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Diffuse Phase Transition of Polycrystalline $(Ba_{0.9}Sr_{0.1})TiO_3$

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Abstract

The results of X-ray diffraction (XRD) and dielectric measurements performed for polycrystalline $(Ba_{0.9}Sr_{0.1})TiO_3$ (BS10T) are presented. Data from these measurements show a presence of diffuse phase transition (DPT) between cubic and tetragonal structure at a temperature of 373 K. The temperature T_m of the maximum of real part permittivity (ε') does not depend on the frequency of the applied electric field. A phase angle, $\Phi \approx -90°$, between current and applied voltage, suggests an occurrence of polar regions (clusters) below 400 K i.e. in the DPT temperature range of and in the paraelectric phase.

Keywords: Dielectric properties, Ferroelectrics, Phase transition, Solid solution

ROZMYTA PRZEMIANA FAZOWA POLIKRYSZTAŁU $(Ba_{0,9}Sr_{0,1})TiO_3$

Przedstawiono wyniki pomiarów rentgenowskich (XRD) i dielektrycznych dla polikrystalicznego $(Ba_{0,9}Sr_{0,1})TiO_3$ (BS10T). Wyniki pomiarów pokazują obecność, w temperaturze 373 K, rozmytej przemiany fazowej (DPT) pomiędzy strukturą regularną i tetragonalną. Temperatura maksimum rzeczywistej składowej przenikalności elektrycznej (ε') nie zależy od częstotliwości elektrycznego pola pomiarowego. Kąt fazowy, $\Phi \approx -90°$, między prądem a przyłożonym napięciem elektrycznym sugeruje występowanie obszarów polarnych (klasterów) poniżej 400 K, tj. w obszarze temperaturowym DPT i w fazie paraelektrycznej.

Słowa kluczowe: właściwości dielektryczne, ferroelektryki, przemiana fazowa, roztwór stały

1. Introduction

Barium strontium titanate ($(Ba_{0.9}Sr_{0.1})TiO_3$ or BS10T) is the solid solution of the following two ferroelectrics: barium titanate ($BaTiO_3$ or BT) and strontium titanate ($SrTiO_3$ or ST). BS10T belongs to the $(A'A'')BO_3$ class of ferroelectric materials. Ba^{2+} and Sr^{2+} ions have identical valence electron configuration.

Widely investigated, BT is applied as capacitor ceramics [1], piezoelectric transducers, and in thermistor and chemical sensors [2-4]. Pure BT occurs in four crystalline structures [5-6]. At high temperatures, BT forms a cubic structure (paraelectric phase). A lowering of the temperature induces the following three structural phase transitions (PT): to tetragonal (T) structure at about 400K, next to orthorhombic structure (O) at ~300 K and finally to rhombohedral (R) structure at ~210 K [7].

Ferroelectric ST may be used in varistors and tunable microwave filters. At very low temperatures ST exhibits piezoelectric and superconducting properties.

ST has cubic structure above 105 K, *i.e.* over the whole temperature range in which the present measurements were performed.

It is know that 10 % substitution of Sr in A sublattice of $BaTiO_3$ stabilizes the cubic structure below the temperature related to the maximum of real part of electric permittivity (T_m). At T_m a structure of BS10T is a mixture of cubic and tetragonal structures. In comparison to pure BT, both T_m temperature and the assigned ε'_{max} values are lower. In both cases however (*i.e.* for BT and BS10T) one observes small values of phase angle between current and voltage, which confirms the presence of polar regions [8-9]. The occurrence of dipole polarization in these regions has been reported elsewhere [10-12] and related to the freezing of the paraelectric phase at cooling to the ferroelectric phase [13].

Small values of the phase angle in a broad temperature region and the reported influence of the Sr concentration on the character of the paraelectric – ferroelectric PT have prompted the authors of this work to undertake systematical studies of the character of phase transition in BS10T. The present studies were performed by means of the XRD method, electron scanning microscopy (SEM) and dielectric spectroscopy. The resulting conclusions can be used in the designing of new ferroelectric materials.

