Dielectric properties of bismuth titanate ceramics containing SiO_2 and Nd_2O_3 as additives[#]

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Abstract

Bismuth-titanate ceramics containing SiO_2 and Nd_2O_3 as additives are synthesized by melt quenching method in the system Bi_2O_3-TiO_2-Nd_2O_3-SiO_2 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} $(\Omega \cdot cm)^{-1}$ at room temperature, dielectric permittivity from 1000 to 3000 and dielectric losses tgδ between 0.0002 and 0.1.

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

I. Introduction

Aurivillius family oxides including $Bi_4Ti_3O_{12}$ 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, mechanochemical 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 $Bi_4Ti_3O_{12}$ ceramics are strongly influenced not only by the method of preparation, but also by the type and portion of additives. The introduction of Nd_2O_3 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 Nd_2O_3 addition is the existence of solid solutions in the system Bi_2O_3-TiO_2-Nd_2O_3. Thus, Kunej *et al*. [19] described the solubility limits of three solid-solutions: $Bi_{(1.6-1.08x)}Nd_xTi_2O_{(6.4+0.3x)}$, $(0.25 < x < 0.96)$, $Nd_{2-x}Bi_xTi_2O_7$, $(0 < x < 0.35)$, and $Bi_{4-x}Nd_xTi_3O_{12}$, $(0 < x < 2.6)$.

In the previous works [20,21] it has been shown that the introduction of 20–40 mol% SiO_2 simulates the partial amorphisation of the samples. The main established phases in the super cooled melt are either $Bi_2Ti_2O_7$ and $Bi_4Ti_3O_{12}$ or only $Bi_4Ti_3O_{12}$, depending on the cooling rate and composition. The other important result was that the simultaneous introduction of SiO_2 and Nd_2O_3 as

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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 Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 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 Bi_2O_3-TiO_2-SiO_2-Nd_2O_3, 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 10^2 °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 Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 at 0, 5, 10 and 20 mol% SiO_2. According to the X-ray data (Fig. 2 and Table 1) several phases are identified including $Bi_2Ti_2O_7$ (JCPDS 32-0118), $Bi_4Ti_3O_{12}$ (JCPDS 73-2181), $Bi_{12}TiO_{20}$, (JCPDS 78-1158) and δ-Bi_2O_3 (JCPDS 27-0052).

The increase of the TiO_2 content (above 50 mol%) and the decrease of the Bi_2O_3 content (below 40 mol%) leads to formation of the main phase $Bi_4Ti_3O_{12}$. At high Bi_2O_3 content (in the range 40–60 mol%) the identified phases are $Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$ and δ-Bi_2O_3. The sample 4 (Fig. 2d) is presented as an example of partially crystalline material as its X-ray diffraction pattern

