



Evolution of electric polarization in paraelectric phase of BaTiO₃

W. Bąk^a, C. Kajtoch^{a,*}, F. Starzyk^b, J. Żmija^c

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

^b Institute of Physics, Cracow University of Technology, ul. Podchorążych 1, 30-084 Kraków, Poland

^c Military University of Technology, ul. Gen. Sylwestra Kaliskiego 2, 00-908 Warszawa 49, Poland

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

Received 10.07.2008; published in revised form 01.10.2008

ABSTRACT

Purpose: The aim of this work has been to study electric properties of polycrystalline BaTiO₃ (BT) at paraelectric phase. On the basis of the obtained results mechanism of dipolar polarization has been discussed.

Design/methodology/approach: Polycrystalline samples of barium titanate were prepared using calcinations method, at the temperature about 1670 K. Dielectric measurements were carried out by means of Quatro Cryosystem 4.0 and Agilent Precision LCR meter HP4284A equipped with WinDETA 5.62 software Novocontrol. The samples were refreshed before measurements by annealing at 700 K. The dielectric measurements were carried out within the frequency range 20 Hz - 1 MHz under cooling with 2 K/min speed.

Findings: The results show occurrence of maxims of dielectric permittivity (ϵ') and phase angle (Φ) within the “cross – over” region. The temperatures related to these maxims depend on the frequency of electric field and are higher for higher frequencies. A positive temperature coefficient (PTC) of conductivity has been found in paraelectric phase of BT.

Research limitations/implications: It has been postulated, on the basis of the obtained results, that at the temperatures above 400 K (paraelectric phase) two types of polarization exist in BT: the polarization due to free dipoles (Pf) and the polarization (Pd) related to polar clusters formed by the dipoles.

Originality/value: The results confirm existence of two types of polarization in paraelectric phase of BaTiO₃.

Keywords: Ferroelectric; Ceramics; Electrical Properties; Phase Transition; Polarization

MATERIALS

1. Introduction

Changes of crystal structure and evolution of cooperative interactions of electric dipoles are of crucial meaning for understanding phenomena in paraelectric phase of ferroelectric materials. They involve phonon-assisted/thermally activated nucleations of ferroelectric domains. They also influence physical properties of low temperature ferroelectric phase and determine a kind of ferroelectric – paraelectric phase transition. This consideration has prompted the authors to undertake the studies on the evolution of electric polarization, at cooling, in paraelectric phase of BaTiO₃ (BT). Such studies can give insight into a

formation of free dipoles and their clustering within “cross – over” region.

Barium titanate exists in 4 structures [1, 2]. In the paraelectric phase, it has a cubic structure. Lowering of the temperature induces, step by step, 3 phase transitions: the first one into tetragonal structure (T) at about 400 K, the next one into orthorhombic structure (O) at about 300 K and finally to rhomboedric one (R) at about 210 K.

The paraelectric – ferroelectric phase transition in BT was a subject of many neutronographic, dilatometric, optical, roentgenographic as well as Raman and infrared investigations [2–7]. The results confirmed the hypothesis of “cross – over” region existence connected with a change of the nature of the structure

evolution from so called “displacive” one (below 650 K) to “order – disorder” type.

Anomalous electric behavior of BT within “cross – over” region can be explained via relation to the formation and clustering of electric dipoles. Clusters appear as a result of short – range interactions between the dipoles. The dipole may be imaged as single elementary cell with ferroactive Ti ion shifted toward (111) direction. The dipole complexes form the chains oriented toward various corners of the cube, so they [4, 5] give no effect in the macro scale. The dipole complexes reveal strong dynamics. This, together with mechanical stresses and high local electric field, oppose their ordering. Polarization, prescribed to the polar regions in the paraelectric phase, is called dipole polarization P_d . Its influence on the thermal expansion of BT in the paraelectric phase is shown in Fig.1.

Dipole polarization was found in many materials. The temperature, at which it appeared, was usually below 650 K (Burns temperature). Spontaneous polarization observed in the ferroelectric phase could be treated as the sum of cooperative polarization and the oriented part of dipole polarization (Fig.1) [2].

