Effect of synthesis route on the microstructure of SiO_2 doped bismuth titanate ceramics#

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Received 16 April 2009; received in revised form 23 October 2009; accepted 27 November 2009

Abstract

Synthesis and characterization of SiO_2 doped bismuth titanate ceramics were investigated. Four investigated compositions belonging to the system Bi_2O_3-TiO_2-SiO_2 are located in the section $Bi_4Ti_3O_{12}$-SiO_2, near by it and in the binary Bi_2O_3-TiO_2 system. Melt quenching was applied for synthesis of SiO_2 doped bismuth titanate ceramics and for the sample $40Bi_2O_3 \cdot 60TiO_2$. The binary sample $70Bi_2O_3 \cdot 30TiO_2$ is prepared by gradient heating of bulk materials near the liquidus temperature (modified solid state reaction). The influence of the thermal treatment on the phase formation and microstructure was evaluated using XRD, EDS and SEM. The binary samples prepared by solid state reaction at low temperature (1000°C) possess poly-phased dense microstructure, while secondary crystallization combined with porosity formation is typical for the sample obtained at high temperature (1150°C). The ternary Bi_2O_3-TiO_2-SiO_2 samples, obtained by supercooling of the melts down to room temperature, are thermally treated at 700, 800°C. They consist of elongated crystals in amorphous matrix. The crystals have lower Bi_2O_3-content and higher TiO_2-content than the nominal batch composition. The XRD data show that the main crystalline phases in the ceramics produced by melt quenching method and solid state reaction are β-Bi_2O_3, $Bi_4Ti_3O_{12}$ and one unknown new phase. It is proved that the applied methods of synthesis are suitable for generation of different microstructures in the bulk SiO_2 doped bismuth titanate ceramics, which is promising basis for modification of their electrical properties.

Keywords*: bismuth titanate, melt quenching, heat treatment, microstructure*

I. Introduction

The application of Aurivillius family of bismuth-based ferroelectric compounds with a layered structure [1] in capacitors, sensors, piezoelectric and electrooptic devices [2–4] is strongly influenced by the method of preparation. Doping with different cations is used to control the point defects. Various low- and high-temperature routes of synthesis are used: sol-gel method [5–7], hydrothermal crystallization [8], metal-organic decomposition [9] and others. Recently crystallization from melts and glasses is also applied [10–14]. This method gives possibility 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 [15]. It is established that the introduction of 20–40 mol% SiO_2 stimulates the partial amorphization of the samples. It is known, that the properties of some ferroelectric ceramics can be enhanced by texturing of their structure as in the case of partial grain orientation in polycrystalline $Bi_4Ti_3O_{12}$ ceramics obtained by sol-gel, magnetic alignment and other methods [16–19]. All these facts motivate our further investigations.

The purpose of the present study is to elucidate the influence of the heat treatment on the phase formation and microstructure of SiO_2 doped bismuth titanate ceramics obtained by melting.

#Paper presented at *6th COST 539 Workshop, Advance Functional Characterization of Nanostructured Materials,* February 23-25, 2009, ICMM-CSIC, Madrid, Spain

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II. Experimental

The selection of compositions with high melting temperatures was made according to the data for the liquidus temperature in the system Bi_2O_3-TiO_2 [13,20, 21] as well as to the glass formation in the system Bi_2O_3-SiO_2 [22,23]. Four compositions (in mol%) were selected: one in the section $Bi_4Ti_3O_{12}$-SiO_2 ($24Bi_2O_3{\cdot}36TiO_2{\cdot}40SiO_2$), the second near by this area

