The value \(m\) (integer or fractional), indicates the number of perovskite building blocks between two fluorite-like bismuth-oxygen layers \((\text{Bi}_2\text{O}_2)^2\) [10]. The place of A position usually is taken by big cations like \(\text{Bi}^{3+}\), \(\text{Sr}^{2+}\), \(\text{Dy}^{3+}\), \(\text{La}^{3+}\) and the B position is mostly occupied by smaller ions like for example \(\text{Fe}^{2+}\), \(\text{Ti}^{4+}\) [11].

Authors, repeatedly indicate, that single-phase samples \(\text{Bi}_{m-1}\text{Fe}_m\text{Ti}_3\text{O}_{3m+3}\) are very difficult to obtained by solid-phase chemical reactions. The reason for this is the multi-stage process of the formation of these compounds and the fact that the thermal stability of the materials in question is low [12]. Therefore, it is still desirable to find a suitable method to obtain this material. The literature reports different ways to obtain the Aurivillius compounds, such as preparing through a modified sol-gel citrate-complexation and precursor film route [13], using Pechini’s method [14,15] or obtaining samples by traditional solid-state technique [16]. The choice of the method as well as technological conditions have significant impact on properties of ceramic materials.

The aim of this work was to study the dielectric properties of six-layered Aurivillius type Bi7Fe3Ti3O21 ceramics obtained in different sintering times. XRD analysis was conducted to study the crystal structure.

2. Experimental

2.1. Technology process

Stoichiometric amount of simple oxides \(\text{Bi}_2\text{O}_3\) (Aldrich 99.9%), TiO2 (Poch 99.9%), Fe2O3 (Sigma-Aldrich 99%) were weighted, preliminarily mixed in the mortar and then milled in the planetary ball mill for \(t = 24\) h (in ethanol). After drying, powders were re-mixed in the mortar. The synthesis was carried out at \(T = 1123\) K for \(t = 4\) h. The next step was to crumble the powders in the mortar and to mill it in ethanol in the planetary...
ball mill for \( t = 24 \text{ h} \) over. After drying and next re-milling in the mortar, pellets were pressed (\( \phi = 10 \text{ mm}, H = 1 \text{ mm}, 200 \text{ MPa} \)). The samples were put and closed into crucibles. The sintering was carried out under the following conditions: \( T = 1263 \text{ K} \) for the several sintering time \( t_s = (4;8;12;16;24) \text{ h} \).

2.2. Investigations

The scanning electron microscope was used to observe the microstructure of the ceramic samples. To confirm a proper stoichiometry of obtained material the energy dispersion spectroscopy (EDS) technique was applied. The crystal structures of all discussed samples were investigated using BRUKER D8 Discover, equipped with a standard CuKa radiator (\( \lambda_{Kα1} = 1.54056 \text{ Å}, \lambda_{Kα2} = 1.54439 \text{ Å} \)), Siemens KFL CU2 K, working at 40 kV voltage and 40 mA current in operating mode. The radiator was equipped with a Göbel FGM2 mirror, allowing to perform the measurements under parallel beam conditions. The Bragg-Brentano diffraction geometry was applied [17]. The diffraction angle of 2\( \theta \) range was set to 15-80° with a step of 0.015° and acquisition time of 2 s per step. All measurements were done at 298 K in the temperature-stabilized Anton Paar HTK 1200N chamber. For the data processing the Crystal Impact Match! application was used. For each diffraction pattern the \( \lambda_{Kα2} \) signal component was deconvoluted and removed, the background was subtracted and

Fig. 1. SEM images of the microstructure of fracture of the Bi\textsubscript{7}Fe\textsubscript{3}Ti\textsubscript{3}O\textsubscript{21} samples sintered from different time a) 4 h b) 8 h c) 12 h d) 16 h and e) 24 h
the data were smoothed using the fast Fourier transform. The phase analyzes were done with support of an ICSD database. For crystallographic calculations the FullPROF ver. 3.0 program was used, which allowed to perform the Rietveld refinement and calculate the precise unit cell parameters, based on a diffraction profile fitting [18]. The reference CIF file used for this analysis was received from the supplementary data given in Ref. [19]. Calculated broadening of diffraction lines, namely full width at half maximum (FWHM) was used to estimate the average crystallite sizes using Debye-Scherrer formula [20]. The standard reference material NIST SRM 660a (LaB₆) was applied as an instrumental standard to eliminate the apparatus broadening component.