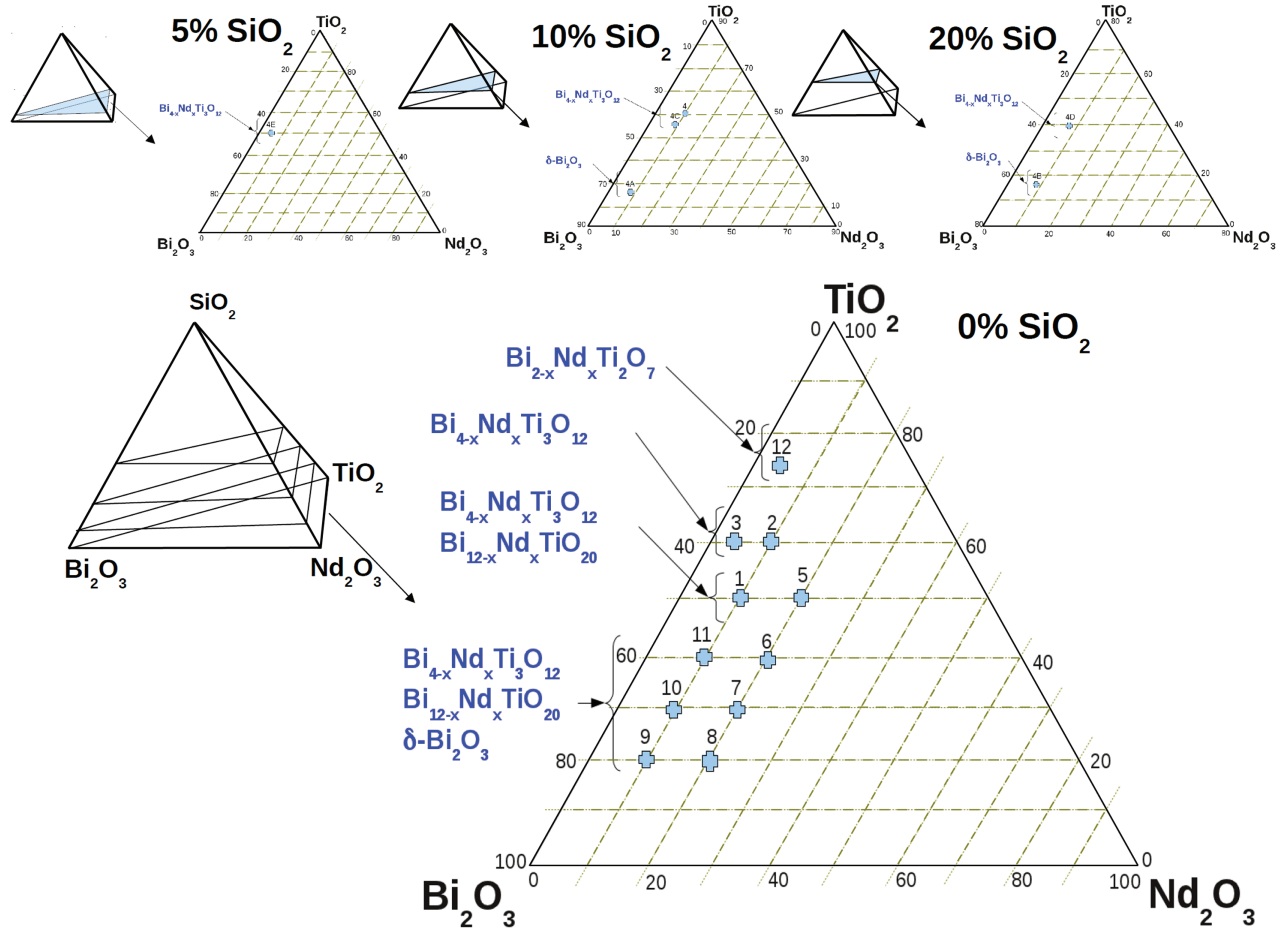


Figure 1. Investigated compositions in the system Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 at selected sections contains 0, 5, 10 and 20 mol% SiO_2

Table 1. Starting compositions and identified phases

Sample	Starting composition [mol%]				Identified phases by XRD
	Bi_2O_3	TiO_2	Nd_2O_3	SiO_2	
1	40	50	10	--	Bi4, Bi12
2	25	65	10	--	Bi4
3	35	60	5	--	Bi4
4	30	50	10	10	Glass + Bi4
5	30	50	20	--	Bi4, Bi12
6	40	40	20	--	Bi4, Bi12, δ
7	50	30	20	--	Bi4, Bi12, δ
8	60	20	20	--	Bi4, Bi12, δ
9	70	20	10	--	Bi4, Bi12, δ
10	60	30	10	--	Bi4, Bi12, δ
11	50	40	10	--	Bi4, Bi12, δ
12	21	72	7	--	P
4A	63	18	10	9	Glass + δ
4B	56	16	20	8	Glass + δ
4C	36	45	10	9	Bi4
4D	32	40	20	8	Bi4
4E	40	50	5	5	Bi4