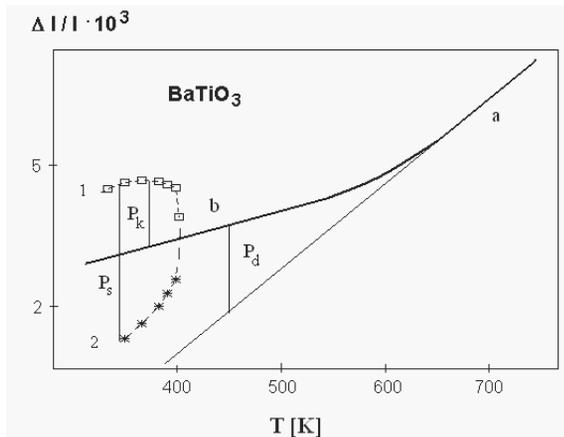


Fig. 1. Thermal expansion of barium titanate during cooling: 1 – without pressure; 2 – under uniaxial pressure $p = 1$ MPa. The data measured with application of the electrical field $E = 2 \cdot 10^5$ V/m; a, b – two ranges of linear dependence in paraelectric phase; P_k – cooperative polarization; P_d – dipole polarization; P_s – spontaneous polarization.

The size of polar clusters, simulated for the temperature close to T_m (maximum values of dielectric permittivity for BT), gave values of the order of 10^{-8} m [8]. The rapid growth of polar regions in the paraelectric phase may be connected with the change of the interaction character. Cooperative character of this interaction manifests itself by increase of the range of the correlation and leads to the creation of the ferroelectric domains (Fig.2).

The present work is aimed at determination of how dielectric properties of pure barium titanate in paraelectric phase change under temperature evolution. The changes are correlated with the polarization. The polarization components are described together with their evolution within “cross – over” region. In the studies, dielectric spectroscopy technique was applied to determine a role of polar phase in the electric conductivity [9-11].

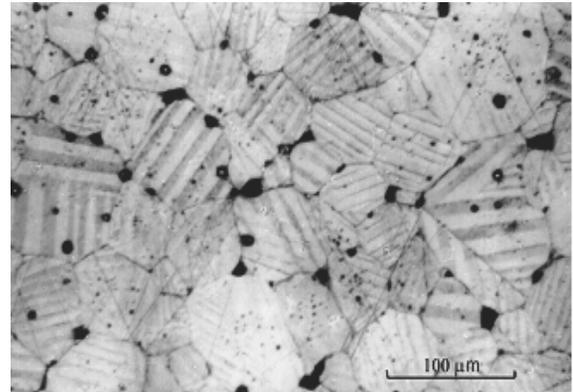


Fig. 2. Polarization microscope image of ferroelectric domains in pure BT.

2. Experimental

Polycrystalline samples of barium titanate were prepared using calcinations method, at the temperature about 1670 K. Dielectric measurements were carried out by means of Quatro Cryosystem 4.0 and Agilent Precision LCR meter HP4284A equipped with WinDETA 5.62 software Novocontrol. The samples were refreshed before measurements by annealing at 700 K. The dielectric measurements were carried out within the frequency range 20 Hz ÷ 1 MHz under cooling with 2 K/min speed.

3. Results and discussion

In this part, the results of dielectric and electric measurements for paraelectric phase of polycrystalline BT samples are presented. The real part of dielectric permittivity $\epsilon'(T)$ was measured within the range 300 K ÷ 723 K (Fig.3). It is the temperature range including paraelectric – ferroelectric phase transition (~ 400 K) and, consequently, the “cross – over” region. The range of the “cross – over” behavior depends strongly on the measuring field frequency. The increase of the frequency shifts the “cross – over” range toward higher temperatures. Simultaneously, the $\epsilon'(T)$ values are lower. The dependence of the phase angle (Φ) on the temperature and the frequency of measuring ac electric field is shown in Fig.4. Above about 400 K, a rapid increase of Φ values (from ~ -90 deg toward ~ 0 deg) is seen. At higher temperatures, for a given frequency, the transient minimum of Φ occurs, followed by local increase. The range of the temperatures with minimal Φ values can be interpreted as that with a dominance of dipolar component of the polarization. It is also seen that the rise of the frequency shifts the local Φ maximum towards higher T. One can postulate, that these local minimum regions are connected with a formation of polar structures within the paraelectric phase and at the paraelectric – ferroelectric phase transition. Fig.5 shows the scheme of the subsequent regions of the formation of free dipoles, arising from free ions, and giving polarization P_f . This kind of polarization has been not reported in the literature.

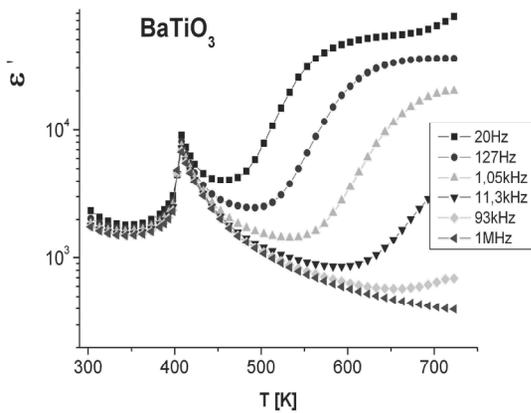


Fig. 3. Dependence of the dielectric permittivity (ϵ') on the temperature (T) and frequency for polycrystalline BT.