2. Experimental

The polycrystalline BS10T was prepared by calcination method at a temperature of ~1620 K. The sample of

10 mm in diameter and 1.2 mm thick was covered with silver electrodes. X-ray measurements were carried out over the range from 10 to 110 degrees, with a step angle 2Theta equal to 0.008 degrees. The microstructure of BS10T was investigated using a Philips SEM 525M electron microscope at room temperature. The dielectric measurements were made automatically (QUATRO KRIO 4.0 with Agilent type 4824A analyzer and BDS 1100). The measurements were made during cooling at a rate of 2 K/min, in the frequency range from 20 Hz to 1 MHz.

3. Results and discussion

Fig. 1 presents the XRD pattern of a polycrystalline BS10T sample at the temperature T_m (373 K) considered as a middle temperature of the phase transformation.

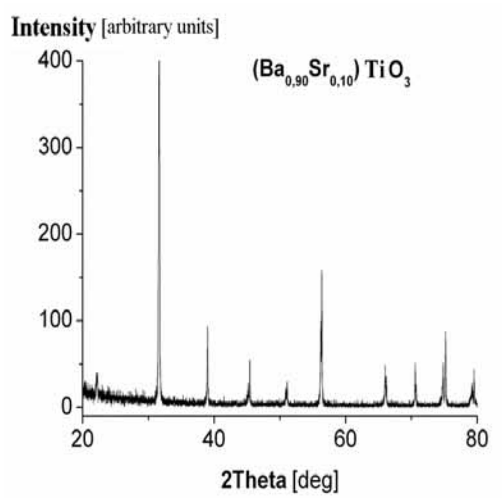

Fig. 1. X-ray pattern of BS10T (373 K, 50.4 % tetragonal phase, 49.6 % cubic phase)
Rys. 1. Dyfraktogram rentgenowski próbki BS10T (373 K, 50,4 % - faza tetragonalna, 49,6 % - faza regularna)

Fig. 2 presents a temperature dependence of the cubic and tetragonal phase contribution in BS10T. It can be seen that T_m coincides with the temperature at which cubic and tetragonal phase ratio equals 1:1.

This means that a small concentration of the ferroactive substitution in the A-sublattice causes a broadening of the temperature region of the phase transition in BS10T, in which a lowering of the symmetry of the crystalline structure occurs.

Figures 3 and 4 present the surface of BS10T sample, obtained by SEM with two different magnifications: $2.2 \cdot 10^2$ and $4 \cdot 10^3$. The layers of structure of the material as well as large crystallites (grains) are visible (Fig. 4). This may be related to the statistical distribution of Ba and Sr ions.

Fig. 5 shows a temperature dependence of $\varepsilon'(T)$ for polycrystalline BS10T measured at cooling. A weakly diffuse paraelectric- ferroelectric phase transition between cubic and tetragonal structure is visible.

The measured T_m temperature does not depend on the field frequency and is shifted to lower temperatures compared to pure BT. This is probably an influence of the presence of Sr in the structure of solid solution; pure ST is a paraelectric material down to 105 K. Therefore, the Sr substitution in sublattice A causes a lowering of the temperature T_m,

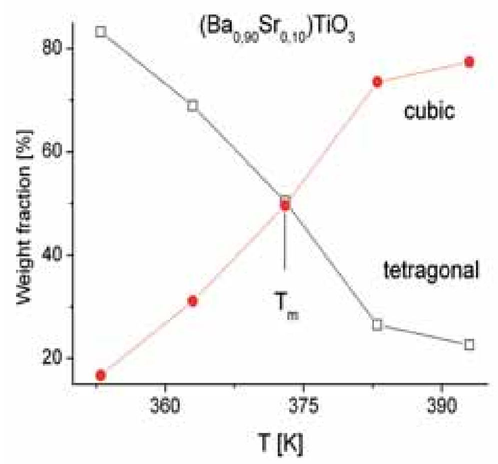

Fig. 2. A weight fraction of cubic and tetragonal phases in BS10T at the temperatures close to T_m.
Rys. 2. Udział fazy regularnej i tetragonalnej w rejonie rozmytej przemiany fazowej BS10T.

