



Electrical characteristics of bismuth titanate glass-ceramics containing SiO_2 and Nd_2O_3

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Abstract

Bismuth-titanate ceramics containing SiO_2 and Nd_2O_3 as additives are synthesized at two different ways of cooling of the melts. The introduction of SiO_2 and Nd_2O_3 leads to more complex crystallization with participation of several phases including $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. 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_2O_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} ($\Omega\cdot\text{cm}$)⁻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_2O_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_2O_3 is also performed. The SiO_2 is introduced to change the melting conditions, while the reason for Nd_2O_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 now, there are no reports for the preparation of glass-ceramics containing the phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by melt quenching with participation of SiO_2 and Nd_2O_3 .

II. Experimental

Bismuth-titanate ceramics containing SiO_2 and Nd_2O_3 as additives were synthesized by quenching from melt. The melting was made from the following pre-

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cursors: TiO_2 , Bi_2O_3 , SiO_2 and Nd_2O_3 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% Al_2O_3 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: $24\text{Bi}_2\text{O}_3\cdot 36\text{TiO}_2\cdot 40\text{SiO}_2$, $30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{SiO}_2$, $50\text{Bi}_2\text{O}_3\cdot 30\text{TiO}_2\cdot 20\text{SiO}_2$ and $30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{Nd}_2\text{O}_3$ (Table 1).

The phase formation was studied by X-ray diffraction analysis (XRD - TUR M62, Cu-K α radiation and Bruker D8 Advanced Diffractometer, Cu-K α 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% SiO_2 (Fig. 1) shows that the introduction of SiO_2 leads to more complex crystallization with participation of several phases, including dominant $\text{Bi}_2\text{Ti}_2\text{O}_7$ ($\text{Bi}_2\text{Ti}_2\text{O}_7$ – JCPDS 32-0118) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$ – JCPDS 73-2181). It

can be seen (Fig. 1) that the fast cooling even favors formation of the pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$ phase and stimulates the partial amorphization of the prepared samples. However, in our previous paper [20] it was confirmed that for samples containing $\geq 40\%$ SiO_2 XRD patterns were close but do not completely coincide with these ones of the phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. That can result from the forma-

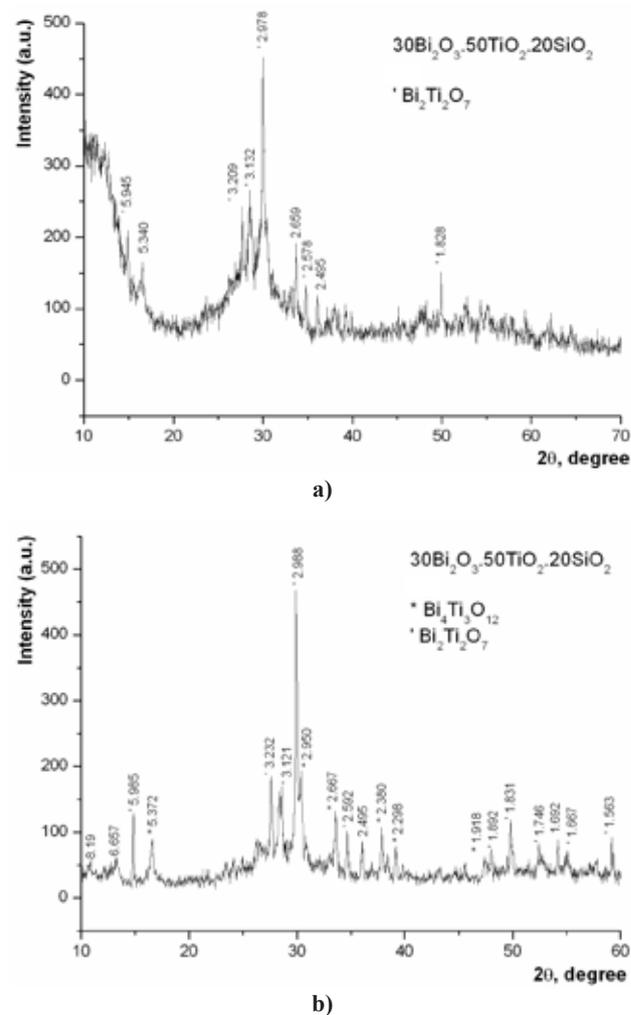


Figure 1. XRD patterns of sample with composition $30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{SiO}_2$ melted at 1300°C: a) fast cooling of the melts (A); b) slow cooling of the melts (B)

Table 1. Conductivity of the samples depending on the composition and method of the measurement