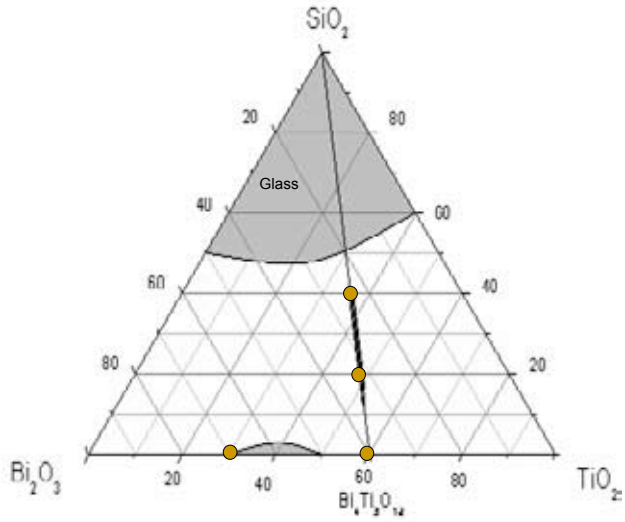

Figure 1. Gibbs triangle of the system Bi_2O_3-TiO_2-SiO_2 with the selected compositions: 1) $24Bi_2O_3{\cdot}36TiO_2{\cdot}40SiO_2$; 2) $33Bi_2O_3{\cdot}47TiO_2{\cdot}20SiO_2$ and 3) $70Bi_2O_3{\cdot}30TiO_2$, 4) $40Bi_2O_3{\cdot}60TiO_2$

($33Bi_2O_3{\cdot}47TiO_2{\cdot}20SiO_2$), and other two in the system Bi_2O_3-TiO_2 ($70Bi_2O_3{\cdot}30TiO_2$ and $40Bi_2O_3{\cdot}60TiO_2$) (Fig. 1). The sample having a model binary composition $70Bi_2O_3{\cdot}30TiO_2$ was prepared with gradient heating of bulk materials near the liquidus temperature (modified solid state reaction) in the temperature range 1000–1150°C for 1 hour. The sample with the composition $40Bi_2O_3{\cdot}60TiO_2$, corresponding to the phase $Bi_4Ti_3O_{12}$, was quenched from melt at 1300°C. The three

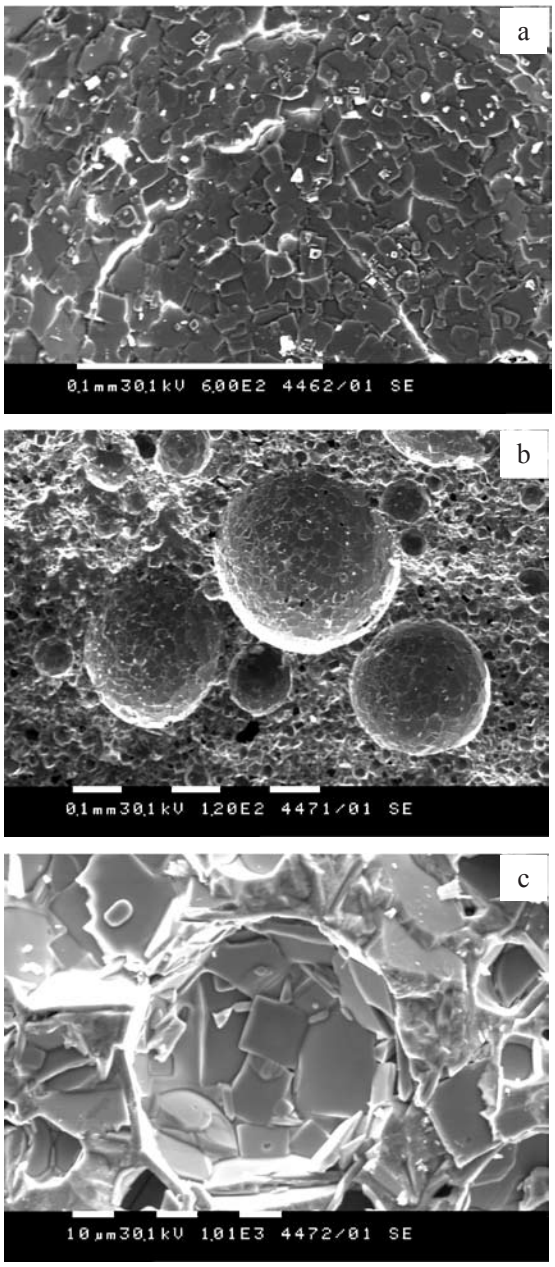

Figure 2. SEM micrographs of sample with composition $70Bi_2O_3{\cdot}30TiO_2$ prepared at: a) 1000°C and b, c) 1150°C

