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Diffused phase transition of polycrystalline $(Ba_{0.80}Sr_{0.20})TiO_3$

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ABSTRACT

Purpose: The purpose of this work was to determinate the influence of the 20% Sr substitutions (in sublattice A) on changes of the character of phase transition (PT) in comparison with pure barium titanate $BaTiO_3$ (BT).

Design/methodology/approach: Polycrystalline samples of $(Ba_{0.80}Sr_{0.20})TiO_3$ (BS20T) were prepared by calcinations method at temperature 1620 K. X-ray measurements were executed from 10 deg to 120 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 Agilent Precision LRC meter HP4824A equipped with WinDETA 5.62 software Novocontrol. Measurements were taken under cooling with 2 K/min speed. Measuring electric field frequency was from the range 20 Hz - 1 MHz.

Findings: The difference between the value of temperature of structural transition (cubic-tetragonal) equal 310K and the temperature Tm (the temperature of maximum of real part electric permittivity) equal 340 K was affirmed. It was affirmed, that 20% substitution of Sr ions changed the type of phase transition. The transition was strongly diffused (DPT). The polar character of this solid solution was also observed in a broad temperature range (in the paraelectric phase too). It is connected with the occurrence of polar regions (clusters).

Research limitations/implications: The results can be used to describe changes of PT in the DPT solid solutions with ferroactive substitutions in sublattice A.

Originality/value: Value of this work relies on the experimental examination of the dielectric properties of $(Ba_{0.80}Sr_{0.20})TiO_3$ (BS20T) solid solution. The temperature of the DPT was calculated. The low value of phase angle is connected with the existence of the polar regions.

Keywords: Barium Strontium Titanate; X-ray spectroscopy; Electron microscopy; Permittivity; Conductivity; Phase transition; Cluster

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MATERIALS

1. Introduction

Barium strontium titanate stannate $(Ba_{1-x}Sr_x)TiO_3$ (BSxT) is the solid solution of the ferroelectric $BaTiO_3$ (BT) and the ferroelectric $SrTiO_3$ (ST) [1,2]. The dielectric behaviour of (BSxT) changes from typical for ferroelectrics (BT) to ferroelectrics with diffuse phase transition (DPT-[3,4]) with increasing Sr substitution. The BS20T was examined in the interval of temperatures from 150K to 500K. Dielectric measurements of BS20T sample showed diffused phase transition at temperature 340 K.

The material, investigated in this paper use as capacitor ceramics, as piezoelectric transducers and as a PTC thermistor and chemical sensors [5-7].

Temperature of 50% contribution of cubic and tetragonal structural phases of BS20T takes place 30 K below temperature T_m (the temperature of maximum of real part of the electric permittivity). This stands in contradiction with typical properties of ferroelectric materials with DPT. They characterize a change or coexistence of two phases high - and low symmetric. The coexistence 1/1 of both phase: cubic C and tetragonal T was, in solid solution of $(Ba_{0.80}Sr_{0.20})TiO_3$ (BS10T) not observed at T_m. The statistical distribution of ions Ba and Sr in sublattice A leads to diffuseness of PF PT but not to the structural PT.

The above mentioned controversies related to properties of material and the character of phase transition was the cause of execution the presented investigations.

2. Experimental

The polycrystalline BS20T-sample was obtained by the calcinations method (1620 K). A sample, about diameter 10mm and thickness 1.5 mm, was painted by silver electrodes. X-ray measurements were executed in range 10-120 degrees from jump angle 2Q even 0,008 degree. The electron microscope Philips SEM 525M was used in order to study the BS20T structure at room temperature.

The dielectric measurements were performed by automatic device (QUATROKRIO 4.0 with analyzer Agilent type 4824A and BDS 1100). The measurements were executed in cooling process with speed 2 K/min in range of frequency from 20 Hz to 1 MHz.

3. Results and discussion

Figure 1 presents the X-ray pattern at temperature 304 K of BS20T sample. It shows peaks of mixed cubic-tetragonal structure. Temperature in this figure is lower about 36 K from temperature T_m. It means, that in temperature T_m = 340 K the structural phase transition does not occur. Lowering of crystallographic symmetry of BS20T solid solution in T_m was not observed.

Figure 2 presents the structure of polycrystalline BS20T obtained with help of the electron microscope at room temperature. Clear crystallites are visible well on it. Their sizes have been carried out since several to a dozen or so micrometers.

Figure 3 presents the temperature dependence of real part of the electric permittivity ε'(T). For all frequencies maximum value of ε' it appears at temperature 340 K. Such situation occurs in ferroelectrics with diffused phase transition (DPT). The grade of broadening of phase transition is combined, in literature, with degree of freezing of paraelectric phase (clusters) to the ferroelectric phase [8].