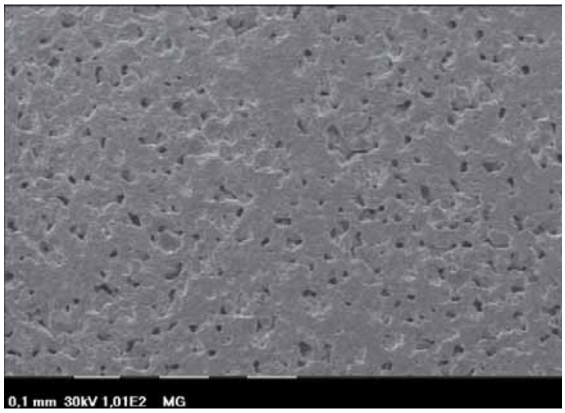

Fig. 3. SEM image of BS10T crystallites (grains); magnification $2.2 \cdot 10^2$.
Rys. 3. Zdjęcie krystalitów (ziaren) BS10T uzyskane metodą SEM przy powiększeniu $2,2 \cdot 10^2$.

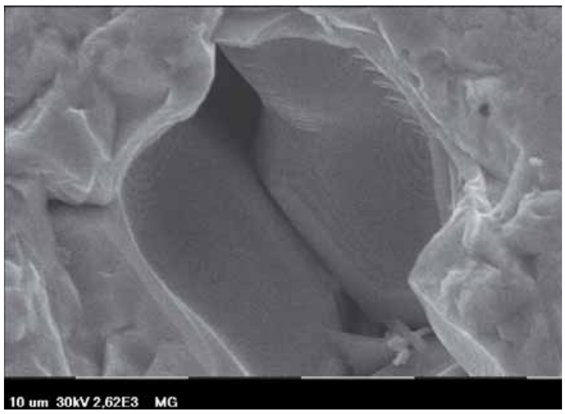

Fig. 4. SEM image of BS10T crystallites (grains); magnification $4 \cdot 10^3$.
Rys. 4. Zdjęcie krystalitów (ziaren) BS10T uzyskane metodą SEM przy powiększeniu $4 \cdot 10^3$.

similar to the effect of the Sn substitution in sublattice B of BTS10 [7]. Both Sr and Sn ions when added to BT causes, to various extent, a diffuseness of phase transition.

In the description of phase transitions in ferroelectric materials the following formula is used [6]:

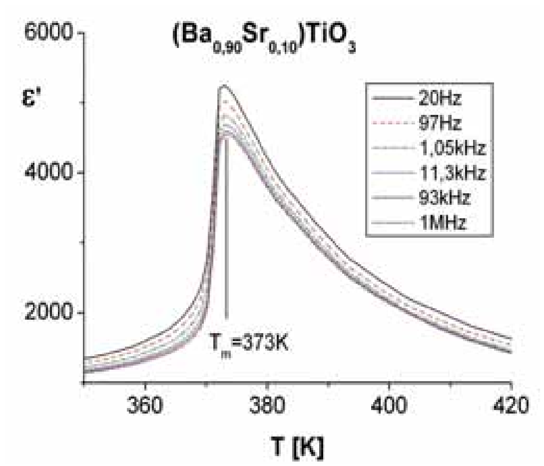

Fig. 5. Real part of electric permittivity ε' for BS10T sample as a function of temperature for various field frequencies.
Rys. 5. Część rzeczywista przenikalności elektrycznej ε' w funkcji temperatury dla BS10T dla różnych częstotliwości pola pomiarowego.

$$\varepsilon'^{-1} = \varepsilon'^{-1}_m + A(T - T_m)^\gamma, \quad (1)$$

where ε'_m is the maximum value of electric permittivity ε', T_m is the temperature of the maximum of electric permittivity ε', A and γ are constant. In the sharp phase transformation, γ assumes value close to 1. In DPT the γ value is close to 2. The γ values for BS10T were calculated from the curves *log* γ ($\gamma = \varepsilon'^{-1} - \varepsilon'^{-1}_m$) versus log*x* ($x = T - T_m$).

