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Electric and dielectric properties of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics modified with special glass in the range of phase transition

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Abstract

Perovskite ceramics $(Ba_{0.6}Pb_{0.4})TiO_3$ modified with PbO-B_2O_3-Al_2O_3-WO_3 special glass was prepared with the conventional mixed oxide method. X-ray diffraction analysis (XRD) of the obtained materials confirmed single-phase and pure tetragonal structure. The Rietveld method was used to determine unit cell parameters. Uniform deformation of the tetragonal parameter was observed with addition of the glass. Dielectric measurements revealed the remarkable influence of special glass admixture on the value of dielectric permittivity and dielectric losses, as well as the Curie temperature. However, the most important achievement of the investigations is obtaining a significant PTCR effect in the sample containing 6 wt.% of special glass admixture.

Keywords: *$(Ba_{0.6}Pb_{0.4})TiO_3$, special glass modifier, dielectric properties, PTCR effect*

I. Introduction

The barium lead titanate is one of the best known ferroelectric materials. The ceramics belonging to the system has various applications in electrics and mechatronics as ceramic capacitors, piezoelectric transducers and actuators [1,2], due to their desirable dielectric, pyroelectric and piezoelectric properties [3–5]. For applications in microelectronics, the anomalous positive temperature coefficient of resistance (PTCR) is of particular interest. $(Ba_{0.35}Pb_{0.65})TiO_3$ and $(Ba_{0.2}Pb_{0.8})TiO_3$ ceramics serve as the example of such materials, however they have a very high Curie point, equal to 360 °C and 420 °C, respectively [6–8]. To sum up, $(Ba_{1-x}Pb_x)TiO_3$ (BPT) ceramics is technologically important and the electrical properties thereof should be tailored to practical applications. One way of such modification is the addition of special glass.

Plenty of well-known ferroelectric systems were modified by glass. The presence of molten glass between growing grains during sintering process significantly influences the properties of obtained materials, which has been broadly and exhaustively described in the literature for different glass-ceramics systems. *Inter alia* Divya and Kumar [9] reported the preparation of $[1\text{-}y](Ba_{0.7}Sr_{0.3})TiO_3$–$y(B_2O_3\text{-}xSiO_3)$ glass-ceramics system with the sol-gel method. The investigations of the possible formation of $(Pb,Ba)TiO_3$ solid solution phase in the glassy matrix of BaO-PbO-TiO_2-B_2O_3-SiO_2 system were describe by Mandal *et al.* [10]. The authors discovered that crystal damping occurs in glass-ceramics solely and exclusively when the glass transition temperature of residual glass is higher than the paraelectric-ferroelectric phase transition temperature of the constituent crystalline phase [10,11]. Shyu and Yang [12] investigated the influence of glass admixture on the Curie temperature (T_c) and the spontaneous deformation of tetragonal perovskite phase. The presence of PbO-Al_2O_3-$2\,SiO_2$ as surface layers around grains promotes the coexistence of coarse and fine perovskite crystallites. The increasing concentration of glass admixture causes an increase in the size of crystallites. Moreover, literature reports indicate that the admixture of glass reduces the sintering temperature due to a viscous sintering effect [13] as well as contributes to crys-

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tallites cleaving processes by the diffusion of impurities and defects of the glass layers. The admixture of glass is also the source of additional ions, which improve the properties of based ceramics.

The present paper describes the influence of PbO-B_2O_3-Al_2O_3-WO_3 special glass modification on the electric and dielectric properties of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics. The mentioned glass significantly improves not only crystallization ability, but it is also a source of W^{6+} ions, which replace titanium ions and make the material more attractive for the applications in the field of electronics.