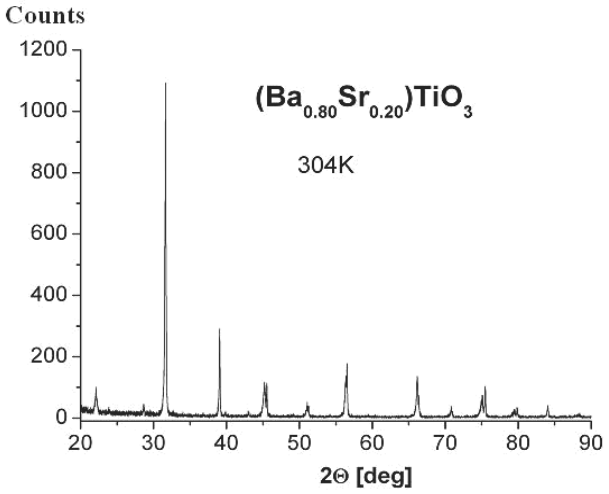

Fig. 1. X-ray pattern of BS20T (304 K)

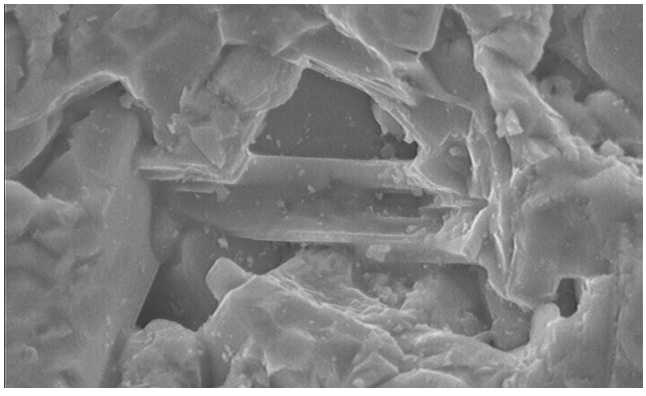

Fig. 2. The crystalline structure of BS20T ceramic obtained by electron microscope (magnification 3.4 x10^3)

Creations of these clusters lead to occurrence of dipolar polarization [9-11]. This is connected with growth of density of domain walls [12, 13]. This has essential influence on measured values of ε'.

The formula 1 describes ferroelectric materials with diffuse phase transition.

$$\varepsilon^{-1} = \varepsilon_m^{-1} + A(T - T_m)^{\gamma} \quad (1)$$

where ε_m is the maximum value of the electric permittivity ε', A and γ are fixed constants. In a diffuse phase transitions the value

of γ is close to 2. These values, from formula 1, were presented in Figure 4 as dependence (logy) on (logx), where:

$$y = \varepsilon^{-1} - \varepsilon_m^{-1} \tag{2}$$

$$x = T - T_m \ . \tag{3}$$

The obtained results show two temperature regions with constant γ_1 and γ_2. Values of these parameters have changed from 1.70 to 1.20 by temperature ca.. 383 K. This temperature is about 21 K higher than temperature T_m. It is equal to the temperature of beginning of quick growth of the phase angle (see Fig. 5). The γ_1 value is close to 2, that suggests typical behaviour for diffused phase transition.

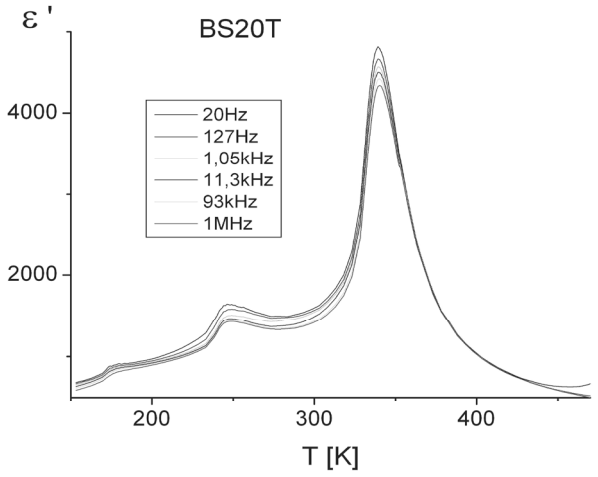

Fig. 3. The temperature dependence of the electric permittivity ε'(T) for BS20T sample

