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SYNTHESIS OF DOPED BISMUTH TITANATE CERAMICS WITH Nd_2O_3 AND SiO_2 AND THEIR ELECTRICAL PROPERTIES

S. Slavov[1], M. Krapchanska[2], E. Kashchieva[1], S. Parvanov[1], Y. Dimitriev[1]

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[1]*University of Chemical Technology and Metallurgy,*
8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria
[2]*Bulgarian Academy of Sciences,*
Institute of Electrochemistry and Energy Systems,
Acad. G. Bonchev Str., Bl. 10,1113 Sofia, Bulgaria
E-mail: stanislavslavov@mail.bg

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 at temperature range 1260 – 1500^oC. 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. The addition of SiO_2 and Nd_2O_3 allows controlling the crystallization, glass formation ability, melting temperature and Curie temperature. Different values of conductivity, dielectric losses and relative permittivity are obtained depending on the composition. Measurements of the electrical conductivity, capacitance and dielectric losses of selected samples are performed by DC resistible bridge and digital capacity meter (with frequency of 1 kHz) using two-terminal method and a suitable sample holder with graphite electrodes. It is established that all investigated samples are dielectric materials with conductivity between 10^{-9} and 10^{-13} $(\Omega\ cm)^{-1}$ at room temperature, dielectric permittivity from 1000 to 3000 and dielectric losses tgδ between 0,0002 and 0,1.

Keywords: *bismuth titanate ceramics, melt quenching, electrical characteristics, microstructure.*

INTRODUCTION

Aurivillius family oxides including $Bi_4Ti_3O_{12}$ are of great interest with their potential use for electronic applications with high temperature piezoelectric properties, and ferroelectrics with high Curie temperature [1]. They are also typical with a large polarization, good fatigue endurance [2, 3] and high losses [4].

Many techniques have been employed for preparing a layered structure of bismuth titanate powders and oriented ceramics. Bismuth-based ferroelectric compounds and phase formation in them are strongly influenced by the method of preparation [5-8].

The main established phases in the system Bi_2O_3-TiO_2 are $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ [9].

S. Kunej et all.was describing the solubility limits in the system Bi_2O_3-TiO_2-Nd_2O_3 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) [10].

In other hands introduction of 20 - 40 mol% SiO_2 simulates the partial amorphization of the samples and the main established phases are either $Bi_2Ti_2O_7$ and $Bi_4Ti_3O_{12}$ or only $Bi_4Ti_3O_{12}$ [11-13].

The introduction of SiO_2 and Nd_2O_3 as additives in bismuth-titanate ceramics and these phases attract attention for obtaining of materials with more effective electrical and dielectric properties [14-20].

These results motivated the purposes of the present work: to prepare by melt quenching method composite materials in the system Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 and the study their electrical properties depending on composition and temperature.

EXPERIMENTAL

The samples are synthesized at fast cooling to room temperature, performed by pouring of the melts between two cooper plates (with temperature gradient of the cooling 10^2 K/s). The melting is made in alumina crucibles at 1260 and 1500°C for 10 – 15 min depending on the composition.

The phase formation is studied by X-ray diffraction analysis (XRD - TUR M62, Cu-Kα radiation and Bruker D8 Advanced Diffractometer, Cu-Kα radiation). 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 performed by DC resistible bridge and digital capacity meter E8-4 (1 kHz) using two-terminal method and a suitable sample holder with graphite electrodes.

RESULTS AND DISCUSSION

The obtained samples may be considered as ceramics and glass-ceramics materials because they have crystalline milk like parts instead of the dark or transparent glass regions (Table 1). According to the X-ray data (Fig. 1) and EDS data (Figs. 2-5) several phases are formed including $Bi_2Ti_2O_7$ ($Bi_2Ti_2O_7$ – JCPDS 32-0118), $Bi_4Ti_3O_{12}$ ($Bi_4Ti_3O_{12}$ – JCPDS 73-2181), $Bi_{12}TiO_{20}$, ($Bi_{12}TiO_{20}$ – JCPDS 78-1158) and δ-Bi_2O_3 (δ-Bi_2O_3 – JCPDS 27-0052).

