Dielectric properties of bismuth titanate ceramics containing SiO₂ and Nd₂O₃ as additives

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Received 27 December 2011; received in revised form 19 June 2012; accepted 4 July 2012

Abstract
Bismuth-titanate ceramics containing SiO₂ and Nd₂O₃ as additives are synthesized by melt quenching method in the system Bi₂O₃-TiO₂-Nd₂O₃-SiO₂ in the temperature range of 1250–1500 °C. The phase composition of the obtained materials is determined by X-ray diffraction analysis and energy dispersive spectroscopy. Using scanning electron microscopy different microstructures are observed in the samples depending on the composition. Different values of conductivity, dielectric losses and relative permittivity are obtained depending on the composition. It is established that all investigated samples are dielectric materials with conductivity between 10⁻⁹ and 10⁻¹³ (Ω·cm)⁻¹ at room temperature, dielectric permittivity from 1000 to 3000 and dielectric losses tanδ between 0.0002 and 0.1.

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

I. Introduction
Aurivillius family oxides including Bi₄Ti₃O₁₂ are of great interest in the last years due to their potential for electronic applications as transducers, capacitors, and acoustic piezo-sensors with high temperature piezoelectric properties (because of its high Curie temperature) [1,2]. Many techniques have been employed for preparing a layered structure of bismuth titanate phases including powders and bulk ceramics: molten salt synthesis, co-precipitation, reactive calcinations, sol-gel synthesis, mecanochemochemical method and others. Between them the crystallisation from melts or glasses [3–6] gives the possibility for easy control of the particle size distribution, morphology and crystallographic orientation. It is well known, that the phase formation and

the properties of Bi₄Ti₃O₁₂ ceramics are strongly influenced not only by the method of preparation, but also by the type and portion of additives. The introduction of Nd₂O₃ as an additive allows the synthesis of materials with improved dielectric and ferroelectric properties, such as high dielectric constant, low dielectric losses, high remnant polarisation and high resistance to fatigue [7–18]. The other advantage of Nd₂O₃ addition is the existence of solid solutions in the system Bi₂O₃-TiO₂-Nd₂O₃. Thus, Kunej et al. [19] described the solubility limits of three solid-solutions: Bi₂(1-x)NdₓTi₂O₇ (0.25 < x < 0.96), NdxBi₂Ti₂O₇ (0 < x < 0.35), and Bi₄Nd₂Ti₃O₁₂ (0 < x < 2.6).

In the previous works [20,21] it has been shown that the introduction of 20–40 mol% SiO₂ simulates the partial amorphisation of the samples. The main established phases in the super cooled melt are either Bi₂TiO₅, or Bi₄Ti₃O₁₂, or only Bi₂TiO₅ depending on the cooling rate and composition. The other important result was that the simultaneous introduction of SiO₂ and Nd₂O₃ as
additives [21] in the bismuth-titanate ceramics changes the glass-formation ability and electrical properties. These results motivated us to continue our experiments in this field. The purposes of the present work are to prepare polycrystalline or glass-ceramic materials in the system Bi₂O₃-TiO₂-SiO₂-Nd₂O₃ by melt quenching method and to study their electrical properties depending on processing temperature and composition.

II. Experimental

The nominal compositions of the selected samples in the system Bi₂O₃-TiO₂-SiO₂-Nd₂O₃, are given in Table 1 and Fig. 1. The melting is done in alumina crucibles at the temperature between 1250 and 1500 °C for 10–15 min depending on the composition. The samples are synthesized by fast cooling to room temperature, performed by pouring of the melts between two cooper plates (with cooling rate nearly 10⁵ °C/s). The phase formation is studied by X-ray diffraction analysis (XRD - TUR M62, Cu-Kα radiation and Bruker D8 Advanced Diffractometer). Chemical composition is determined by energy dispersive spectroscopy (EDS, EDAX 9900). The microstructure is observed by scanning electron microscopy (SEM-525M, Philips). The electrical conductivity, capacitance and dielectric losses of the selected samples are measured by DC resistible bridge and digital capacity meter E8-4 (1 kHz) using the two-terminal method and a suitable sample holder with graphite electrodes.

