Characterization of the Dielectric Parameters of Monophase Polycrystalline Bismuth Titanate Pyrochlore (Bi2Ti2O7) Ceramics and Glass-Ceramics

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Abstract

Pyrochlore compounds have a number of technological applications, such as dielectrics for high-frequency and magnetoelectric devices. In bulk materials, they exhibit stimulated cation arrangement and good long-distance order within the pyrochlore framework. Bismuth titanate ceramics containing SiO2 and Nd2O3 were synthesized in the Bi2O3-TiO2-SiO2-Nd2O3 system using the melt-quenching method. In a previous study, the phase composition of selected samples was determined by X-ray diffraction (XRD) analysis and the microstructure was studied by scanning electron microscopy (SEM). The preparation of monophase polycrystalline materials was concluded. Infrared Fourier-transformed spectroscopy (FTIR) was applied in order to identify the structure. The electrical conductivity, as well as the dielectric losses and dielectric constants of selected samples were determined, and the influence of the phase composition on the dielectric characteristics was evaluated. The combination of the pyrochlore phase with the amorphous phase represented by the structural groups Bi-O-Si and Si-O-Si exerts a grain boundary strengthening effect.

Keywords: bismuth titanate pyrochlore, glass ceramics, dielectric characteristics.

1. Introduction

The pyrochlore of $Bi_2Ti_2O_7$ was first reported by Knop et al. [1] in 1968 devoted to $A_2Ti_2O_7$ titanates. The Bi_2O_3 - TiO_2 phase diagram, was first published by Speranskaya [2]. In the work of Subramanian et al., the study of $A_2Ti_2O_7$ titanates [3] showed that the compound $Bi_2Ti_2O_7$ should have an ideal stoichiometric composition. However, the stability of this structure is mainly due to the addition of certain impurities and it was proved on the basis of ion radii studies that the pure compound $Bi_2Ti_2O_7$ is outside the stability range of the pyrochlorine structure.

The applications of the pyrochlore phase have been outlined by a number of authors [4-8]. The methods for the synthesis of the pyrochlore phase ($Bi_2Ti_2O_7$) when doped with La, Sm, aiming to achieve innovative microwave properties, are discussed there. When synthesizing the materials, mainly sol-gel and laser deposition methods are used to obtain monophase pyrochlore-based materials. For example, by using oxides such as Bi_2O_3, TiO_2 and La_2O_3, and sintering at temperatures from 800 to 1200 °C [9], the phases $Bi_4Ti_3O_{12}$, $La_2Ti_2O_7$, $Bi_2Ti_2O_7$ and La_2TiO_5 have been identified.

With these compositions, the following values for ε_r(max): 130, 145, 147, 186, 168, 101 and for the dielectric losses tanδ: 0.022, 0.023, 0.024, 0.022, 0.017, 0.014, were respectively measured in a temperature range of 670, 508, 424, 246, -137, -149 °C.

An alternative type of disorder, cooperative tetrahedral tilt, also exists for compounds such as $Bi_2Ti_2O_7$ which is attributed to single-pair effects [11,12,13]. Thus, because of this disorder, the ferroelectric behavior of these material, is attributed to the presence of impurities.

The present study reports the synthesis of bismuth titanate ceramics containing SiO_2 and Nd_2O_3 in the Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 system by applying the melt-quenching technique. The preparation of monophase polycrystalline materials is envisaged. Infrared Fourier-transformed spectroscopy (FTIR) was applied in order to identify the structure. The phase composition was determined by X-ray diffraction (XRD) analysis and the microstructure - by scanning electron microscopy (SEM). The electrical conductivity, as well as the dielectric losses and dielectric constants of selected samples were determined, and the influence of the phase composition on the dielectric characteristics was evaluated.

2. Experimental

Sample preparation

For the synthesis reagent grade powder raw materials were used. The samples were prepared by using conventional high temperature and subsequent quenching method. The bathes of 100 gr. are heated up in a corundum crucible up to 1450°C in a SiC firnace and then soaked for h at this temperature. The melts were subsequently quenched to room temperature on a brass plate without pressing. The respective compositions are given in Table 1.

