



Structural and dielectric properties of polycrystalline $(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{TiO}_3$

C. Kajtoch ^{a,*}, M. Gabryś ^a, W. Tejchman ^b, B. Handke ^c

^a Institute of Physics, Pedagogical University, ul. Podchorążych 2, 30-084 Kraków, Poland

^b Institute of Biology, Pedagogical University, ul. Podchorążych 2, 30-084 Kraków, Poland

^c Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland

* Corresponding author: E-mail address: ckajtoch@ap.krakow.pl

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ABSTRACT

Purpose: This work is aimed to determination of the influence of Sr – ferroactive substitution on physical properties and character of phase transitions (PT) in barium titanate BaTiO_3 (BT).

Design/methodology/approach: Polycrystalline samples of BST-10 were prepared by means of calcination method at the ~ 1600 K. Roentgenogram of BST-10 was made within the angles from 10 deg to 110 deg with the 0.008 deg step. Images of the morphology of the samples were taken by means of electron microscope Philips SEM 525M at room temperature. Dielectric measurements were performed with application of Quatro Cryosystem 4.0 and Agilent Precision LCR meter HP4284A equipped with WinDETA 5.62 software Novocontrol. Measurement were taken under cooling with 2 K/min speed. Measuring electric field frequency was from the range 20 Hz-1 MHz.

Findings: Dielectric spectroscopy in the frequency domain was applied to measure complex dielectric permittivity and other dielectric functions of ferroelectric polycrystalline $(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{TiO}_3$ (BST-10). It was established that 10% substitution of Sr in BST-10 solid solution did not change the character of the phase transitions. The temperatures of the phase transitions were correlated with low temperature of PT in SrTiO_3 (ST). Similar properties of Ba and Sr ions were taken into consideration. The dipolar character of solid solution was also observed in paraelectric phase.

Practical implications: Obtained results can be used to model the effects of ferroactive and nonferroactive substitutions in the A and B subnets of perovskite ferroelectrics.

Originality/value: An attempt to correlate low phase angle values observed in the paraelectric phase of BST-10 with high dielectric permittivity and the occurrence of polar regions.

Keywords: Ceramics; Ferroelectric; Dielectric properties; Phase transition; Dielectric relaxation spectroscopy

PROPERTIES

1. Introduction

$(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{TiO}_3$ solid solution (BST-10) belongs to ferroelectric materials of the $(A'A'')\text{BO}_3$ type. Both constituents of this solution are ferroelectrics. Widely investigated barium titanate is applied as capacitor ceramic [1], as piezoelectric transducer, termistor [2, 3] and chemical sensor. Strontium titanate may be used in varistors and tunable microwave filters. At

very low temperatures strontium titanate exhibits piezoelectric and superconducting properties. Pure barium titanate (BT) occurs in four structures [4, 5]. At high temperatures (paraelectric phase), BT forms cubic structure. The temperature lowering induces 3 phase transitions: at about 400 K to tetragonal (T) structure, next at ~ 300 K to orthorhombic structure (O) and finally at ~ 210 K to rhombohedral (R) structure. Strontium titanate (ST) has cubic structure above 105 K [6] i.e. in the whole temperature range where the present measurements have been performed.

This work is aimed at the determination of an influence of the ferroelectric components BT and ST on physical properties of BST-10 as well as a character and temperatures of PT in this material. Composition 10% of SrTiO_3 has been chosen for the investigations in order to compare the results with the properties of $\text{Ba}(\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_3$ [7] which has Sn instead of Ti at the same stoichiometry. The 10% of the admixture of nonferroelectric BaSnO_3 stabilizes the cubic structure below average temperature (T_m) of the phase transition. ST within this temperatures range also occurs at cubic structure. Strontium atom behaves in this structure as ferroactive ion. Simultaneously, Ba and Sr have similar electron configuration. This is why a comparison of $(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{TiO}_3$ and $\text{Ba}(\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_3$ and analysis of the influence of „ferroactive” and „non-ferroactive” ions on the crystal structure may be useful in explanation of ferroelectric behaviour of perovskites.

2. Experimental

Polycrystalline samples of BST-10 were prepared by means of calcination method at the ~ 1600 K. Roentgenogram of BST-10 was made within the angles from 10 deg to 110 deg with the 0.008 deg step. Images of the morphology of the samples were taken by means of electron microscope Philips SEM 525M at room temperature. Dielectric measurements were performed with application of Quatro Cryosystem 4.0 and Agilent Precision LCR meter HP4284A equipped with WinDETA 5.62 software Novocontrol. Measurement were taken under cooling with 2 K/min speed. Measuring electric field frequency was from the range 20 Hz-1 MHz.

3. Results and discussion

Results of roentgenographic measurement (Fig. 1), taken for BST-10 at room temperature, confirm tetragonal crystal structure (P4/mmm). The content of this structure approaches 100%.