The measurements of the temperature dependencies of dielectric permittivity were performed with the use a computerized measuring system, where the integral part was an Agilent E4980A LCR meter.

3. The results and discussion

Several different sintering times were applied at the final sintering process. The difference in technical conditions determined changes in properties of discussed ceramic material. Figure 1 exhibits SEM images of ceramic materials densified at different time. The grains of ceramics which were finally sintered for the shortest time are well developed and show platelet – like structure, which is characteristic for Bi₇Fe₃Ti₃O₂₁ [21]. Such a shape is typical for Aurivillius bismuth layered compounds due to the preferential growth of the a–b crystalline plane [22]. Plates are randomly oriented and their size is not homogenous, however the domination of larger grains is visible. The microstructure is completely changed as far as longer times of final sintering are concerned. The platelet-like grains completely disappeared, and much smaller grains with rounded edges developed. The tendency is changed for samples which were sintered for 24 hours.

The EDS spectrum is shown in Figure 2. The qualitative EDS analysis confirms the presence of following elements: bismuth, iron, titanium and oxygen. The presence of undesirable impurities has not been registered. The scan has been done on 50 points of several grains – the stoichiometry changes slightly from “point to point”. However, the average stoichiometry obtained for the surface of all grains is in a good agreement with theoretical one. The Table 1 presents results of EDS analysis concerning Bi₇Fe₃Ti₃O₂₁ ceramics sintered for 4 h.

The influence of sintering time length on the crystal structure of Bi₇Fe₃Ti₃O₂₁ ceramics has been studied by XRD. The complete set of the powder diffraction patterns with the reference ICSD card for investigated samples are shown in Figure 3. The unit cell parameters and estimated crystallite sizes were presented in Table 2.

The comparison of obtained results has shown that the increase of sintering time insignificantly influence on the crystallographic parameters, which has had tendency to decrease with increase in tₛ. The effect of technological conditions on the change in crystallite size is more visible. It decreases from about 58 nm to 35 nm.

Figure 4 shows the temperature characteristics of dielectric constant obtained for discussed ceramics. The broad maximum visible in ε(T) dependencies in temperature range between 500 K and 530 K is attributed, by other authors, to space charge polarization [21,23,24]. The contribution of polarization of the space charge decreases with temperature.

As the sinter time increases, the discussed maximum increases, reaching the highest value for 12 hours of sintering times (Table 3). Then, the value of maximum is reduced – this behavior can be associated with changes in the concentration of space charge. Above 700 K, the value of dielectric permittiv-

![Fig. 2. EDS emission spectrum Bi₇Fe₃Ti₃O₂₁ ceramics sintered for t = 4 h](image)

### Table 1

<table>
<thead>
<tr>
<th>Oxide formula</th>
<th>Determined oxide content from EDS [wt.%]</th>
<th>Theoretical oxide content [wt.%]</th>
<th>The difference between the theoretical and determined oxide content [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂O₃</td>
<td>76.7</td>
<td>77.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12.6</td>
<td>11.4</td>
<td>1.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>10.8</td>
<td>11.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Sintering time [h]</th>
<th>Unit cell parameters [Å]</th>
<th>V [Å³]</th>
<th>Crystallite size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>5.492(6) 5.540(1) 57.724(3)</td>
<td>1756.52</td>
<td>58</td>
</tr>
<tr>
<td>8</td>
<td>5.477(1) 5.490(1) 57.493(5)</td>
<td>1728.74</td>
<td>56</td>
</tr>
<tr>
<td>12</td>
<td>5.482(1) 5.491(1) 57.396(3)</td>
<td>1727.72</td>
<td>48</td>
</tr>
<tr>
<td>16</td>
<td>5.482(1) 5.492(1) 57.361(3)</td>
<td>1726.98</td>
<td>35</td>
</tr>
<tr>
<td>24</td>
<td>5.475(7) 5.497(5) 57.383(4)</td>
<td>1727.63</td>
<td>40</td>
</tr>
<tr>
<td>Ref. [19]</td>
<td>5.4699 5.4924 57.5510</td>
<td>1729.00</td>
<td>—</td>
</tr>
</tbody>
</table>
Dielectric permittivity rises again, which is associated with the increasing in high
temperature conductivity.