III. Results and discussion

3.1 Phase formation

The obtained samples are identified as polycrystalline ceramics (Table 1, samples 1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 4C, 4D, 4E) or partially crystallized materials (glass-ceramics) because they have visually crystalline milk like parts and dark or transparent glass regions (Table 1, samples 4, 4A, 4B). These results are also shown in the investigated sections of the system Bi₂O₃-TiO₂-SiO₂-Nd₂O₃ at 0, 5, 10 and 20 mol% SiO₂. According to the X-ray data (Fig. 2 and Table 1) several phases are identified including Bi₂Ti₂O₇ (JCPDS 32-0118), Bi₄Ti₃O₁₂ (JCPDS 73-2181), Bi₁₂TiO₂₀ (JCPDS 78-1158) and δ-Bi₂O₃ (JCPDS 27-0052).

The increase of the TiO₂ content (above 50 mol%) and the decrease of the Bi₂O₃ content (below 40 mol%) leads to formation of the main phase Bi₄Ti₃O₁₂. At high Bi₂O₃ content (in the range 40–60 mol%) the identified phases are Bi₂Ti₂O₇, Bi₁₂TiO₂₀ and δ-Bi₂O₃. The sample 4 (Fig. 2d) is presented as an example of partially crystalline material as its X-ray diffraction pattern...
Table 1. Starting compositions and identified phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting composition [mol%]</th>
<th>Identified phases by XRD</th>
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<tr>
<td></td>
<td>Bi₂O₃</td>
<td>TiO₂</td>
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<tr>
<td>1</td>
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</tr>
<tr>
<td>4E</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

P: Bi₂Ti₂O₇, Bi₄: Bi₄Ti₃O₁₂, Bi₁₂: Bi₁₂TiO₂₀, δ: δ-Bi₂O₃

Figure 2. XRD patterns of samples with different compositions: a) 40Bi₂O₃·50TiO₂·10Nd₂O₃ melted at 1450 °C and fast cooled, b) 30Bi₂O₃·50TiO₂·20Nd₂O₃ melted at 1500 °C and fast cooled, c) 40Bi₂O₃·50TiO₂·5SiO₂·5Nd₂O₃ melted at 1450 °C and fast cooled, and d) 30Bi₂O₃·50TiO₂·10SiO₂·10Nd₂O₃ melted at 1450 °C and fast cooled
shows the peaks of Bi₄Ti₃O₁₂ phase and an amorphous halo. Additional information about the microstructure was obtained by SEM imaging (Fig. 3). The main observed phase is a solid-solution Bi₄₋ₓNdₓTi₃O₁₂, in which the content of Nd₂O₃ varies between 9–18 mol%. These results are in agreement with the data of Kunej et al. [19]. They determined the upper solubility boundary to be 26 mol% Nd₂O₃ instead of Bi₂O₃ in the structure of Bi₄Ti₃O₁₂. In Fig. 3d it is shown that the amorphous phase contains Bi₂O₃ (around 23–26 mol%), TiO₂ (about 51–52 mol%), SiO₂ (around 12–13 mol%) and Nd₂O₃ (9–12 mol%).

3.2 Electrical characteristics

To compare the electrical properties, we selected four samples from the system Bi₂O₃-TiO₂-SiO₂-Nd₂O₃ with similar content of Bi₂O₃ and TiO₂. The compositions of the first two of them are 30Bi₂O₃·50TiO₂·ₓSiO₂·ₚNd₂O₃, (ₓ=10, 0; ₚ=10, 20) and the second two are formulated as: 40Bi₂O₃·50TiO₂·ₓSiO₂·ₚNd₂O₃, (ₓ=5, 0; ₚ=5, 10). Additionally we measured the electrical properties of two samples synthesized in our previous studies: 30Bi₂O₃·50TiO₂·20SiO₂, and 40Bi₂O₃·50TiO₂·10SiO₂ [21,22]. Arrhenius plots showing the temperature dependence of the conductivity are presented in Fig. 4. It is shown that the glass-crystalline sample containing 20 mol% SiO₂ possesses the highest value of the conductivity.