Sample	Method of cooling and view of the sample	σ , ($\Omega\cdot\text{cm}$) ⁻¹	Method of measurement
1	$24\text{Bi}_2\text{O}_3\cdot 36\text{TiO}_2\cdot 40\text{SiO}_2$ heat treated, glass ceramic	$1.77\cdot 10^{-6}$	AC impedance
2a	$30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{SiO}_2$ heat treated, glass ceramic	$3.54\cdot 10^{-7}$	AC impedance
2b	$30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{SiO}_2$ fast cooling, partially crystallized	$8.32\cdot 10^{-6}$	DC method
2c	$30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{SiO}_2$ slow cooling, glass ceramics	$2.20\cdot 10^{-9}$	DC method
3a	$50\text{Bi}_2\text{O}_3\cdot 30\text{TiO}_2\cdot 20\text{SiO}_2$ fast cooling, partially crystallized	$2.77\cdot 10^{-9}$	DC method
3b	$50\text{Bi}_2\text{O}_3\cdot 30\text{TiO}_2\cdot 20\text{SiO}_2$ slow cooling, glass ceramics	$2.54\cdot 10^{-9}$	DC method
4	$40\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 10\text{Nd}_2\text{O}_3$ fast cooling, glass ceramics	$2.75\cdot 10^{-9}$	DC method
5	$30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{Nd}_2\text{O}_3$ fast cooling, glass ceramics	$1.15\cdot 10^{-7}$	DC method

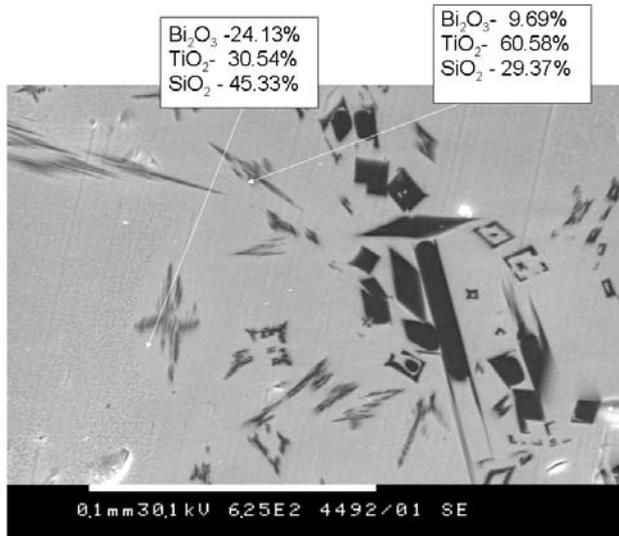
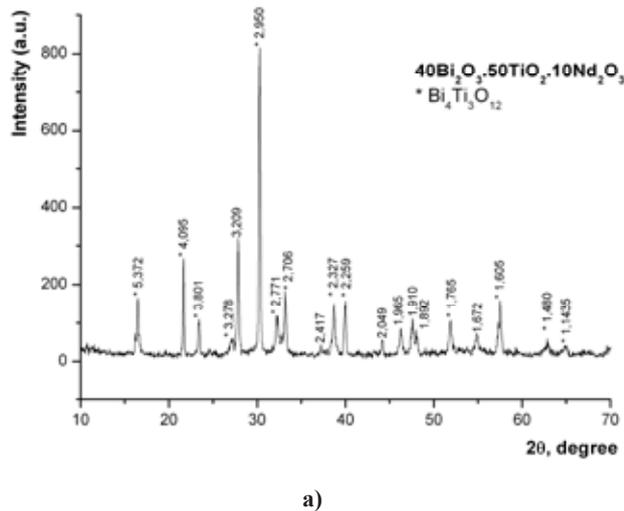
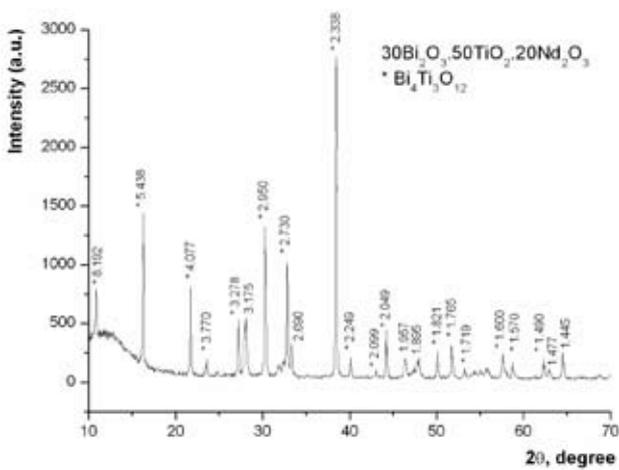


Figure 2. SEM micrographs and EDS data of melt quenched sample with composition $24\text{Bi}_2\text{O}_3\cdot 36\text{TiO}_2\cdot 40\text{SiO}_2$ heat treated at 700°C



a)



b)

Figure 3. XRD patterns of samples melted at 1450°C and fast cooled with composition: a) $40\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 10\text{Nd}_2\text{O}_3$ and b) $30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{Nd}_2\text{O}_3$

tion of solid solution with the bismuth-titanate phase or from the appearance of a new phase. Crystallization behaviour of the sample $24\text{Bi}_2\text{O}_3\cdot 36\text{TiO}_2\cdot 40\text{SiO}_2$ 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 Bi_2O_3 -content and increased TiO_2 -content in comparison with the nominal batch composition, as it was established also in our previous studies [20].