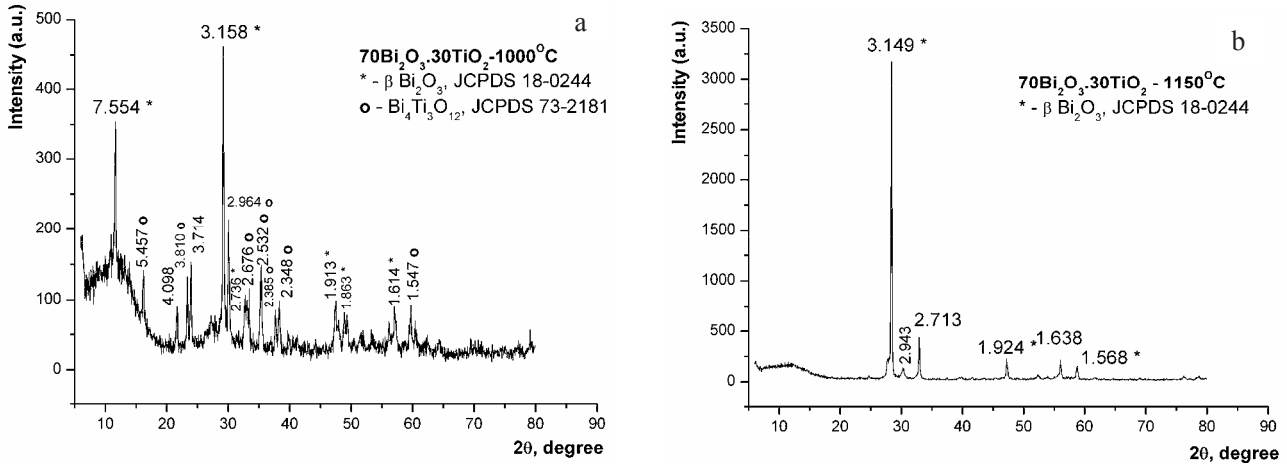

Figure 3. XRD patterns of sample with composition $70Bi_2O_3{\cdot}30TiO_2$ prepared at: a) 1000°C and b) 1150°C

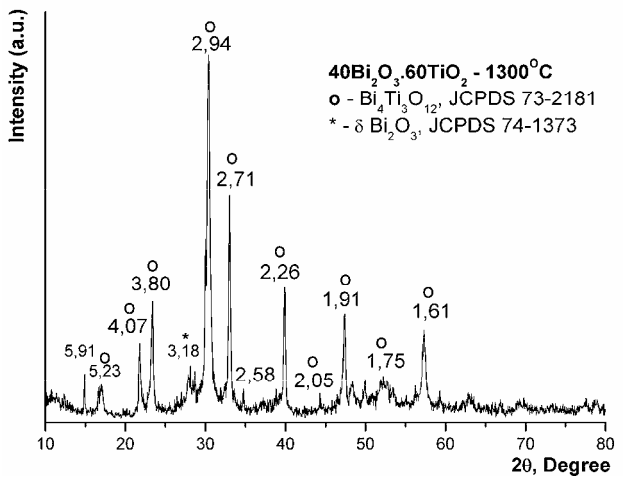

Figure 4. XRD patterns of sample with composition $40Bi_2O_3{\cdot}60TiO_2$ prepared at 1300°C

component samples with SiO_2 were melted in alumina crucibles at 1250°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 supercooling of the melts to room temperature was performed by pouring them between two steel plates. Heat treatment was applied at different temperatures in order to obtain crystalline phases from supercooled samples.

For all samples the phase formation was studied by X-ray diffraction analysis (XRD - TUR M62, Cu-Kα radiation) and energy dispersive spectroscopy (EDS - EDAX 9900). The microstructure was observed by scanning electron microscopy (SEM - 525M, Philips). For the EDS analysis the samples were prepared by mechanical polishing and covered with thin carbon film, while the SEM observations were made on fresh fractured surfaces also covered with thin carbon film.

III. Results and discussion

The investigation started with a model binary composition $70Bi_2O_3{\cdot}30TiO_2$ obtained by solid state reaction with heating for 1 hour in the temperature range 1000–1150°C. The SEM analysis illustrates the formation of different microstructures in the sample sintered at low-temperature, 1000°C (Fig. 2a). Secondary crystallization combined with porosity formation is observed after the high-temperature (1150°C) treatment (Fig. 2b), where clearly shaped cubic-like crystals are formed. The sample prepared at low-temperature is poly-phased one and its XRD data contains the patterns of the phase β-Bi_2O_3 and some patterns of other non-identified phases (Fig. 3a). The main crystalline phase is β-Bi_2O_3 (Fig. 3b) for the sample treated at 1150°C.