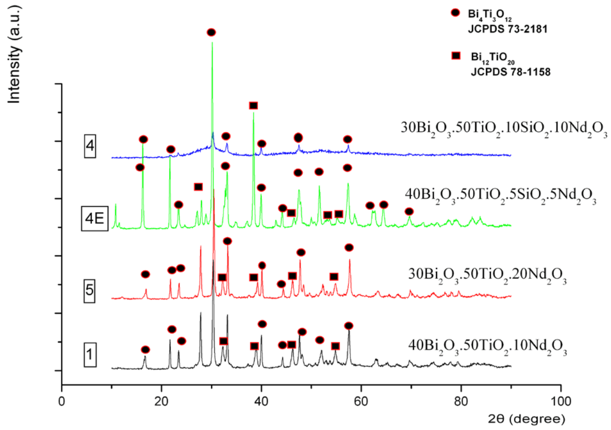

Fig. 1. XRD patterns of sample with composition $40Bi_2O_3.50TiO_2.10Nd_2O_3$, $30Bi_2O_3.50TiO_2.20Nd_2O_3$, $40Bi_2O_3.50TiO_2.5SiO_2.5Nd_2O_3$, $30Bi_2O_3.50TiO_2.10SiO_2.10Nd_2O_3$.

Increasing TiO_2 content (above 50 mol %) and decreasing Bi_2O_3 content (below 40 mol %) lead to formation of adventitious 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 [6 - 8].

Addition of Nd_2O_3 doesn't essentially change the phase formation [10, 13].

Table 1. Starting compositions, visual observations, method of cooling for selected samples.

Sample		Visual observation	Method of cooling
A	$30Bi_2O_3.50TiO_2.20SiO_2$	Black with milky regions	T_m=1400 °C Fast Cooling
4	$30Bi_2O_3.50TiO_2.10SiO_2.10Nd_2O_3$	Dark silver	T_m=1450 °C Fast Cooling
5	$30Bi_2O_3.50TiO_2.20Nd_2O_3$	Milk silver with yelow additives	T_m=1500 °C Fast Cooling
B	$40Bi_2O_3.50TiO_2.10SiO_2$	Black with milky regions	T_m=1260 °C Fast Cooling
4E	$40Bi_2O_3.50TiO_2.5SiO_2.5Nd_2O_3$	Milk silver	T_m=1450 °C Fast Cooling
1	$40Bi_2O_3.50TiO_2.10Nd_2O_3$	Dark yelow with silver additives	T_m=1450 °C Fast Cooling

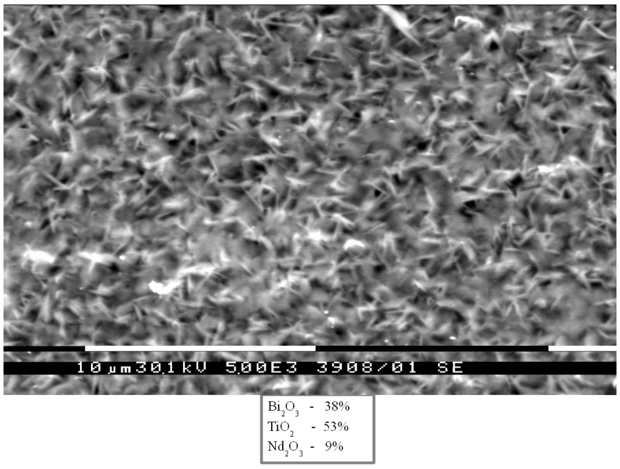

Fig. 2. SEM micrograph and EDS data of sample with composition $40Bi_2O_3.50TiO_2.10Nd_2O_3$ melted at 1450°C and fast cooled.

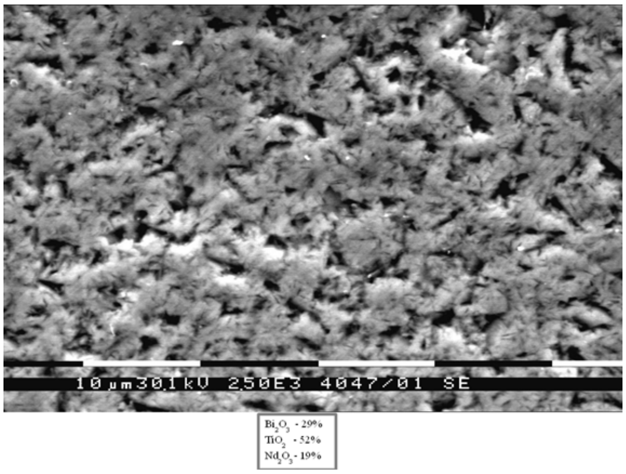

Fig. 3. SEM micrograph and EDS data of sample with composition $30Bi_2O_3.50TiO_2.20Nd_2O_3$ melted at 1500°C and fast cooled.