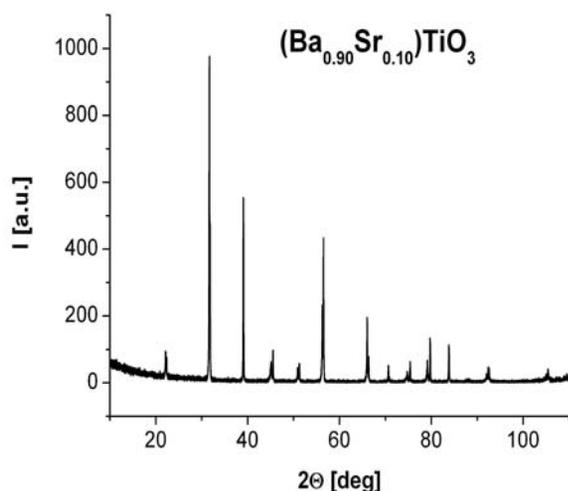


Fig. 1. Diffractogram of polycrystalline BST-10 sample

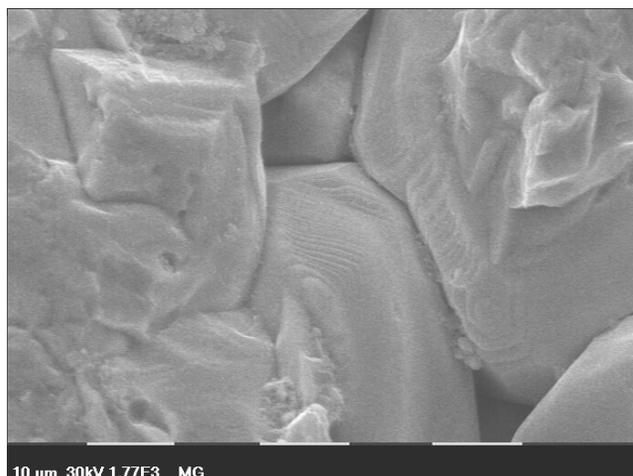


Fig. 2. SEM image of polycrystalline BST-10, magnification 1.77×10^3

Lattice constants are: $a = b = 0.39862$ nm, $c = 0.40207$ nm. They are close to the values for pure BT. Theoretical density for BST-10 equals 5.9 g/cm^3 . The real value for the obtained sample equals about 83% of the theoretical density.

SEM image of the BST-10 sample (Fig. 2) shows well formed crystallites. Surface bands can be seen in some crystallites. They can be related to layered structure of the investigated material. The temperature dependences of real component of dielectric permittivity $\epsilon'(T)$ are shown in Fig. 3 (for BT) and in Fig. 4 (for BST-10). In both cases three peaks exist within the investigated temperature range. The respective peaks relate to the phase transition sequence C – T – O – R. Temperatures of PT in BST-10 are lower of 10-30K in comparison to those for pure BT.

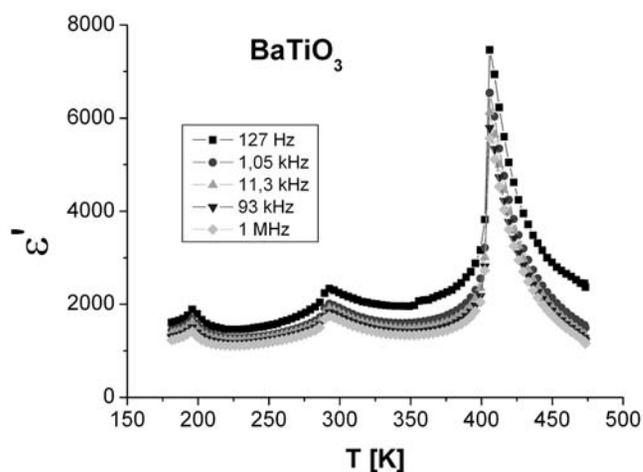


Fig. 3. Temperature dependence of dielectric permittivity ϵ' for polycrystalline BT

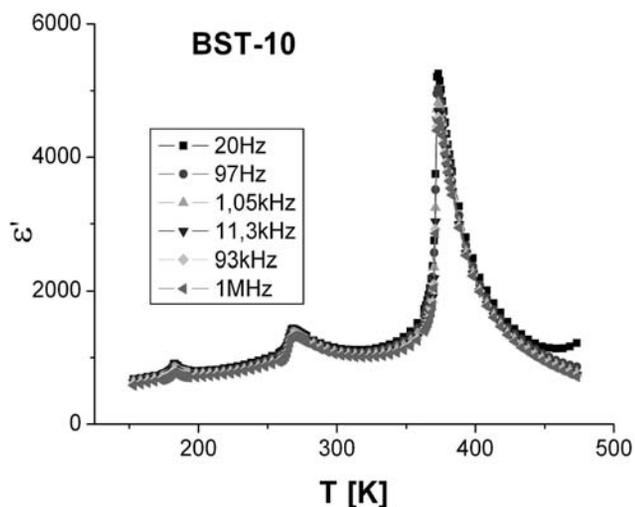


Fig. 4. Temperature dependence of dielectric permittivity ϵ' for polycrystalline BST-10

The observed shift corresponds to lower temperatures of PT in pure ST than in BT. Deeper analysis of the experimental results allows concluding that all PT have diffuse character. The temperatures of $\epsilon'(T)$ peaks are independent of the frequency.