P: $Bi_2Ti_2O_7$, Bi4: $Bi_4Ti_3O_{12}$, Bi12: $Bi_{12}TiO_{20}$, δ: δ-Bi_2O_3

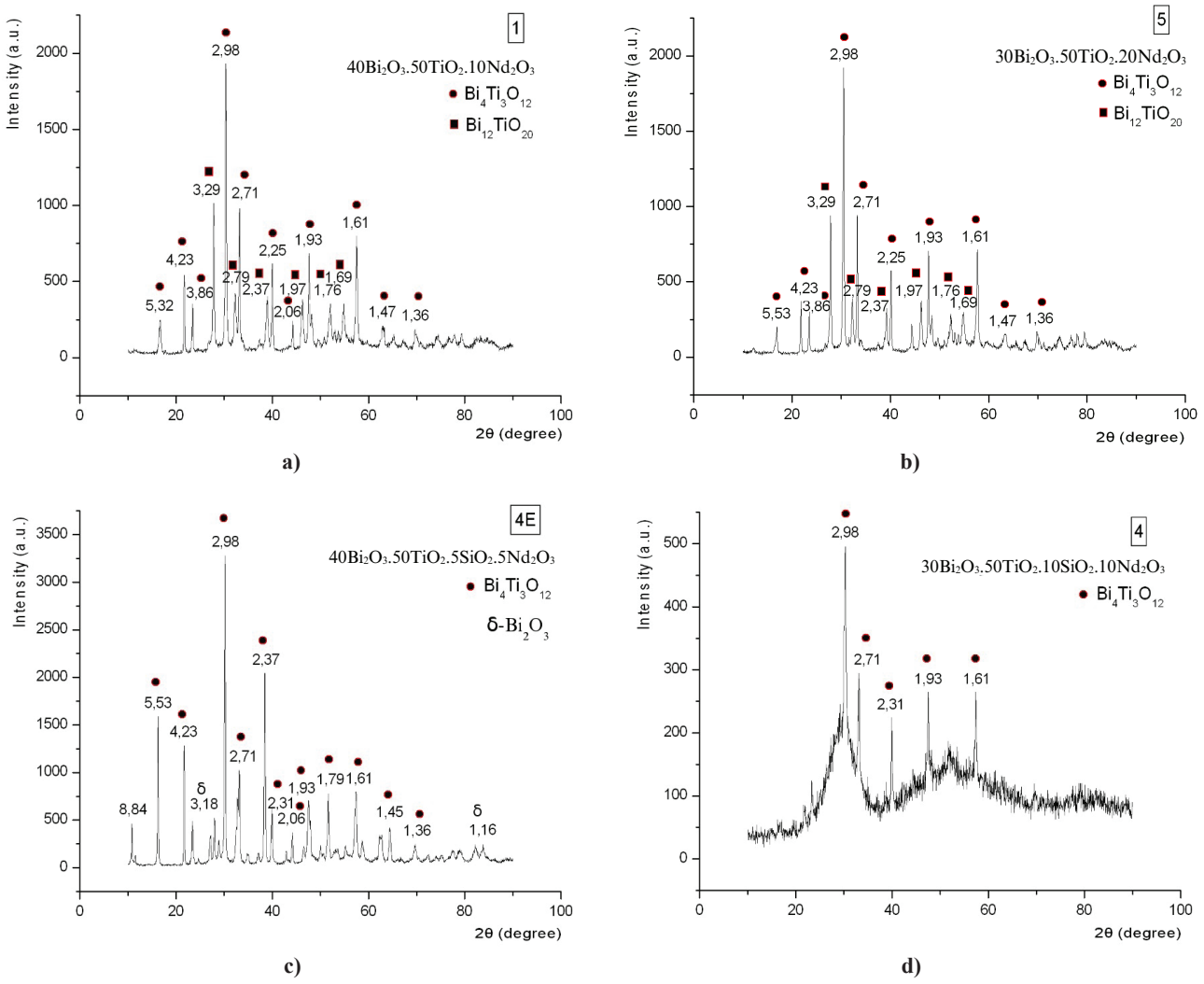


Figure 2. XRD patterns of samples with different compositions: a) $40Bi_2O_3 \cdot 50TiO_2 \cdot 10Nd_2O_3$ melted at 1450 °C and fast cooled, b) $30Bi_2O_3 \cdot 50TiO_2 \cdot 20Nd_2O_3$ melted at 1500 °C and fast cooled, c) $40Bi_2O_3 \cdot 50TiO_2 \cdot 5SiO_2 \cdot 5Nd_2O_3$ melted at 1450 °C and fast cooled, and d) $30Bi_2O_3 \cdot 50TiO_2 \cdot 10SiO_2 \cdot 10Nd_2O_3$ melted at 1450 °C and fast cooled