Moreover, the value of dielectric permittivity shows strong
frequency dependences, which is particularly visible at the
maximum (Figure 5). The degree of dispersion defined as the
difference between maximum value of permittivity measured at
0.1 kHz and measured at 1 MHz changed significantly (Table 3).

For low frequencies on presented characteristics in the range
of temperature between 600 K and 800 K minimum is visible.
The diagram of natural logarithm of the measuring frequency
versus the reciprocal temperature $T_{\text{min}}$, at which the minima in
the $\varepsilon(T)$ curves occur, is shown in Figure 6.

$$f = f_0 \exp \left( - \frac{E_a}{kT_{\text{min}}} \right)$$

(1)

The activation energy $E_a$ of the process, which takes place in
the sample, was determined by using formula (1). The obtained
values are collected in Table 4.

The values of $E_a$ point out that the process is probably con-
nected with the space charge polarization. At low temperature
charges are trapped, however the increase in temperature causes
gradually release of the space charge. Due to the thermal genera-
tion, electrons are released as first. This causes the appearance
of nonscreening dipole moments connected with the ions charge.
The discussed dipoles give rise to the observed increase of di-
electric permittivity in the low frequency range.

<table>
<thead>
<tr>
<th>Sintering time [h]</th>
<th>$\varepsilon$ at room temperature (300K)</th>
<th>$\tan\delta$ at room temperature (300K)</th>
<th>$T_{\text{max}}$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>$\Delta\varepsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>234</td>
<td>0.570</td>
<td>526</td>
<td>3630</td>
<td>8933</td>
</tr>
<tr>
<td>8</td>
<td>245</td>
<td>0.569</td>
<td>513</td>
<td>2021</td>
<td>15875</td>
</tr>
<tr>
<td>12</td>
<td>263</td>
<td>0.625</td>
<td>534</td>
<td>8619</td>
<td>22203</td>
</tr>
<tr>
<td>16</td>
<td>235</td>
<td>0.578</td>
<td>542</td>
<td>5997</td>
<td>5427</td>
</tr>
<tr>
<td>24</td>
<td>295</td>
<td>0.600</td>
<td>503</td>
<td>3123</td>
<td>12036</td>
</tr>
</tbody>
</table>
4. Conclusions

Multiferroic six-layer Aurivillius type Bi$_7$Fe$_3$Ti$_3$O$_{21}$ ceramics was obtained by conventional mixed oxides method. The synthesis took place at the temperature $T = 1123$ K, and time of it was equal $t = 4$ h. The conditions of the final sintering process was carried out at $T = 1263$ K while the time conditions were change in the range $t_s = (4;8;12;16;24)$ h. The difference

![Fig. 5. Real part of dielectric permittivity as a function of temperature for several sintering time a) $t_s = 4$ h, b) $t_s = 8$ h, c) $t_s = 12$ h, d) $t_s = 24$ h, e) $t_s = 24$ h](image)

<table>
<thead>
<tr>
<th>Sintering time [h]</th>
<th>$E_a$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.12</td>
</tr>
<tr>
<td>8</td>
<td>1.21</td>
</tr>
<tr>
<td>12</td>
<td>1.30</td>
</tr>
<tr>
<td>16</td>
<td>1.71</td>
</tr>
<tr>
<td>24</td>
<td>1.12</td>
</tr>
</tbody>
</table>

TABLE 4

The activation energy of the process taking place in the samples
in sintering time determined changes in the microstructure of discussed ceramic materials. Shape of grains drastically changed from platelet-like grains (sintering time $t_s = 4$ h) to completely different rounded edges shape (longer sintering time). Prolonging the sinter time caused a significant reduction in the size of the crystallites, without significantly affecting the parameters of the unit cell. Dielectric measurements revealed the broad maximum visible in $\varepsilon(T)$ dependencies in the temperature range between 500 K and 530K, which can be connected to the space charge polarization. Additionally in the range of temperature between 600 K-800 K, for low frequencies on $\varepsilon(T)$ characteristic the local minimum is visible, which temperature is strongly dependent on frequency. The process responsible for the behavior has activation characters. The determined activation energy indicated that the process is connected with the relaxation of ions dipoles giving rise to the observed increase of $\varepsilon$ in the low frequency range.

Acknowledgement

This work was partially supported by the University grant "New crystalline and composite materials for optics and photonics"., UGB 521-9000-00-000, funds for year 2020.

REFERENCES