Structural studies

In previous work [10], the preparation of single-phase ceramic and glass-ceramic materials was reported, for which the phase compositions and structure were identified by XRD and IR. Thus, by utilizing the melt-quenching method, an economically sound technique for the preparation of Nd-doped pyrochlore materials and the preparation of single-phase ceramic and glass-ceramic materials containing the pyrochlore phase is demonstrated. Single-phase polycrystalline products containing more than 70 mol% TiO_2, which correspond to the pyrochlorine phase $Bi_2Ti_2O_7$ and for sample 3 containing more than 50 mol% SiO_2, which correspond to the pyrochlorine phase $Bi_2Si_2O_7$, have been obtained from the melt. It can be assumed that Bi and Nd ions are simultaneously participating in the phase composition by forming a solid substitution solution as shown according to XRD.

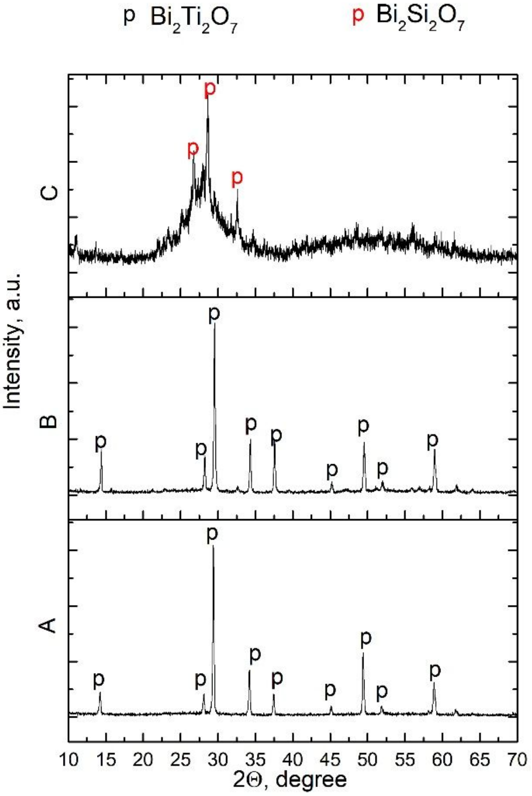

Figure 1. XRD patterns of samples 1, 2 and 3 [10].

For all three samples (Figure 2), according to Kojima et al [14, 15, 16, 17, 18] the occurrence of series of layered bismuth compounds could be suggested. Furthermore,in sample 1, according Jagannath Roy[19] the existence of antisymmetric stretching vibrations Si-O-Si could be assumed. In the glass ceramic sample 3 (featuring $Bi_2Si_2O_7$ crystal pyrochlorine phase) there is an absence or minimal content of Si-O-Si-bonds, which, according to some authors, is explained by the replacement [20, 21] with BiO_6 polyhedral structures and polymerized SiO_4 groups.

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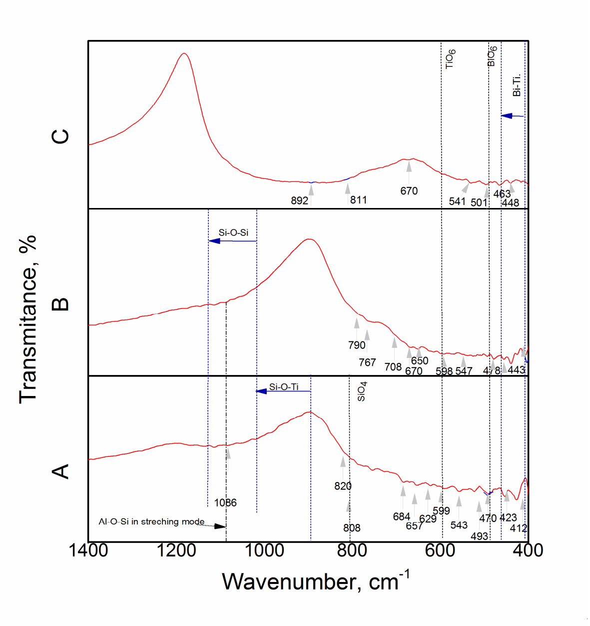

Figure 2. IR spectra of samples 1, 2 and 3 [10].

Table 1. Batch composition, phase composition and melting conditions (soaking temperatute and quenching temperature) of selected samples in the system Bi_2O_3-TiO_2-SiO_2-Nd_2O_3 [10].