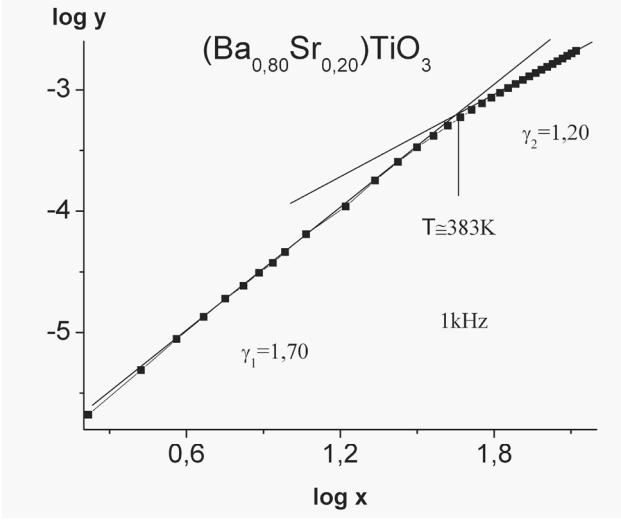

Fig. 4. Dependence (logy) on (logx) by 1 kHz for polycrystalline BS20T

Figure 5 presents the temperature dependence of phase angle Φ(T) for BS20T. Local maxima of Φ behave similarly like maxima of ε'(T).

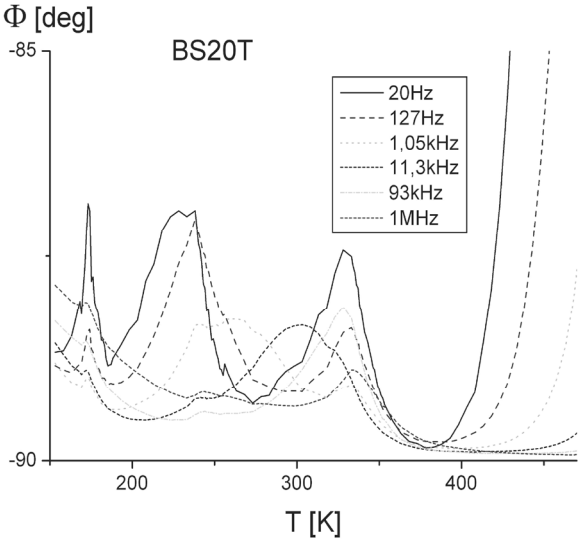

Fig. 5. The dependence of the phase angle Φ as temperature function for BS20T sample

Below temperature 400 K the value of the phase angle belongs to the interval from -90 deg to -87 deg. The increase of temperature causes the violent increase of the phase angle until to value 0 deg. The quickest increase occurs for small frequencies. This is connected with small sizes of polar regions and the short-range interactions that are present during the structural and electric coordination in clusters.

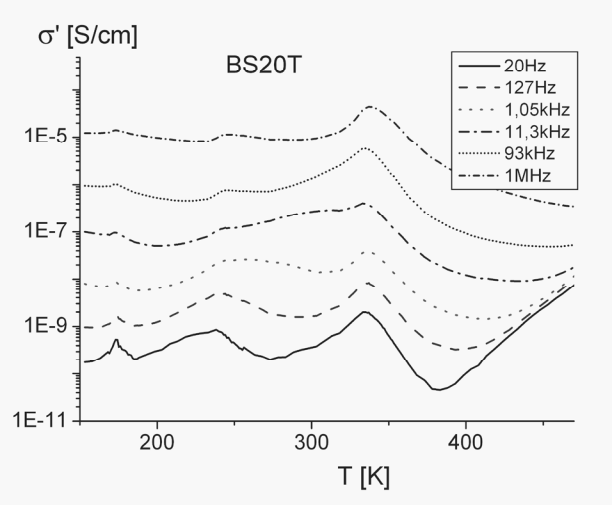

Fig. 6. Function σ'(T) for BS20T sample

The low values of phase angle suggest existence of clusters in broad temperature region. They give contribution to dipolar

polarization P_d. In this range of temperatures the superiority of dipole-like conductivity over other conductivity types takes place. In high temperatures and low frequencies the increase of part of the electron-like conductivity is present.

Figure 6 shows dependence of the electric conductivity $\sigma(T)$ on temperature. For frequency from 20 Hz to 1 MHz the PTC (the positive coefficient of the electric resistance) effect was observed at temperatures near PF PT.

Increase frequency 5 orders of size leads to the same growth of electric conductivity.

Observed effect PTC is probably connected with reconstruction of structure of polar regions [14-16]. Strong increase of their liability in area of phase transition is connected with their joining in larger complexes (micro domain). The processes of freeing and the trapping of charges (the electrons) during phase transition are connected with strong growth of electric susceptibility and the occurrence of the PTC effect.

4. Conclusions

In BS20T the structural transition was not observed in surroundings of temperature T_m. Polar properties (phase angle $\Phi = -90^0$) in whole range of temperatures suggests the existence of polar regions.

In $\varepsilon'(T)$ and $\sigma'(T)$ measurements independence of temperature T_m from frequency of the applied electric field was confirmed. This fact suggests occurrence of the diffused phase transition (DPT).

It suggests that the system of clusters is created.

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