Electrical characteristics of bismuth titanate glass-ceramics containing SiO$_2$ and Nd$_2$O$_3$

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Abstract

Bismuth-titanate ceramics containing SiO$_2$ and Nd$_2$O$_3$ as additives are synthesized at two different ways of cooling of the melts. The introduction of SiO$_2$ and Nd$_2$O$_3$ leads to more complex crystallization with participation of several phases including Bi$_4$Ti$_3$O$_{12}$. It is proved that the applied methods of synthesis are suitable for generation of different microstructures in the bulk doped bismuth titanate ceramics, which is promising basis for modification of their electrical properties. The increasing of SiO$_2$ content improves the glass formation ability and addition of Nd$_2$O$_3$ stimulates the crystallization. The conductivity of selected samples is determined by impedance analyzer in the frequency range from 10 to 100 kHz and DC resistible bridge using two-terminal method. All investigated samples are dielectrics with conductivity $10^{-6}$–$10^{-9}$ (Ω·cm)$^{-1}$.

Keywords: bismuth titanate, melt quenching, electrical characteristics, microstructure

I. Introduction

The application of Aurivillius family of bismuth-based ferroelectric compounds with a layered structure [1] in capacitors, sensors, piezoelectric and electro-optic devices [2–4] is strongly influenced by the method of preparation. Between them the crystallization from melts and glasses recently is also applied [5–9]. This method gives possibility for doping with different cations to improve the properties. It allows also to control the particle size evolution during the transition from amorphous to crystalline state and to achieve suitable crystallographic orientation in the polycrystalline materials.

In our previous study, the phase formation in the system Bi$_2$O$_3$–TiO$_2$–SiO$_2$ from fast quenched melts is investigated [10]. It is established that the introduction of 20–40 mol% SiO$_2$ stimulates the partial amorphization of the samples. It was proved that by melt quenching it is possible to modify the microstructure and to control the crystallization process in bismuth titanate ceramics. These results motivate our future investigations.

The purpose of the present study is to elucidate the influence of the cooling rate and additional heat treatment on the phase formation and microstructure of bismuth titanate ceramics with addition of SiO$_2$, obtained by melting. Full replacement of SiO$_2$ with Nd$_2$O$_3$ is also performed. The SiO$_2$ is introduced to change the melting conditions, while the reason for Nd$_2$O$_3$ addition to bismuth titanate is that this oxide is more effective in improving the electrical properties [11–19]. According to our knowledge, up to know, there are no reports for the preparation of glass-ceramics containing the phase Bi$_4$Ti$_3$O$_{12}$ by melt quenching with participation of SiO$_2$ and Nd$_2$O$_3$.

II. Experimental

Bismuth-titanate ceramics containing SiO$_2$ and Nd$_2$O$_3$ as additives were synthesized by quenching from melt. The melting was made from the following pre-
cursors: TiO₂, Bi₂O₃, SiO₂ and Nd₂O₃ in alumina crucibles at 1250–1500°C. The contact between the samples and crucible during the melting was about 15 min. as after longer exposition (3–5 hours) contamination with 3–5 mol% Al₂O₃ was detected. The samples were prepared by two cooling rates of the melts: i) fast cooling to room temperature, performed by pouring of the melts between two cooper plates (samples with notation A) and ii) slow cooling of the melts in the crucibles (samples with notation B). The selected compositions are: 24Bi₂O₃·36TiO₂·40SiO₂, 30Bi₂O₃·50TiO₂·20SiO₂, 50Bi₂O₃·30TiO₂·20SiO₂ and 30Bi₂O₃·50TiO₂·20Nd₂O₃ (Table 1).

The phase formation was studied by X-ray diffraction analysis (XRD - TUR M62, Cu-Kα radiation and Bruker D8 Advanced Diffractometer, Cu-Kα radiation). Chemical composition was determined by energy dispersive spectroscopy (EDS, EDAX 9900). The microstructure was observed by scanning electron microscopy (SEM - 525M, Philips).

The conductivity of selected samples was measured by impedance analyzer in the 10–100 kHz frequency range (Hewlett-Packard HP4192A) and DC resistible bridge using two-terminal method and a suitable sample holder with graphite electrodes.

### III. Results and discussion

#### 3.1 Structural characterization

Depending on the cooling rate, more or less well separated amorphous regions are visually observed. They are distinguished because the crystals are milk-like, while the glass part is dark or transparent in some samples. For this reason all obtained samples may be considered as glass-ceramics. However, after the slow cooling higher crystallization of the prepared samples is observed (Fig. 1).

XRD analysis of the samples containing 20 mol% SiO₂ (Fig. 1) shows that the introduction of SiO₂ leads to more complex crystallization with participation of several phases, including dominant Bi₂Ti₂O₇ (Bi₂Ti₂O₇ – JCPDS 32-0118) and Bi₄Ti₃O₁₂ (Bi₄Ti₃O₁₂ – JCPDS 73-2181). It can be seen (Fig. 1) that the fast cooling even favors formation of the pyrochlore Bi₂Ti₂O₇ phase and stimulates the partial amorphization of the prepared samples. However, in our previous paper [20] it was confirmed that for samples containing ≥ 40% SiO₂ XRD patterns were close but do not completely coincide with these ones of the phase Bi₄Ti₃O₁₂. That can result from the forma-