№	Composition, mol%				t_m, °C/ t, min	Phases, according to XRD
	Bi_2O_3	TiO_2	SiO_2	Nd_2O_3		
1	19	66	8	7	1450/ 20	$Bi_2Ti_2O_7$
2	23	66	4	7	1450/ 20	$Bi_2Ti_2O_7$
3	45	0	50	5	1100/ 15	Glass + $Bi_2Si_2O_7$

Electrical properties investigation

Electrical measurements are done by using an impedancemeter Zahner IM6, Zahner Elektrik Kronach. Germany and two-contacting points measurement. After silver electrodes were applied onto the base of their disc-shaped surface, the samples were mounted in the holder and then connected to the impedance analyzer. The impedance modulus and the phase angle were measured as a function of frequency in the range from 100 Hz to 100 kHz at room temperature. Taking into account the sample geometry, the conductivity as well as several dielectric characteristics of the measured samples was estimated and the obtained results are summarized for the different compositions studied in Figs. 1 – 3 and Table 1.

It was established that the obtained monophase and polycrystalline materials based on the pyrochlore phase have the following characteristics: Samples 1 and 3 have similar dielectric constants up to 2000, while Sample 2 has a 7 times higher value of the parameter ε' (Figure 4).

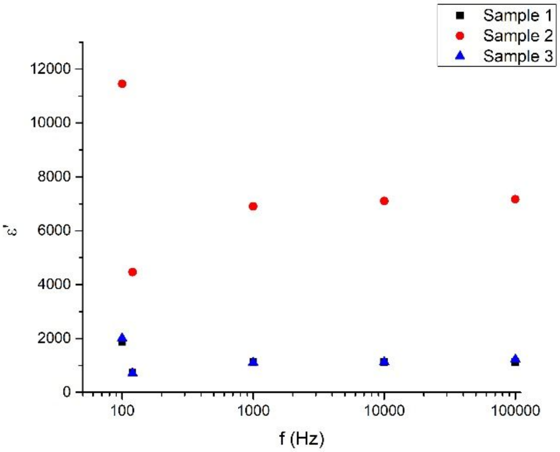

Figure 4. Graphical representation of the real part of the dielectric permittivity, ε’ vs frequency of samples 1, 2 and 3

This phenomenon is attributed to the bonding of cubic pyrochlore block structures in line-stacked layers of the phase $Bi_2Ti_2O_7$ (Sample 2)[10].

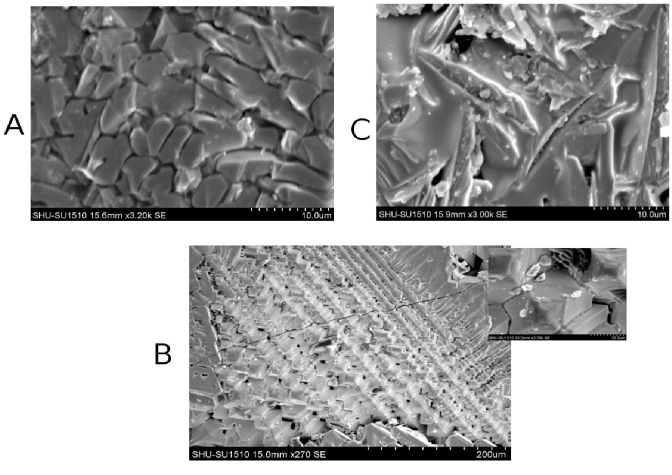

Figure 3. SEM micrographs of the fractured C-covered crosss-section of samples: A (sample 1), B (sample 2) and C (sample 3) [10].

At the same time, the dielectric losses, as seen in Figures 6 and 7 show stability as a function of the frequency for samples 2 and 3. At frequencies higher than 100 kHz, sample 2 demonstrates an increase in the dielectric losses (ε"), which is probably due to an increase in the vibrational effects on the boundary of the grains between the $Bi_2Ti_2O_7$ phase and the glassy phases with the different Bi-Si and Si-O-Si structural groups. According to Figure 6, all samples have low losses in the interval from 0 to 100 kHz, i.e. these are below 0.5.

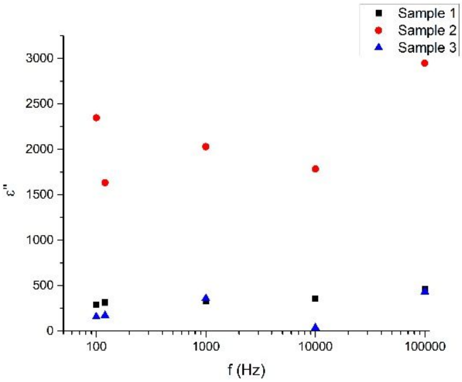

Figure 5. Graphical representation of the imaginary part of dielectric permittivity, ε'' vs frequency of samples 1, 2 and 3.