II. Experimental procedure

The process of making special modified glass commenced with the weighting stoichiometric quantities of PbO, B_2O_3, Al_2O_3 and WO_3 which were subsequently milled and mixed together with an agate mortar for 2 h. Melting of the oxides was carried out at 900 °C. Consecutively, the liquid mixture solidified rapidly after being poured onto a steel surface. Consequently, the congealed glass was crushed and milled in a planetary mill for 1 h. At the same time, the fabrication process of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics was carried out on the basis of the following formula:

$$BaCO_3 + 2\,PbO + 5\,TiO_2 \longrightarrow 5\,(Ba_{0.6}Pb_{0.4})TiO_3 + 3\,CO_2\uparrow \quad (1)$$

Proper amounts of oxides and carbonates ($BaCO_3$, PbO and TiO_2) were weighed and milled in planetary mill with the usage of ethanol as a mixing medium. The obtained powder was dried and pressed into pellets. The synthesis process was carried out at T = 950 °C for 4 h. Next, the obtained material was crushed and milled again. The final part of the technological process involved the introduction of the special glass admixture into the base material, in the quantities of 2, 4, 6 and 8 wt.% of the basic ceramics powder. The combined powders were milled in a planetary mill for 24 h in ethanol medium, dried and uniaxially pressed (at 10 MPa) into pellets. First sintering was carried out at T = 1050 °C for 4 h and consecutively the milling procedures were repeated. Final sintering was conducted at T = 1200 °C for 4 h. In both sintering steps, the pressed pellets were placed in a double crucible with some amount of PbO, in order to avoid the loss of PbO caused by its sublimation and to maintain the established composition.

The obtained samples became the basic material for further study and analysis. The crystalline structure of the obtained ceramic samples was tested with the usage of X-ray diffraction (XRD). Measurements were performed on powdered samples using a high resolution INEL Diffractometer with filtered Cu Kα_1 radiation (40 kV, 30 mA). Microstructure of the discussed ceramics was tested with scanning electron microscope (SEM; JEOL JSM-7100 TTL LV, Japan). Grain size measurements were performed on the fractured surface of ceramic samples, which were coated with gold to provide electrical conductivity and to avoid any charging effects. The investigations of dielectric permittivity as a function of temperature were carried out in the range of 0.1–20 kHz by using Quadtech 9200 LCR meter. DC electric conductivity as a function of temperature was investigated with an automatic system based on Keithley 6485 picoammeter.

III. Results and discussion

3.1. Crystal structure

XRD studies were carried out in order to determine the influence of special glass admixture on the crystal structure of the obtained ceramics. X-ray diffraction patterns of the discussed materials are presented in

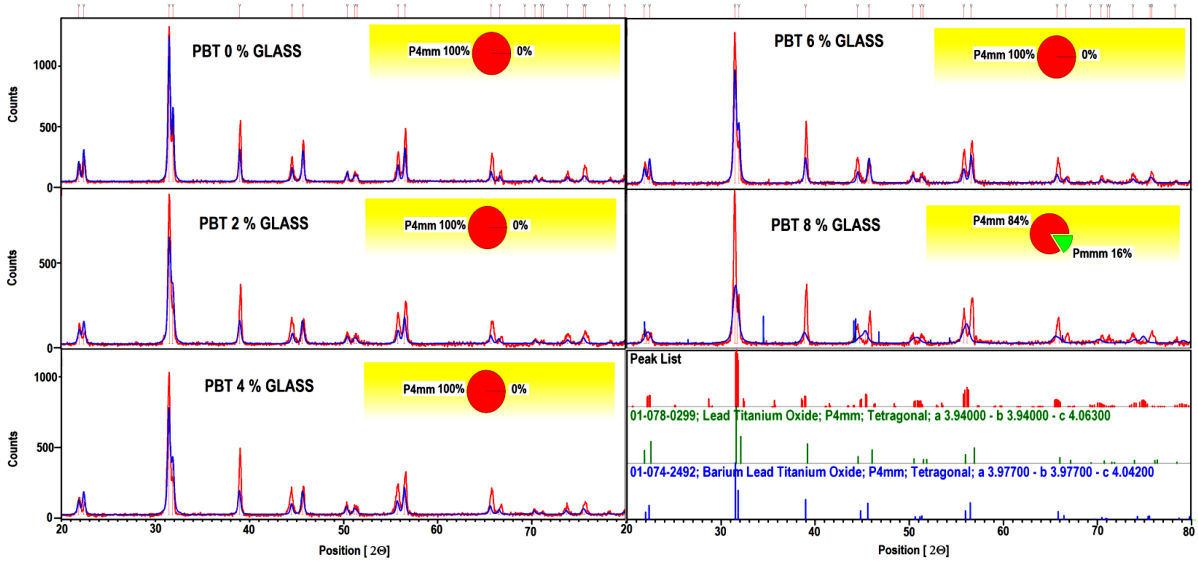

Figure 1. Evolution of X-ray diffraction peaks of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics with increasing concentration of PbO-B_2O_3-Al_2O_3-WO_3 glass