![Figure 1. XRD patterns of sample with composition 30Bi₂O₃·50TiO₂·20SiO₂ melted at 1300°C: a) fast cooling of the melts (A); b) slow cooling of the melts (B)](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method of cooling and view of the sample</th>
<th>σ, (Ω·cm)⁻¹</th>
<th>Method of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24Bi₂O₃·36TiO₂·40SiO₂ heat treated, glass ceramic</td>
<td>1.77·10⁻⁶</td>
<td>AC impedance</td>
</tr>
<tr>
<td>2a</td>
<td>30Bi₂O₃·50TiO₂·20SiO₂ heat treated, glass ceramic</td>
<td>3.54·10⁻⁷</td>
<td>AC impedance</td>
</tr>
<tr>
<td>2b</td>
<td>30Bi₂O₃·50TiO₂·20SiO₂ fast cooling, partially crystallized</td>
<td>8.32·10⁻⁶</td>
<td>DC method</td>
</tr>
<tr>
<td>2c</td>
<td>30Bi₂O₃·50TiO₂·20SiO₂ slow cooling, glass ceramics</td>
<td>2.20·10⁻⁶</td>
<td>DC method</td>
</tr>
<tr>
<td>3a</td>
<td>50Bi₂O₃·30TiO₂·20SiO₂ fast cooling, partially crystallized</td>
<td>2.77·10⁻⁶</td>
<td>DC method</td>
</tr>
<tr>
<td>3b</td>
<td>50Bi₂O₃·30TiO₂·20SiO₂ slow cooling, glass ceramics</td>
<td>2.54·10⁻⁶</td>
<td>DC method</td>
</tr>
<tr>
<td>4</td>
<td>40Bi₂O₃·50TiO₂·10Nd₂O₃ fast cooling, glass ceramics</td>
<td>2.75·10⁻⁶</td>
<td>DC method</td>
</tr>
<tr>
<td>5</td>
<td>30Bi₂O₃·50TiO₂·20Nd₂O₃ fast cooling, glass ceramics</td>
<td>1.15·10⁻⁷</td>
<td>DC method</td>
</tr>
</tbody>
</table>
tion of solid solution with the bismuth-titanate phase or from the appearance of a new phase. Crystallization behaviour of the sample $24\text{Bi}_2\text{O}_3\cdot36\text{TiO}_2\cdot40\text{SiO}_2$ was additionally investigated. Thus, it is observed that after the slow cooling, the amorphous microstructure is transformed to glass-ceramic one and after additional heat treatment at 700°C for 5 hours the amount of crystalline phase increases. According to the EDS analysis (Fig. 2) the crystals and matrix differ in composition: the separated crystals are with decreased $\text{Bi}_2\text{O}_3$-content and increased $\text{TiO}_2$-content in comparison with the nominal batch composition, as it was established also in our previous studies [20].

The addition of $\text{Nd}_2\text{O}_3$ up to 20% decreases the glass formation trend and raises the melting temperature up to 1500°C. XRD results, presented in Fig. 3, show that addition of already 10 mol% stabilize $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase, which is completely different behaviour in comparison to the samples containing 20 mol% $\text{SiO}_2$. In the sample containing 20 mol% $\text{Nd}_2\text{O}_3$, the phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, texturing in the plane (001) was detected after fast cooling (Fig. 3). According to EDS data (Fig. 4), the sample contains pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase and crystals of the bismuth titanate with $\text{Bi}_2\text{O}_3$ partially replaced by $\text{Nd}_2\text{O}_3$ (Fig. 4).

### 3.2 Electrical properties

Conductivity of the samples depending on the composition, cooling method and method of measurement are presented in Table 1. The conductivity of all samples is in the rage $10^{-6}$–$10^{-9}$ (Ω·cm)$^{-1}$ and the materials may be considered as dielectrics. The sample $24\text{Bi}_2\text{O}_3\cdot36\text{TiO}_2\cdot40\text{SiO}_2$ with the largest amount of $\text{SiO}_2$ has highest conductivity, whereas the samples $50\text{Bi}_2\text{O}_3\cdot30\text{TiO}_2\cdot20\text{Nd}_2\text{O}_3$ with the largest amount of $\text{Bi}_2\text{O}_3$ have lowest conductivity. It also can be seen that the slow cooling and addition of $\text{Nd}_2\text{O}_3$ promote crystallisation, but decrease conductivity.
The dependency $Z = f(Z')$ (Fig. 5) shows one not well distinguished semicircle. The semicircular in the complex plane yield to an arc, whose centre is displaced below the real axis, due to the presence of distributed elements and a relaxation process resulting from the trapped states. The semicircle is ascribed to originate from the grain boundary and nonzero intercept corresponding to the resistance of the grain, with no semicircle corresponding to electrode-sample interface [21]. More detail analysis of the electrical data will be the subject in a new investigation.

IV. Conclusions

The investigation carried out shows that depending on the conditions of the melting and additional heat treatment of the super cooled samples, different polyphase glass-ceramics materials with various microstructures could be obtained in the systems Bi$_2$O$_3$-TiO$_2$-SiO$_2$ and Bi$_2$O$_3$-TiO$_2$-Nd$_2$O$_5$. The presence of several phases is established, mainly Bi$_4$Ti$_3$O$_12$ and Bi$_2$Ti$_2$O$_7$. All investigated samples are dielectrics with conductivity in the range $10^{-6}$–$10^{-9}$ (Ω·cm)$^{-1}$. These results are promising basis for control and modification of the electrical properties of the bismuth titanate glass-ceramics doped with SiO$_2$ and Nd$_2$O$_5$.

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References