In addition, it can be assumed that in order to achieve stable dielectric parameters, the stabilization of the phases of the pyrochlore $Bi_2Ti_2O_7$ and $Bi_2Si_2O_7$ by replacing the Bi ions by the Nd at the A-site in the structures $A_2Ti_2O_7$ and $A_2Si_2O_7$ possesses an important role [22].

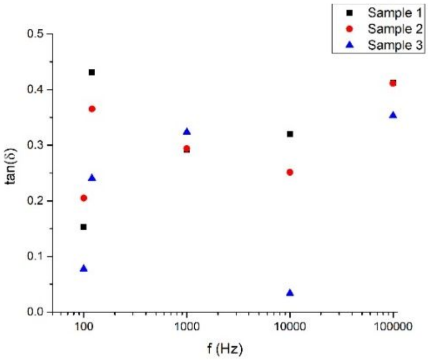

Figure 6. Spectra with dielectric losses vs frequency of samples: 1, 2 and 3

These data are confirmed by the measured conductivity values, which for Samples 1 and 3 remain low, with an upper limit of 0.002 S/m, while for Sample 2, it increases to 0.016 for frequencies of 100 kHz (Figure 7). This behavior is explained by the influence of Bi-Si and Si-O-Si structural groups [10]. It is noteworthy mentioning that the glass-crystal sample has similar dielectric characteristics to the crystal sample 1 containing the $Bi_2Ti_2O_7$ phase, which is probably due to the dominant influence of the dielectric characteristics of the amorphous phase containing mainly Bi-Si and Si-O-Si structural groups.

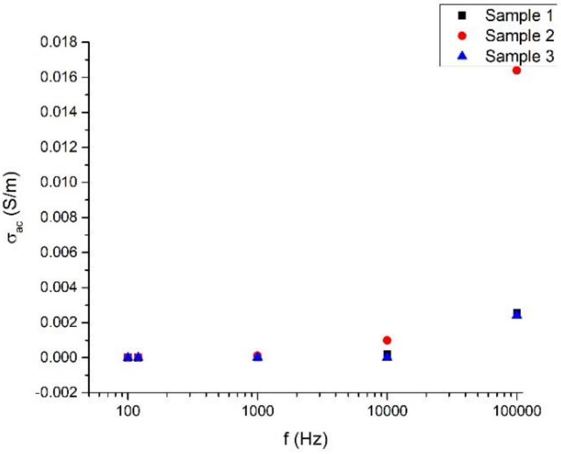

Figure 7. Conductivity vs frequency of samples: 1, 2 and 3

These dielectric parameters can be explained by another phenomenon proposed by Parker [23,24] concerning the influence of the rutile TiO_2 crystals on the dielectric constant ε'. The focus of these studies is on the high oxidation state of TiO_2, which reduces the frequency dependence of the dielectric constant, according to the oxygen oxidation state, which for peroxites and pyrochlores is −1, of the components given by the general structural formula of pyrochlore) $A_2^{3+}Ti_2^{4+}O_6O^-$, according to Roth [25].

3. Conclusion

In the frequency range from 0 to 100 kHz, all investigated compositions show stable behavior in terms of dielectric parameters and conductivity.

When comparing the crystalline Sample 1 ($19Bi_2O_3.66TiO_2.8SiO_2.7Nd_2O_3$) and the glass-crystalline Sample 3 ($45Bi_2O_3.50SiO_2.5Nd_2O_3$), their electrical characteristics demonstrate minimal frequency dependence and corresponding potential for high-frequency capacitor applications. For Sample 2 ($23Bi_2O_3. 66TiO_2.4SiO_2.7Nd_2O_3$), the frequency dependence of the electrical characteristics is significant at low frequencies (≤ 20 kHz) after which it becomes insignificant up to 100 kHz, making this composition potential candidate for the preparation of low frequency dielectric devices. This behavior of Sample 2, is attributed to its structure where the addition of up to 66 mol % TiO_2 determines the bonding of cubic pyrochlore block structures in the line-stacked layers of the phase $Bi_2Ti_2O_7$. Furthermore, the combination of the pyroclore phase with the amorphous phase, represented by the Bi-Si and Si-O-Si structural groups, exerts grain boundary strengthening effect.

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