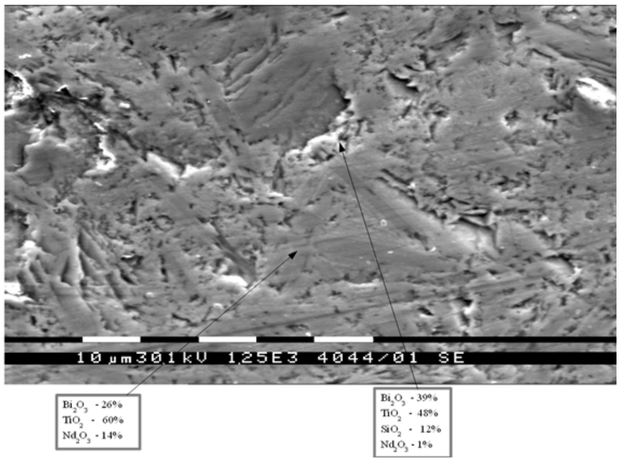

Fig. 4. SEM micrograph and EDS data of sample with composition $40Bi_2O_3.50TiO_2.5SiO_2.5Nd_2O_3$ melted at 1450°C and fast cooled.

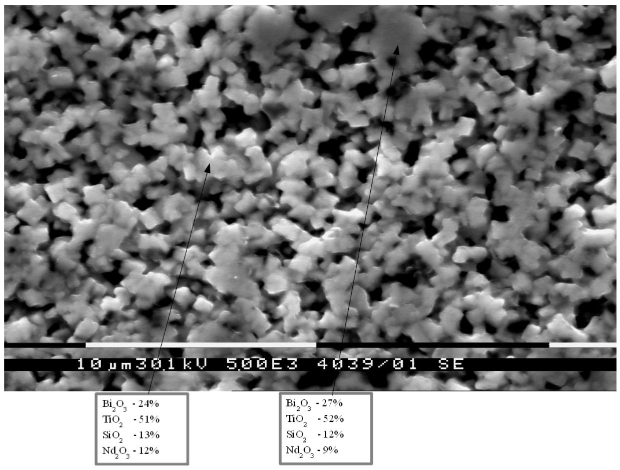

Fig. 5. SEM micrograph and EDS data of sample with composition $30Bi_2O_3.50TiO_2.10SiO_2.10Nd_2O_3$ melted at 1450 °C and fast cooling.

The formation of the phases $Bi_2Ti_2O_7$ and $Bi_4Ti_3O_{12}$ is strongly influenced not only by the composition and melting temperature but also by the cooling rate [13].

To make comparison of the electrical properties we selected four samples of the system Bi_2O_3-TiO_2-SiO_2-Nd_2O_3, with similar content of Bi_2O_3 and TiO_2. The first two of them are in combination $30Bi_2O_3$-$50TiO_2$-$xSiO_2$-yNd_2O_3, (x=10, 0; y=10, 20) and the second two respectively: $40Bi_2O_3$-$50TiO_2$-$xSiO_2$-yNd_2O_3, (x=5, 0; y=5, 10). Additionally we measured the electrical properties of two samples, synthesized in our previous study [13]: $30Bi_2O_3$-$50TiO_2$-$20SiO_2$, and $40Bi_2O_3$-$50TiO_2$-$10SiO_2$.

Arrhenius plot of the conductivity and dielectric losses in dependence on the temperature are presented in Fig. 6.

Increasing of the Nd_2O_3 content up to 10 mol % increases the activation energy and increasing of the SiO_2 content up to 10 mol % decreases the activation energy. Co-addition of SiO_2 and Nd_2O_3 till 5 mol % leads to activation energy with value close to 1 eV in the temperature range 500 – 830°C. The next increasing to 10 mol % of the SiO_2 and Nd_2O_3 content leads to activation energy to 1,7 eV in temperature range 500 - 830°C, that process is typical for decreasing of hole mobility [21, 22].

Doting with Nd_2O_3 decreases the conductivity and increases the melting point and Curie temperature (Fig. 7),

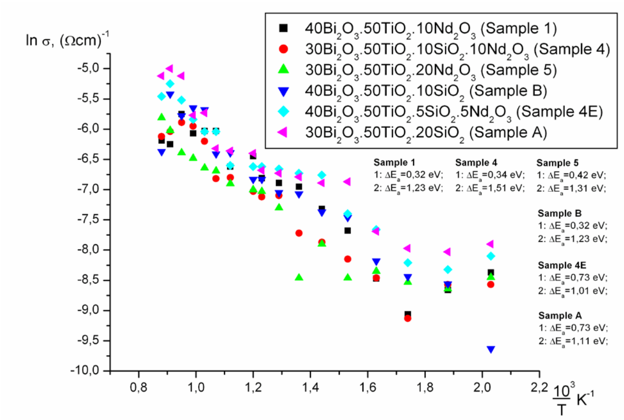

Fig. 6. Arrhenius plot of the conductivity in dependence on the temperature for samples with compositions $30Bi_2O_3.50TiO_2.20SiO_2$, $30Bi_2O_3.50TiO_2.10SiO_2.10Nd_2O_3$, $30Bi_2O_3.50TiO_2.20Nd_2O_3$, $40Bi_2O_3.50TiO_2.10SiO_2$, $40Bi_2O_3.50TiO_2.5SiO_2.5Nd_2O_3$, and $40Bi_2O_3.50TiO_2.\ 10Nd_2O_3$.

