Bi$_{12}$TiO$_{20}$ crystallization in a Bi$_2$O$_3$-TiO$_2$-SiO$_2$-Nd$_2$O$_3$ system

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Abstract. Polycrystalline mono-phase bismuth titanate was produced by free cooling from melts heated to 1170 °C. The control over the initial amounts in the starting compositions in the system Bi$_2$O$_3$/TiO$_2$/SiO$_2$/Nd$_2$O$_3$ and over the thermal gradient of the heat process resulted in the formation of specific structures and microstructures of monophase sillenite ceramics. The main phase Bi$_{12}$TiO$_{20}$ belongs to the amorphous network groups based on oxides of silicon, bismuth and titanium. In this work, we demonstrated a way to control the crystalline and amorphous phase formation in bulk poly-crystalline materials in the selected system.

1. Introduction

Bismuth-titanate-based materials became very popular in recent years with a number of important applications, such as capacitors, sensors [1], piezoelectric, electro-optical and pyroelectric materials, relaxers, FERAM and DRAM storage devices and semiconductor devices [2].

The most popular methods for preparation are solid-state reactions, co-preparation, molten salt synthesis, mechanochemical synthesis. Addition of suitable additives is one way to modify their properties by controlling the phase formation. Jose Pineda-Flores et al. [3] have studied the ways to modify the properties of bismuth-titanate-based materials by controlling the phase formation and adding suitable additives, as Pr, Nd, Gd. Murugan et al. [4] discussed the glass-phase content influence on the dielectric properties of novel low-permittivity, fine-grain, pore-free and nano-structured materials. In general, the properties of bulk ceramic materials are affected by the phases involved, the grains size, the amount of glass phase and the grain boundary effects [5]. In the present work, we explored the possibility to obtain monophase polycrystalline ceramics using a bismuth-silicate amorphous network as a boundary-matrix in order to control the properties of these new bismuth-titanate materials.

2. Experimental

The synthesis of the bulk materials of the Bi$_2$O$_3$-TiO$_2$-SiO$_2$-Nd$_2$O$_3$ system began by homogenizing for 15 min the starting oxides (Bi$_2$O$_3$, TiO$_2$, SiO$_2$ and Nd$_2$O$_3$, Alfa Aesar 99.99%). The melting was done in aluminum crucibles in a KTM-GSL1700X SiC tube furnace at a temperature of 1170°C.

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This study was part of a larger experiment aimed at obtaining monophase polycrystalline samples by melting and controlled cooling to room temperature. In the selected system, it is possible to obtain the following phases: Bi$_4$Ti$_3$O$_{12}$, Bi$_2$Ti$_2$O$_7$, Bi$_2$Si$_2$O$_7$, Bi$_{12}$TiO$_{20}$, Bi$_{12}$SiO$_{20}$, depending on the starting composition and the melting temperature. The remaining starting oxides (table 1) were selected with the idea of obtaining only one crystalline phase. Bi$_{12}$TiO$_{20}$, in combination with a Bi/Si/O amorphous network. In order to control the temperature gradient of the free cooling, it was carried out in graphite crucibles.

### Table 1. Starting phase composition and melting conditions of selected samples in the system Bi$_2$O$_3$-TiO$_2$-SiO$_2$-Nd$_2$O$_3$.

| Sample index | Initial oxide composition (Raw materials in mol %) | t, °C / time, min | Phases obtained after melting, according to X-Ray Diffraction |
|--------------|--------------------------------------------------|-------------------|-------------------------------------------------------------|
| A | Bi$_2$O$_3$ TiO$_2$ SiO$_2$ Nd$_2$O$_3$ | 1170/15 | Bi$_{12}$TiO$_{20}$ |
| B | Bi$_2$O$_3$ TiO$_2$ SiO$_2$ Nd$_2$O$_3$ | 1170/15 | Bi$_{12}$TiO$_{20}$ |
| C | Bi$_2$O$_3$ TiO$_2$ SiO$_2$ Nd$_2$O$_3$ | 1170/15 | Bi$_{12}$TiO$_{20}$ |

The phase composition was determined by X-ray diffraction using a Ridacu D/MAX2500V + PC apparatus, CuKa radiation (1.5406 Å). The microstructure was observed by scanning electron microscopy (SEM Hitachi SU1510). The structure of the samples was examined by Thermo Nicolet – Avatar 370 FT-IR equipment.

3. Results and discussion
As seen in the X-ray patterns (figure 1) only one phase, Bi$_{12}$TiO$_{20}$, was present in the three samples chosen. The SEM images (figure 2) show that the samples examined had a similar dense microstructure,
without visible cracks or cavities. The formation of separate crystals of different size is also seen.

According to the IR spectra (figure 3), the structures of samples A and B are similar; the band at about 830 cm\(^{-1}\) is associated with the symmetric vibrations of the Ti-O linkages; and that at 600 cm\(^{-1}\), with asymmetric and deformation vibrations of the TiO\(_6\) octahedron [6]. Betch and White [7] reported that the band of 850 cm\(^{-1}\) is related to symmetric vibrations of Ti-O bonds in addition to Nd together with the TiO\(_6\) octahedral. The bands around 560 cm\(^{-1}\) and 820 cm\(^{-1}\) characterize a complex combination of a MO\(_4\) tetrahedral and a BiOn polyhedral [8], typical for the sillenite phase Bi\(_{12}\)TiO\(_{20}\). On the other hand, the bands near 900-800 cm\(^{-1}\) and 900-1000 cm\(^{-1}\), and the band near 1050-1100 cm\(^{-1}\) are typical for structures with four terminal oxygens SiO\(_4\) [13]. Jagannath Roy et al. [14] reported that the appearance of antisymmetric stretching vibrations of Si-O-Al and Si-O-Si networks can be connected with the peaks around 832 cm\(^{-1}\) and 1112 cm\(^{-1}\).

The formation of a multi-component amorphous matrix with Si-O-Si linkages (1034 cm\(^{-1}\), 1098 cm\(^{-1}\)), BiO\(_6\) (480 cm\(^{-1}\)), Si-O-Ti linkages (900 cm\(^{-1}\), 1034 cm\(^{-1}\)) and of depolymerized SiO\(_2\) groups (890 cm\(^{-1}\), 920 cm\(^{-1}\)) is due to the increased amount of SiO\(_2\) in the starting composition of sample C. Thus, the different crystal sizes observed in he SEM images could be due to different SiO\(_2\) content. In this sense, the results obtained by us directly correspond to the literature data, namely, that besides the formation of the sillenite bismuth-titanate phase Bi\(_{12}\)TiO\(_{20}\), bismuth-silicate and titanium-silicate multi-component amorphous structures are formed.

4. Conclusions
In this work we have investigated
1. The possibility to obtain monophase Bi\(_{12}\)TiO\(_{20}\) polycrystalline ceramics,
2. The type and composition of the bismuth-silicate amorphous network as boundary-matrix between the crystalline phases.

This investigation indicates a way to create new monophase polycrystalline materials of the system Bi\(_3\)O\(_3\)-TiO\(_2\)-SiO\(_2\)-Nd\(_2\)O\(_3\) using melting and controlled cooling to room temperature.

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