The increase of the Nd₂O₃ content up to 10 mol% increases the activation energy and the increase of the SiO₂ content up to 10 mol% decreases the activation energy. Co-addition of SiO₂ and Nd₂O₃ up to 5 mol% leads to the activation energy with value close to 1 eV in the temperature range of 1.2–2×10³ K⁻¹. Further increase of the SiO₂ and Nd₂O₃ content to 10 mol% leads to the activation energy of 1.7 eV in temperature range 1.2–2×10³ K⁻¹.

The sample containing 20 mol% SiO₂ is characterised by higher dielectric constant (Fig. 5). The decrease of the SiO₂ content from 20% to 10% leads to the decrease of the dielectric constant (ε), but the mixed samples containing SiO₂ and Nd₂O₃ have higher dielectric constant at 820 °C.

More experiments need to be done in order to verify dielectric behaviour of these ceramics, which are now in course.
IV. Conclusions

The investigation carried out confirms that depending on the melting conditions of the super-cooled melt different poly-phase glass-ceramic materials with various microstructures could be obtained containing mainly the bismuth titanate phases in the system Bi\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2}-Nd\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}. The addition of Nd\textsubscript{2}O\textsubscript{3} in the samples leads to the increase of the melting temperature and decreases the tendency to form glassy structure. It is established that all investigated samples are dielectric materials with conductivity between 10\textsuperscript{-9} and 10\textsuperscript{-13} (Ω·cm\textsuperscript{-1}) at room temperature, dielectric permittivity in the range of 1000 to 3000 and dielectric losses tanδ between 0.0002 and 0.1. Addition of SiO\textsubscript{2} and Nd\textsubscript{2}O\textsubscript{3} in the samples leads to essential changes of dielectric losses and conductivity.

Acknowledgements: The study was performed with financial support of UCTM, Sofia under Grant № 10979/2012.

References
5. K. Gerth, Ch. Russel, “Crystallization of Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} from glasses in the system Bi\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}/B\textsubscript{2}O\textsubscript{3}

![Figure 4. Arrhenius plots showing the temperature dependence of the conductivity for samples with different compositions: a) 30Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·20SiO\textsubscript{2} (sample A), 30Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·10SiO\textsubscript{2}·10Nd\textsubscript{2}O\textsubscript{3} (sample 4) and 30Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·20Nd\textsubscript{2}O\textsubscript{3} (sample 5) and b) 40Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·10SiO\textsubscript{2} (sample B), 40Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·5SiO\textsubscript{2}·5Nd\textsubscript{2}O\textsubscript{3} (sample 4E) and 40Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·10Nd\textsubscript{2}O\textsubscript{3} (sample 1).](image)

![Figure 5. Plot of the relative permittivity and dielectric losses in dependence on the temperature for samples with different compositions: a) 30Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·20SiO\textsubscript{2} (sample A), 30Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·10SiO\textsubscript{2}·10Nd\textsubscript{2}O\textsubscript{3} (sample 4) and 30Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·20Nd\textsubscript{2}O\textsubscript{3} (sample 5) and b) 40Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·10SiO\textsubscript{2} (sample B), 40Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·5SiO\textsubscript{2}·5Nd\textsubscript{2}O\textsubscript{3} (sample 4E) and 40Bi\textsubscript{2}O\textsubscript{3}·50TiO\textsubscript{2}·10Nd\textsubscript{2}O\textsubscript{3} (sample 1).](image)