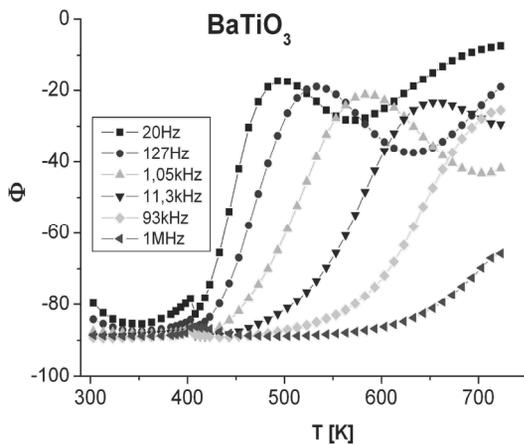


Fig. 4. Dependence of the phase angle (Φ) on the temperature (T) and frequency for polycrystalline BT.

The only confirmations of P_f has been observed in dielectric studies and piroelectric current measurements performed at high temperatures. According to the results, the lowering of the temperature induces polar cluster creation [12]. It means that the behavior of the material is determined by short range electric interactions. At the phase transition, the interactions become long – range and mutual ones (of the ferroelectric character), which leads to the nucleation of the ferroelectric domains.

The T_s in Fig.5 denotes the synthesis temperature, which for BT equals ~ 1200 K. Below this temperature, free charge carriers are present in the sample. These are electrons and ions. They form electronic and ionic conductivity components, as confirmed by the phase angle values $\Phi \approx 0$ and high conductivity σ' (Fig.6). The lowering of T below T_a causes the transition into the A1 region where electric dipoles create. It leads to the creation of P_f polarization, as postulated in this work. It is also manifested by a occurrence of the local minimum of the phase angle (Fig.4), local minimum of σ' and local minimum of σ'' . Further lowering of the temperature results in the creation of the polar clusters where

short – range electric interactions prevail. The contribution of the polar clusters in the conductivity is small (lowering of σ'' , increase of σ' and approaching 0 by Φ). Simultaneously, the strong increase of so called dipolar polarization takes place, which has been confirmed in dilatometric [2, 3] and optical studies [6] (A2 region). Close to the temperature of the paraelectric – ferroelectric phase transition T_c , the softening of the ferroelectric mode occurs. It originates from the delocalization of the ferroactive Ti ion and causes freezing the dynamics of the dipole clusters and the increase of the correlation range. The behavior of the material becomes more susceptible to the external field. Further increase of the correlation length leads to the paraelectric – ferroelectric phase transition and the ferroelectric domains growth. It is reflected by the local minima of σ' and σ'' . It is also connected with the structure lability within the phase transition region where local increase of the number of free charges takes place.

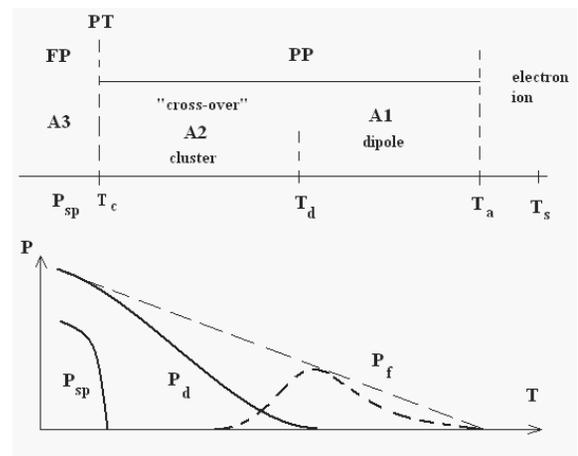


Fig. 5. Evolution of the polarization within paraelectric (PP) and ferroelectric phases (FP) of BT: T_s – temperature of the synthesis; A1 – the range of free dipoles related to the polarization P_f ; A2 – the range of the clusters related to the polarization P_d ; A3 – the range of the ferroelectric phase with the spontaneous polarization P_{sp} .

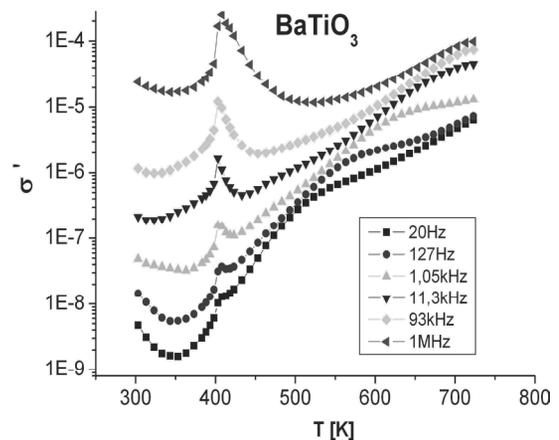


Fig. 6. Temperature dependence of electric ac conductivity (σ') for polycrystalline BT sample.