The addition of Nd_2O_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% SiO_2 . In the sample containing 20 mol% Nd_2O_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 Bi_2O_3 partially replaced by Nd_2O_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 range 10^{-6} – 10^{-9} ($\Omega\cdot\text{cm}$)⁻¹ and the materials may be considered as dielectrics. The sample $24\text{Bi}_2\text{O}_3\cdot 36\text{TiO}_2\cdot 40\text{SiO}_2$ with the largest amount of SiO_2 has highest conductivity, whereas the samples $50\text{Bi}_2\text{O}_3\cdot 30\text{TiO}_2\cdot 20\text{SiO}_2$ with the largest amount of Bi_2O_3 have lowest conductivity. It also can be seen that the slow cooling and addition of Nd_2O_3 promote crystallisation, but decrease conductivity.

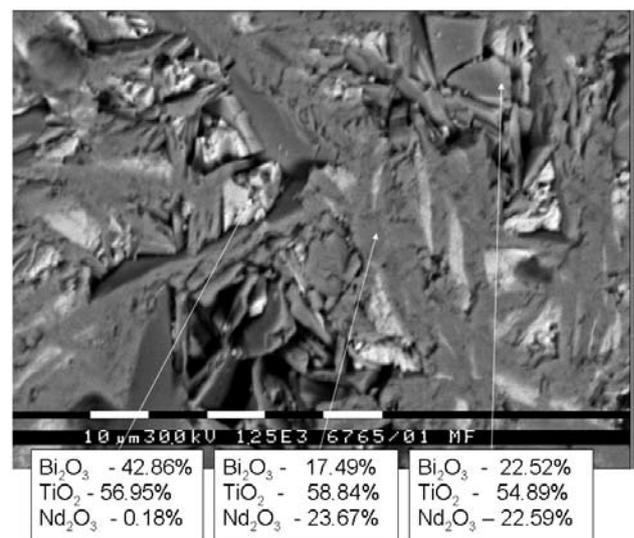


Figure 4. SEM micrographs and EDS data of melt quenched sample with composition $30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{Nd}_2\text{O}_3$ melted at 1450°C

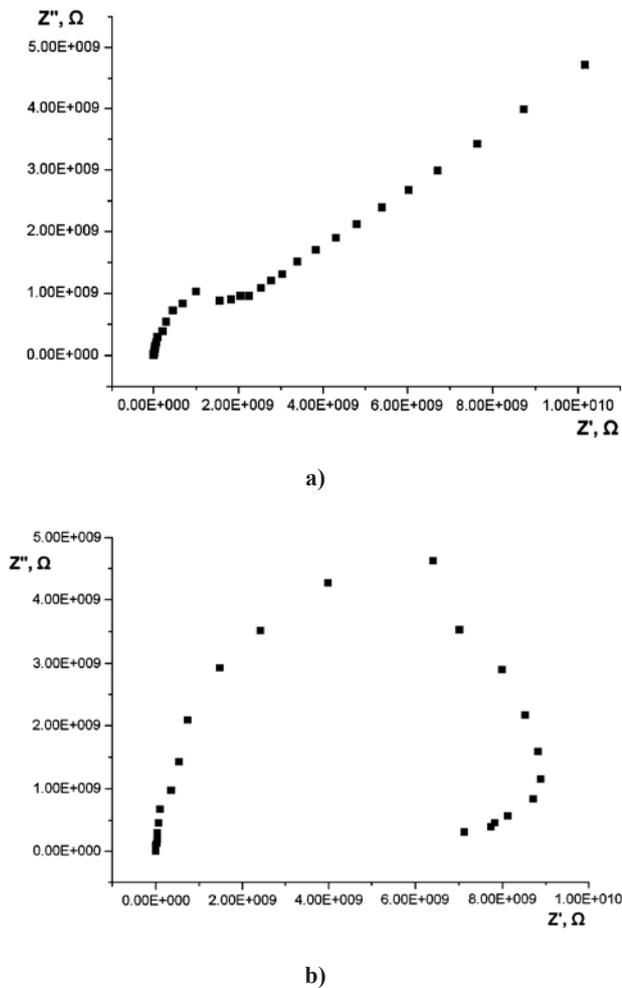


Figure 5. Impedance analysis of the dependency $Z''=f(Z')$ of the samples with compositions: a) $24\text{Bi}_2\text{O}_3\cdot 36\text{TiO}_2\cdot 40\text{SiO}_2$, b) $30\text{Bi}_2\text{O}_3\cdot 50\text{TiO}_2\cdot 20\text{SiO}_2$

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 poly-phase glass-ceramics materials with various microstructures could be obtained in the systems $\text{Bi}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ and $\text{Bi}_2\text{O}_3\text{-TiO}_2\text{-Nd}_2\text{O}_3$. The presence of several phases is established, mainly $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_2\text{Ti}_2\text{O}_7$. All investigated samples are dielectrics with conductivity in the range $10^{-6}\text{-}10^{-9} (\Omega\cdot\text{cm})^{-1}$. These results are promising ba-

sis for control and modification of the electrical properties of the bismuth titanate glass-ceramics doped with SiO_2 and Nd_2O_3 .

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