Table 1. Value of lattice parameters, deformation coefficient, theoretical and experimental density of special glass modified $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics

Sample	Lattice parameter		V	δ_T	ρ_t	ρ_{exp}
	a [nm]	c [nm]	[nm^3]		[kg/m^3]	[kg/m^3]
PBT – 0% glass	0.3959	0.4057	6.3588	0.0247	6869.7	5743
PBT – 2% glass	0.3958	0.4059	6.3587	0.0258	6869.8	5826
PBT – 4% glass	0.3957	0.4061	6.3586	0.0262	6869.9	6131
PBT – 6% glass	0.3955	0.4063	6.3553	0.0273	6873.5	6348
PBT – 8% glass	0.3954	0.4065	6.3552	0.0280	6873.6	6411

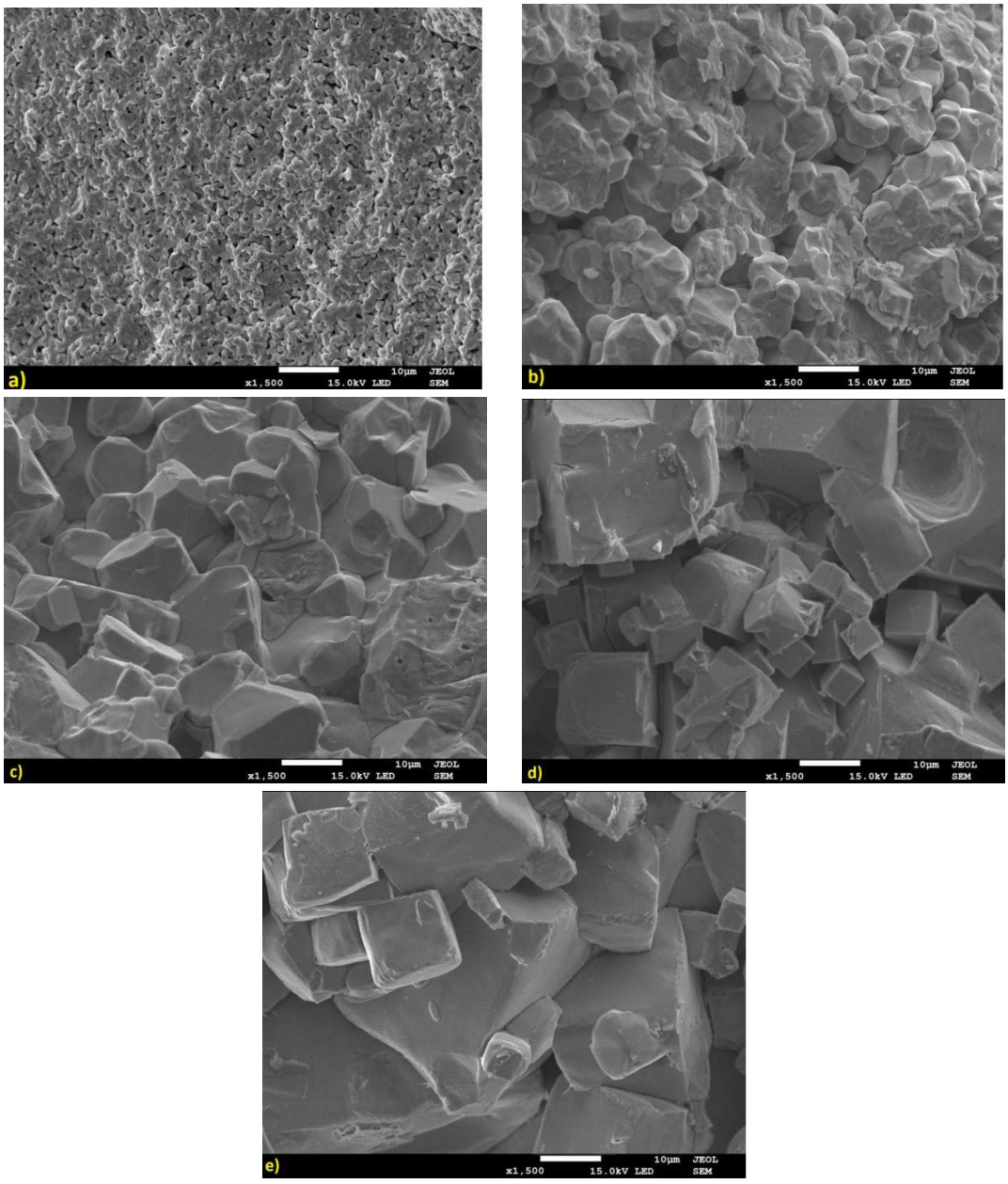

Figure 2. SEM images of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics with: a) 0, b) 2, c) 4, d) 6 and e) 8 wt.% of glass

Fig. 1. The intensity of diffraction maxima decreased with the increase of glass modifier amount. The location and intensity of all diffraction lines in the range of measured angle were compared with the reference patterns from JPCDS-ICDD database. The results of the analysis indicate that at room temperature, the materials are single-phase and exhibit a tetragonal structure ($a = b \neq c, \alpha = \beta = \gamma = 90°$). The symmetry of the crystal lattice may be described by space group ($P4mm$) belonging to the class of tetragonal bipyramids and has four planes of symmetry intersecting in a fourfold symmetry axis of the pole. The Rietveld method was used to determinate the unit cell parameters, volume (V) and uniform deformation of the tetragonal pa-

rameter ($\delta_T = |1 - c/a|$). The values of δ_T coefficients for all ceramics are collected in Table 1.

The observed change of δ_T indicates that the admixture of lead-boron glass is connected with a simultaneous decrease of a parameter and an increase of the c unit cell parameter, resulting in a unit cell volume change (Table 1). The observed reduction of V with the increase of glass admixture amount can be attributed to the partial substitution of Ti^{4+} ions with W^{6+} ions. The process may be described with the following chemical reaction:

$$(Ba^{2+}_{1-x}Pb^{2+}_{x})Ti^{4+}O^{2-}_{3} + yW^{6+}O^{2-}_{3} \longrightarrow (Ba^{2+}_{1-x}Pb^{2+}_{x})(Ti^{4+}_{1-y}W^{6+}_{y})O^{2-}_{3} + ye^{-} \quad (2)$$