shows the peaks of $Bi_4Ti_3O_{12}$ phase and an amorphous hallo. Additional information about the microstructure was obtained by SEM imaging (Fig. 3). The main observed phase is a solid-solution $Bi_{4-x}Nd_xTi_3O_{12}$, in which the content of Nd_2O_3 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% Nd_2O_3 instead of Bi_2O_3 in the structure of $Bi_4Ti_3O_{12}$. In Fig. 3d it is shown that the amorphous phase contains Bi_2O_3 (around 23–26 mol%), TiO_2 (about 51–52 mol%), SiO_2 (around 12–13 mol%) and Nd_2O_3 (9–12 mol%).

3.2 Electrical characteristics

To compare the electrical properties, we selected four samples from the system Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 with similar content of Bi_2O_3 and TiO_2. The compositions of the first two of them are $30Bi_2O_3{\cdot}50TiO_2{\cdot}xSiO_2{\cdot}yNd_2O_3$, ($x$=10, 0; y=10, 20) and the second two are formulated as: $40Bi_2O_3{\cdot}50TiO_2{\cdot}xSiO_2{\cdot}yNd_2O_3$, ($x$=5, 0; y=5, 10). Additionally we measured the electrical properties of two samples synthesized in our previous studies: $30Bi_2O_3{\cdot}50TiO_2{\cdot}20SiO_2$, and $40Bi_2O_3{\cdot}50TiO_2{\cdot}10SiO_2$ [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% SiO_2 possesses the highest value of the conductivity.

The increase of the Nd_2O_3 content up to 10 mol% increases the activation energy and the increase of the SiO_2 content up to 10 mol% decreases the activation energy. Co-addition of SiO_2 and Nd_2O_3 up to 5 mol% leads to the activation energy with value close to 1 eV in the temperature range of $1.2–2\times10^3$ K^{-1}. Further increase of the SiO_2 and Nd_2O_3 content to 10 mol% leads to the activation energy of 1.7 eV in temperature range $1.2–2\times10^3$ K^{-1}.

The sample containing 20 mol% SiO_2 is characterised by higher dielectric constant (Fig. 5). The decrease of the SiO_2 content from 20% to 10% leads to the decrease of the dielectric constant (ε_r), but the mixed samples containing SiO_2 and Nd_2O_3 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.