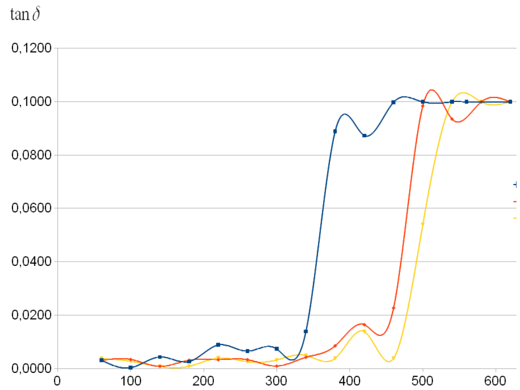

Fig. 8. Plot of the dielectric losses in dependence on the temperature for samples with compositions $30Bi_2O_3.50TiO_2.20SiO_2$, $30Bi_2O_3.50TiO_2.10SiO_2.10Nd_2O_3$ and $30Bi_2O_3.50TiO_2.20Nd_2O_3$.

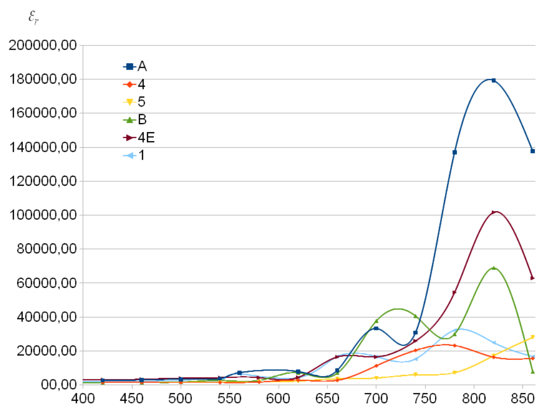

Fig. 7. Plot of the relative permittivity in dependence on the temperature for samples with compositions $30Bi_2O_3.50TiO_2.20SiO_2$, $30Bi_2O_3.50TiO_2.10SiO_2.10Nd_2O_3$, $30Bi_2O_3.50TiO_2.20Nd_2O_3$, $40Bi_2O_3.50TiO_2.10SiO_2$, $40Bi_2O_3.50TiO_2.5SiO_2.5Nd_2O_3$, and $40Bi_2O_3.50TiO_2.10Nd_2O_3$.

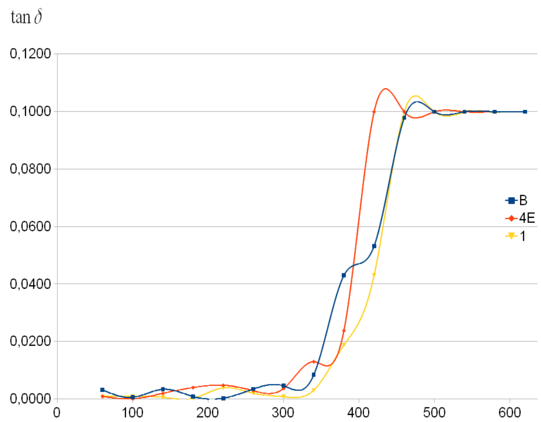

Fig. 9. Plot of the dielectric losses in dependence on the temperature for samples with compositions $40Bi_2O_3.50TiO_2.10SiO_2$, $40Bi_2O_3.50TiO_2.5SiO_2.5Nd_2O_3$, and $40Bi_2O_3.50TiO_2.10Nd_2O_3$.

especially for the sample containing 20 mol % Nd_2O_3.

Apex in the thermal dependence of dielectric losses (Figs. 8 and 9) is may be connected to increasing of ionic mobility.

CONCLUSIONS

This investigation shows that by the applied method of the melting may be produced different poly-phase bismuth titanate glass-ceramic materials in the system Bi_2O_3-TiO_2-Nd_2O_3-SiO_2. Addition of Nd_2O_3 in the samples increase of the melting temperature and decreases of glass-formation tendency. It is established that all investigated samples are dielectric materials with conductivity between 10^{-9} and 10^{-13} $(\Omega\ cm)^{-1}$ at room temperature, dielectric permittivity from near 1.10^3 to 3.10^3 and dielectric losses tgδ between 0,0002 and 0,1. Co-addition of SiO_2 and Nd_2O_3 in the samples leads to generally changes of dielectric losses and conductivity.

Acknowledgements

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