The sample with composition corresponding to the phase $Bi_4Ti_3O_{12}$ ($40Bi_2O_3{\cdot}60TiO_2$) was quenched from the melt at 1300°C. The XRD analysis shows mainly the formation of the phase $Bi_4Ti_3O_{12}$ without texturing effects (Fig. 4). The melt quenched sample with composition

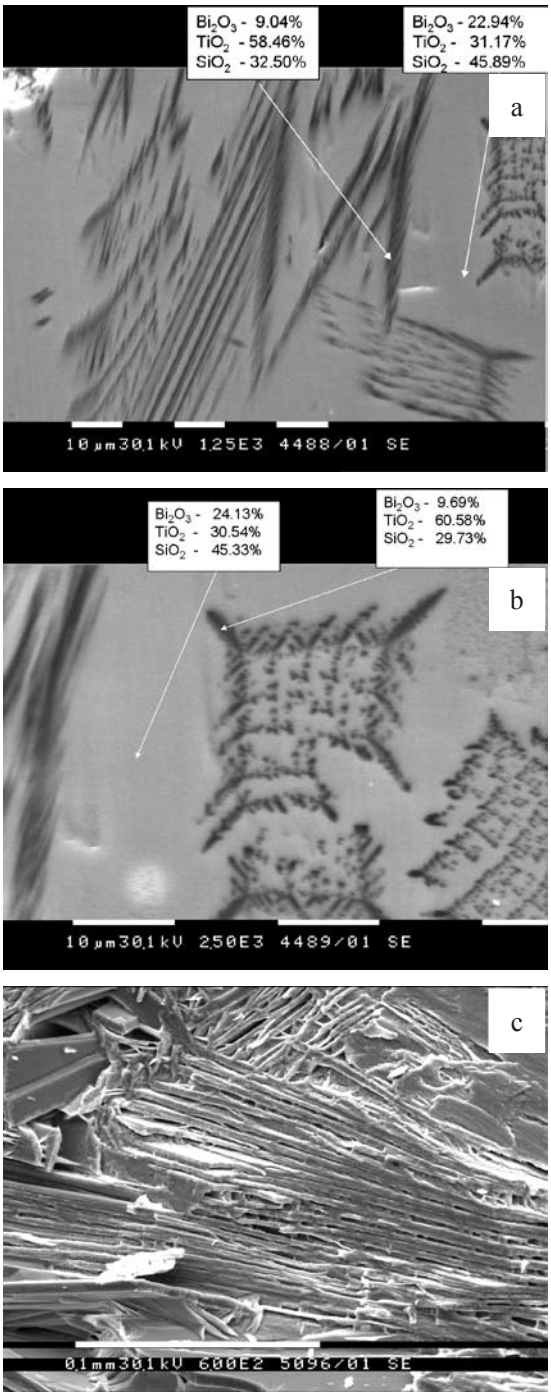

Figure 5. SEM micrographs and EDS data of melt quenched sample with composition $24Bi_2O_3{\cdot}36TiO_2{\cdot}40SiO_2$: a, b) heat treated at 700°C; c) heat treated at 800°C

$24Bi_2O_3{\cdot}36TiO_2{\cdot}40SiO_2$ after subsequent thermal treatment at 700°C, consists of elongated crystals in amorphous matrix (Fig. 5). According to the EDS analysis, the crystals and matrix differ in composition: the crystals have lower Bi_2O_3-content and higher TiO_2-content in comparison to the nominal composition (Figs. 5a,b). For all detected EDS analysis the statistical uncertainty is less than 4–5 mol%. Full crystallization combined with predominating orientation of the crystals is achieved after batch heat treatment for 5 hours at 800°C (Fig. 5c). Before the thermal treatment according to the XRD results,