Temperature dependence of $\epsilon''(T)$ for BST-10 is shown in Fig. 5. Maximum values of $\epsilon''(T)$ relate exactly to the temperatures of the respective PT (Fig. 4). There is not any shift of these temperatures with the frequency. The lack of the frequency dependence of ϵ'' confirms the diffuse character of all phase transitions including those in BT.

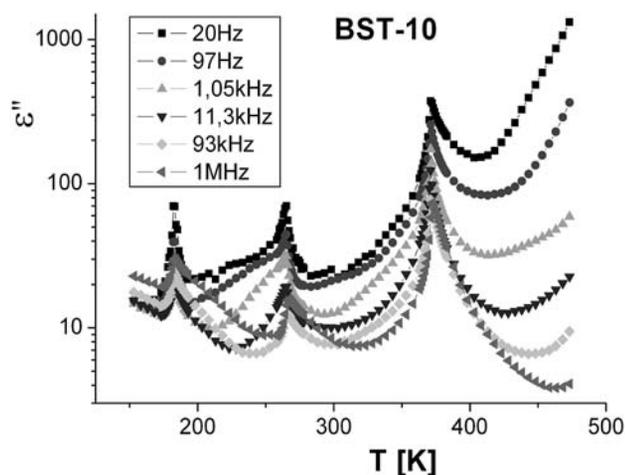


Fig. 5. Temperature dependence of dielectric permittivity ϵ'' for polycrystalline BST-10

Temperature dependence of phase angle $\Phi(T)$ is shown in Fig. 6. In this case, the lack of frequency dependence and the

same PT temperature sequence is seen. Below 400 K, the measured values of the phase angle fall down from -90 deg to 85 deg. It means that these are electric dipoles which have crucial influence on the electrical properties of polycrystalline BST-10.

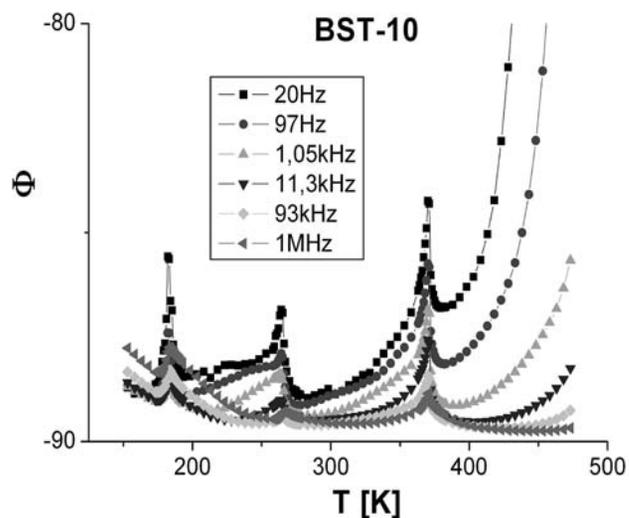


Fig. 6. Temperature dependence of phase angle Φ for polycrystalline BST-10

A nature of such dipoles moments may be connected with electron configurations of the ferroactive Ti ion. The dipoles form clusters. They are created at high T and are a source of dipolar polarization P_d [8-10] related to the short range interdipolar interaction. Growth of the clusters and their long range collectivization lead to the creation of ferroelectric domains. This takes place at the temperatures close to paraelectric – ferroelectric PT.

4. Conclusions

The results of structural and dielectric measurements performed for BST-10 are presented. The analysis confirms that 10% substitution of ferroactive Sr^{2+} instead of Ba^{2+} ions (in the A subnet of the perovskite ABO_3) does not change strongly physical properties in comparison to pure BT. It leads only to lowering of PT - temperatures. ST has a paraelectric character within the investigated temperature range. But it does not lead to freezing of the paraelectric cubic phase below the temperature of paraelectric – ferroelectric phase transition. Such behaviour remains in contradiction to $\text{Pb}(\text{Cd}_{1/3}\text{Nb}_{1/3})\text{O}_3$ [11] and BST-10. In the BST-10 case, the nonferroactive Sn ions make the transition to the tetragonal structure impossible.

Polycrystalline BST-10 may find many practical application, so do other known ferroelectric materials [12-15]. A change of the concentration of the ferroactive Sr ions shifts the temperature of work of electromechanical elements based on $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ without changing other physical properties.

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