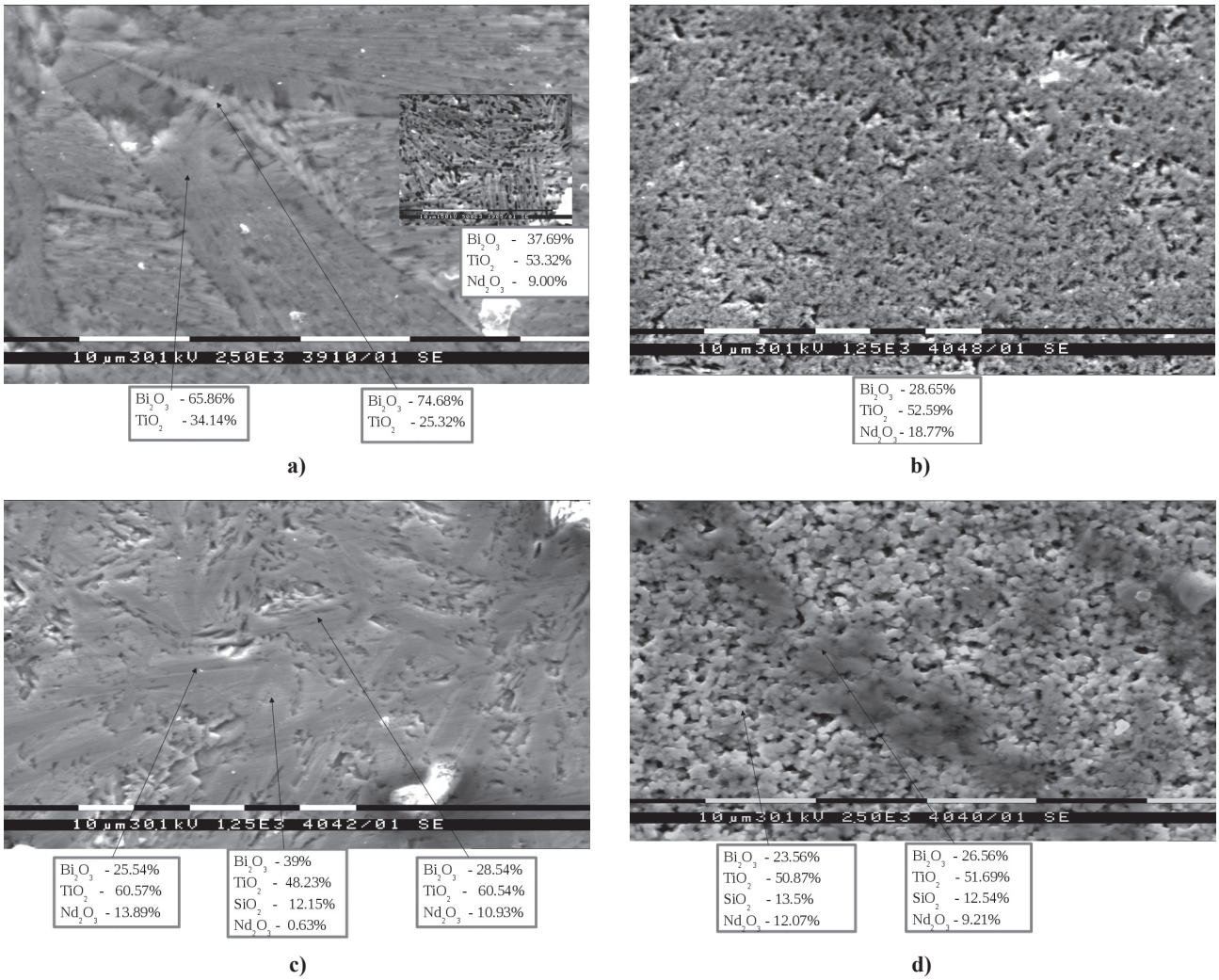
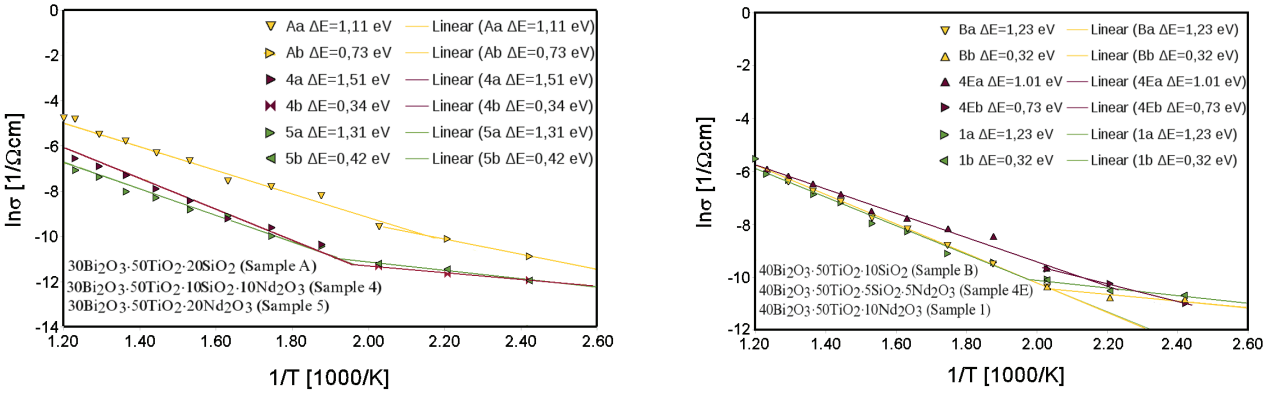
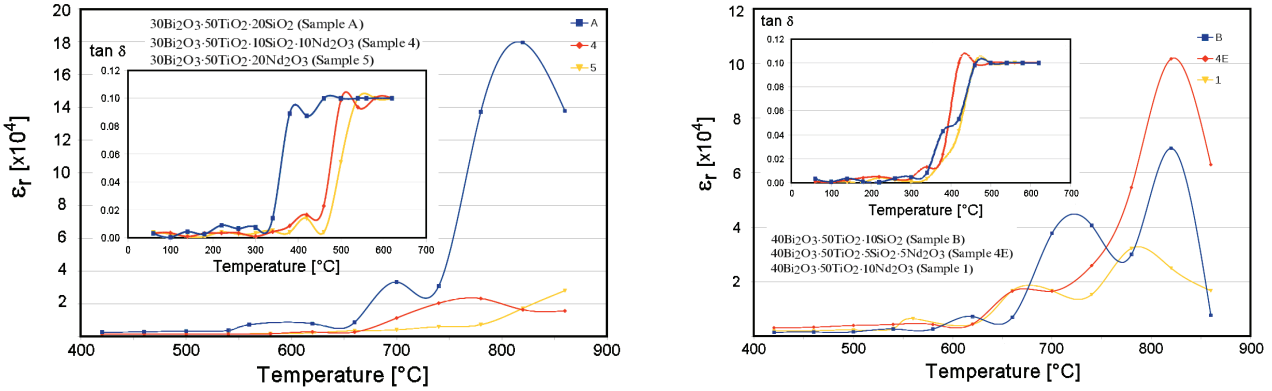


