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$Bi_{12}TiO_{20}$ crystallization in a Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 system

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Abstract. Polycrystalline mono-phase bismuth titanate was produced by free cooling from melts heated to 1170 ºC. The control over the initial amounts in the starting compositions in the system $Bi_2O_3/TiO_2/SiO_2/Nd_2O_3$ 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 on order to control the properties of these new bismuth-titanate materials.

2. Experimental

The synthesis of the bulk materials of the Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 system began by homogenizing for 15 min the starting oxides (Bi_2O_3, TiO_2, SiO_2 and Nd_2O_3, Alfa Aesar 99.99%). The melting was done in aluminum crucibles in a KTM-GSL1700X SiC tube furnace at a temperature of 1170ºC.

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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: $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$, $Bi_2Si_2O_7$, $Bi_{12}TiO_{20}$, $Bi_{12}SiO_{20}$, 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_2O_3-TiO_2-SiO_2-Nd_2O_3.

Sample index	**Initial oxide composition (Raw materials in mol %)**				**t, ºC / time, min**	**Phases obtained after melting, according to X-Ray Diffraction**
	Bi_2O_3	TiO_2	SiO_2	Nd_2O_3		
A	77	14	0	9	1170/15	$Bi_{12}TiO_{20}$
B	74	14	3	9	1170/15	$Bi_{12}TiO_{20}$
C	74	3	14	9	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 Nikolet – 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,

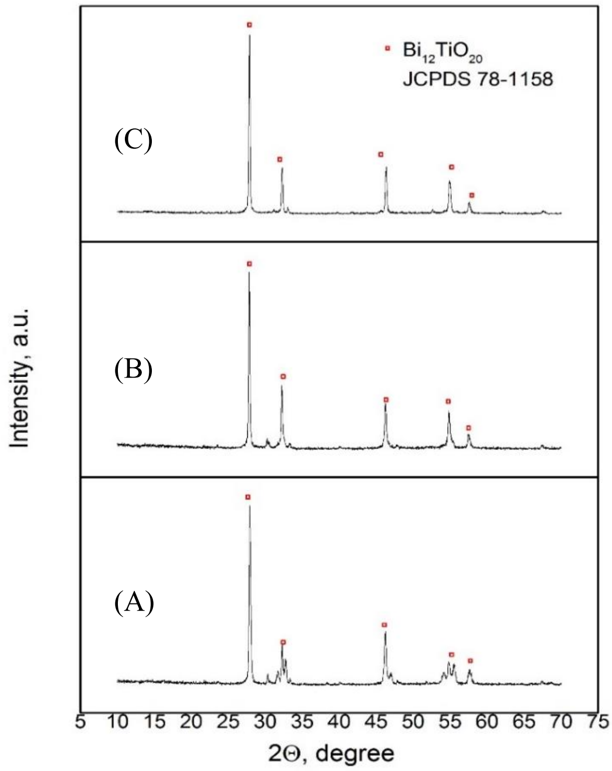

Figure 1. XRD patterns of samples A, B and C.

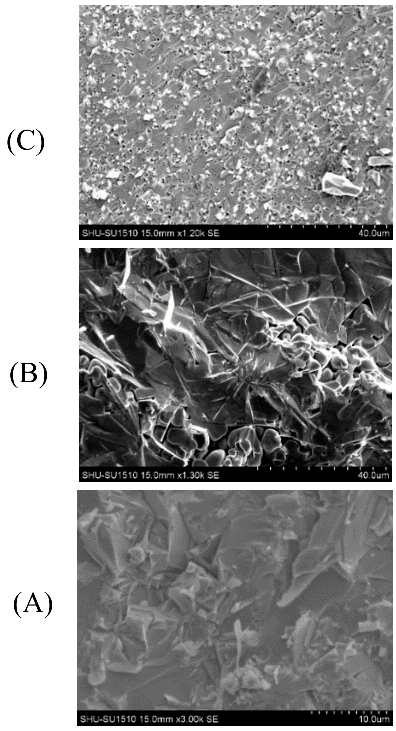

Figure 2. SEM images of samples A, B and C.

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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}.

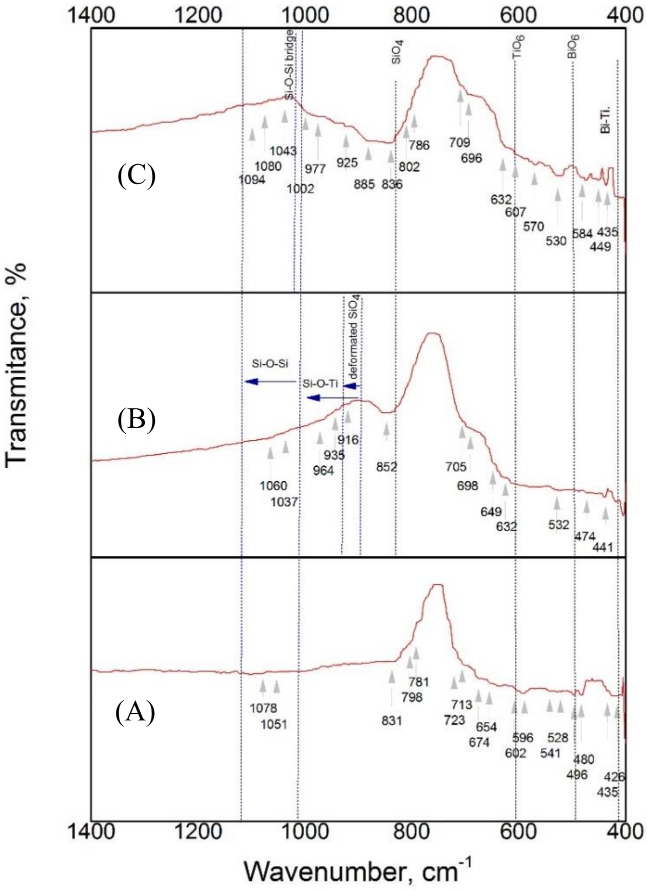

Figure 3. IR spectra of samples A, B and C.

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_4 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_2O_3-TiO_2-SiO_2-Nd_2O_3 using melting and controlled cooling to room temperature.

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