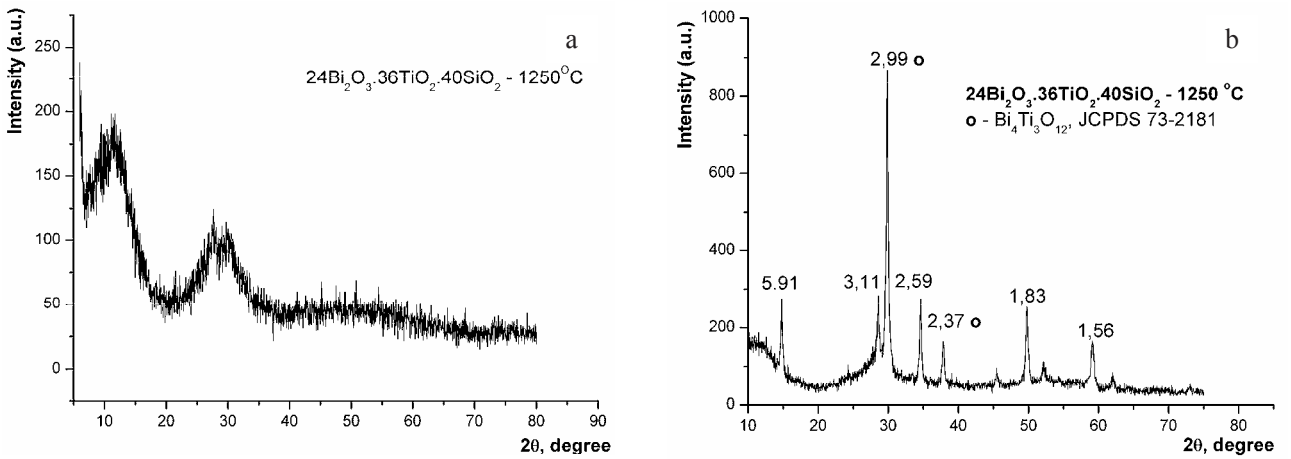

Figure 6. XRD patterns of sample with composition $24Bi_2O_3{\cdot}36TiO_2{\cdot}40SiO_2$: a) without thermal treatment; b) after heating for 5 h at 600°C and for 5 h at 700°C

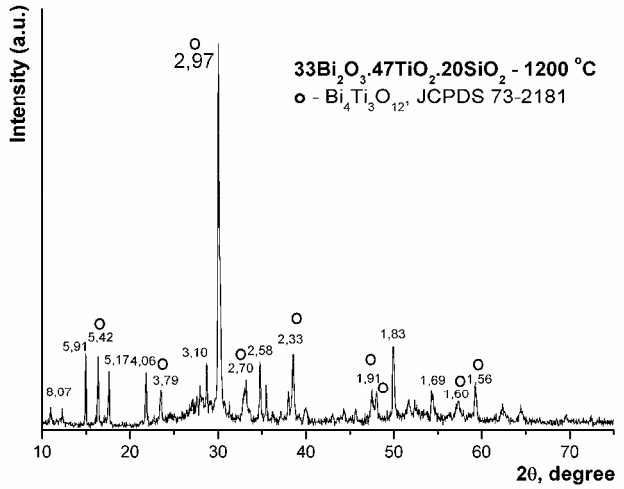

Figure 7. XRD patterns of sample with composition $33Bi_2O_3{\cdot}47TiO_2{\cdot}20SiO_2$

the sample was amorphous (Fig. 6a), but after long heating, the crystallization has been achieved (Fig. 6b) and a new phase having XRD patterns close to those of the phase $Bi_4Ti_3O_{12}$ appears. The decreasing of the SiO_2-content leads to more complex crystallization with participation of several phases including $Bi_4Ti_3O_{12}$ and some unknown phase (Fig. 7).

IV. Conclusions

The investigation shows for the first time that depending on the conditions of the melting and additional heat treatment of the supercooled samples, different poly phased ceramic materials with various microstructures could be obtained in the system Bi_2O_3-TiO_2-SiO_2. Formation of the phase $Bi_4Ti_3O_{12}$, Bi_2O_3-polymorphs and one unknown phase was established. These results are promising basis for control and modification of the electrical properties of the obtained bulk SiO_2 doped bismuth titanate ceramics.

Acknowledgements: The research was supported by UCTM, Sofia, Bulgaria under grand 10663/2009 and COST 539.

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