High contribution of the polarization in the processes within the A2 range is confirmed by the phase angle value close to 0. In the ferroelectric phase there exist ferroelectric domains characterized by the spontaneous polarization P_s . It is connected with the collectivization (P_d) of the clusters created in the “cross – over” region and also with the dipole moment increase related to the displacive effects.

4. Conclusions

The presented results show that a full model of polarization should be based on the cooperative polarization (i.e. dipolar polarization originating from the free dipoles) as a primary component. Such model allows broadening of the interpretation of the results of the electrical measurements performed in the paraelectric phase. The measurements, taken within broader temperature range, have enabled evaluating the changes of the polarization components (free, dipolar – P_d , cooperative – P_k , spontaneous – P_s) in the paraelectric phase and at the paraelectric – ferroelectric phase transition of BT.

It seems that better understanding of the nature of the polarization in ferroelectric materials will be possible in further studies of the nanocomposites [13-17].

References

- [1] Landolet-Boersnstein, New Series 3/3 Springer-Verlag, Berlin-Heidelberg-Nev York, 1969.
- [2] C. Kajtoch, Doctor's thesis Martin-Luther-University Halle-Wittenberg, 1990.
- [3] C. Kajtoch, Dipolar polarisation in $Ba(Ti_{1-x}Sn_x)O_3$, *Ferroelectrics* 172 (1995) 465-468.
- [4] R. Comes, M. Lambert, A. Guinier, The chain structure of $BaTiO_3$ and $KNbO_3$, *Solid State Communication* 6 (1968) 715-719.
- [5] K. Itoh, L.Z. Zeng, E. Nakamura, N. Mishima, Crystal structure of $BaTiO_3$ in the cubic phase, *Ferroelectrics* 63 (1985) 29-37.
- [6] G. Burns, F.H. Dacol, Polarization in the cubic phase of $BaTiO_3$, *Solid State Communication* 42 (1982) 9-12.
- [7] K. Tkacz-Śmiech, A. Koleżyński, W. Jastrzębski, Phase transitions in $BaTiO_3$ from IR auto – correlation spectrum, *Ferroelectrics* 315 (2005) 73-81.
- [8] C. Kajtoch, C. Kuś, M. Burzyńska, Influence of Sn – substitution on the polar region in $Ba(Ti_{1-x}Sn_x)O_3$, *Ferroelectrics* 140 (1993) 293-297.
- [9] W. Bąk, F. Starzyk, C. Kajtoch, E. Nogas-Ćwikiel, Elevated temperature induced dispersion phenomena in $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$, *Archives of Materials Science and Engineering* 29/1 (2008) 5-9.
- [10] F. Starzyk, W. Bąk, C. Kajtoch, M. Gabryś, Influence of electric field DC-component on AC-response of ferroelectric powder, *Archives of Materials Science and Engineering* 29/1 (2008) 36-39.
- [11] C. Kajtoch, W. Bąk, F. Starzyk, M. Gabryś, Study of phase transition specific in polycrystalline $Pb(Cd_{1/3}Nb_{1/3})O_3$, *Archives of Materials Science and Engineering* 29/1 (2008) 20-23.
- [12] F. Gervais, Displacive – order – disorder crossover in ferroelectrics, *Ferroelectrics* 53 (1984) 91-98.
- [13] C. Kajtoch, Electric conductivity of $Ba(Ti_{1-x}Sn_x)O_3$ solid solution, *Materials Science and Engineering* B64 (1999) 25-28.
- [14] C. Kajtoch, Phase transformations in polycrystalline $Ba(Ti_{1-x}Sn_x)O_3$, *Journal of Technical Physics* 38/3 (1997) 557-561.
- [15] J. Ravez, A. Simon, Non-Stoichiometric Perovskites Derived from $BaTiO_3$ with a Ferroelectric Relaxor Behaviour, *Physica Status Solidi (a)* 178 (2000) 793-797.
- [16] A. Buchacz, Influence of piezoelectric on characteristics of vibrating mechatronical system, *Journal of Achievements in Materials and Manufacturing Engineering* 17 (2006) 229-232.
- [17] A. Buchacz, A. Wróbel, Piezoelectric layer modelling by equivalent circuit and graph method, *Journal of Achievements in Materials and Manufacturing Engineering* 20 (2007) 299-302.