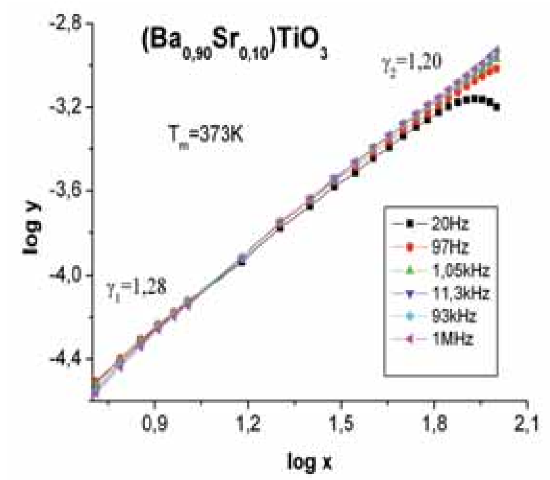

Fig. 6. Logy versus logx for BS10T measured at various field frequencies.
Rys. 6. Zależność logy od logx dla próbki BS10T przy różnych częstotliwościach pola pomiarowego.

The calculated values of γ exponent are contained between 1.20 and 1.28. This testifies that we have a transformation of weakly diffused character. On the other hand it remains in contradiction to the coexistence of the cubic and the tetragonal phases over a broad range of temperatures and needs further studies.

The value of the phase angle close to -90° (Fig. 7) over a broad temperature range testifies to the polar character of this material.

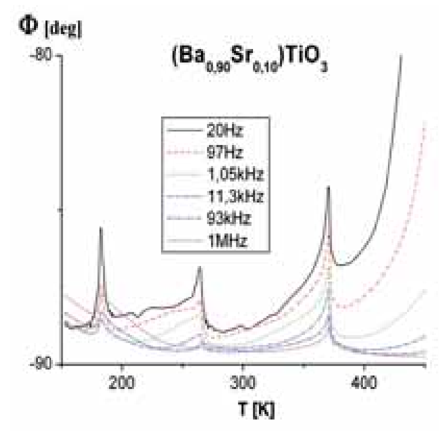

Fig. 7. Temperature dependence of phase angle Φ for the BS10T sample [7] at various field frequencies.
Rys. 7. Zależność kąta fazowego od temperatury Φ dla próbki BS10T [7] przy różnych częstotliwościach pola pomiarowego.

4. Conclusions

The present work reports the results of structural and dielectric measurements of BS10T. It is confirmed that a 10 % substitution of the ferroactive ions Sr (in sublattice A) leads to a lowering of the temperature of paraelectric – ferroelectric PT.

In the presented range of temperatures, ST is a paraelectric material. However, it does not lead to freezing the cubic structure below the temperature of the paraelectric – ferroelectric PT. This behaviour is different compared to $Pb(Cd_{1/3}Nb_{2/3})O_3$ [14] and $Ba(Ti_{0.9}Sn_{0.1})O_3$. In the latter case, nonferroactive Sn ions make transition of BTS10 to tetragonal structure impossible near T_m.

A 10 % concentration of Sr ions in sublattice A of BS10T leads, however, to broadening of the temperature region of coexistence of cubic and tetragonal phases, which is connected to the occurrence of polar regions.

Due to the small value of $\gamma \approx 1.2$ at the paraelectric – ferroelectric PT, BS10T can be classified as the material with the weakly diffused phase transition.

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