Figure 3. SEM micrograph and EDS data of samples with different compositions: a) $40Bi_2O_3{\cdot}50TiO_2{\cdot}10Nd_2O_3$ melted at 1450 °C and fast cooled, b) $30Bi_2O_3{\cdot}50TiO_2{\cdot}20Nd_2O_3$ melted at 1500 °C and fast cooled, c) $40Bi_2O_3{\cdot}50TiO_2{\cdot}5SiO_2{\cdot}5Nd_2O_3$ melted at 1450 °C and fast cooled and d) $30Bi_2O_3{\cdot}50TiO_2{\cdot}10SiO_2{\cdot}10Nd_2O_3$ melted at 1450 °C and fast cooling



a) b)

Figure 4. Arrhenius plots showing the temperature dependence of the conductivity for samples with different compositions: a) $30Bi_2O_3 \cdot 50TiO_2 \cdot 20SiO_2$ (sample A), $30Bi_2O_3 \cdot 50TiO_2 \cdot 10SiO_2 \cdot 10Nd_2O_3$ (sample 4) and $30Bi_2O_3 \cdot 50TiO_2 \cdot 20Nd_2O_3$ (sample 5) and b) $40Bi_2O_3 \cdot 50TiO_2 \cdot 10SiO_2$ (sample B), $40Bi_2O_3 \cdot 50TiO_2 \cdot 5SiO_2 \cdot 5Nd_2O_3$ (sample 4E) and $40Bi_2O_3 \cdot 50TiO_2 \cdot 10Nd_2O_3$ (sample 1)



a) b)

Figure 5. Plot of the relative permittivity and dielectric losses in dependence on the temperature for samples with different compositions: a) $30Bi_2O_3 \cdot 50TiO_2 \cdot 20SiO_2$ (sample A), $30Bi_2O_3 \cdot 50TiO_2 \cdot 10SiO_2 .10Nd_2O_3$ (sample 4) and $30Bi_2O_3 \cdot 50TiO_2$ $20Nd_2O_3$ (sample 5) and b) $40Bi_2O_3 \cdot 50TiO_2 \cdot 10SiO_2$ (sample B), $40Bi_2O_3 \cdot 50TiO_2 \cdot 5SiO_2 \cdot 5Nd_2O_3$ (sample 4E) and $40Bi_2O_3 \cdot 50TiO_2 \cdot 10Nd_2O_3$ (sample 1)

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_2O_3-TiO_2-Nd_2O_3-SiO_2. The addition of Nd_2O_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^{-9} and 10^{-13} $(\Omega \cdot cm)^{-1}$ at room temperature, dielectric permittivity in the range of 1000 to 3000 and dielectric losses tgδ between 0.0002 and 0.1. Addition of SiO_2 and Nd_2O_3 in the samples leads to essential changes of dielectric losses and conductivity.

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