Tungsten ions are smaller than the titanium ions – the atomic radius of tungsten is 0.137 nm, and the ionic radius for W^{2+} is 0.042 nm, whereas the titanium atomic radius and ionic radius are 0.1460 nm and 0.0605 nm, respectively. The observed decrease of BPT unit cell volume might be a direct confirmation of the incorporation of tungsten ions in $(Ba_{0.6}Pb_{0.4})TiO_3$ lattice. On the basis of the results of XRD measurements and the weight of unit cell theoretical density (ρ_t) was determined, whereas the Archimedes displacement method was used to obtain experimental density (ρ_{exp}). Values for both densities are given in Table 1. The admixture of glass caused a growth of the ρ_{exp}/ρ_t ratio and improved the quality of ceramics. The aforementioned may be attributed to the phenomena which occurred during the sintering processes. At high sintering temperature the added glass forms a liquid phase, which has two roles: fills empty places and assists the process of grains movement. As a result, the volume occupied by grains decreases significantly and the content of pores reduces drastically.

The microstructure of the ceramics is shown in Fig. 2. The microstructure of the pure $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics is characterized by small grains with a rounded shape. Moreover, the grain boundaries are not very well developed. The addition of 2 wt.% of special glass changed the microstructure. Namely, the ceramics consists of larger grains, which are well-shaped and angular. The angular shape of grains is also characteristic for the ceramics with 4 wt.% of glass. Higher concentration of admixture results in a change of the shape into cubic grains. An increase in grain size occurs simultaneously. Changes of grains size caused by glass admixture were described by other authors [14,15]. Moreover, SEM images revealed that during the process of fracturing of the ceramics modified with special glass fractures occurred through grains (transcrystalline cracks), which indicates significant hardness of the ceramics and a high degree of packing.

3.2. Electric and dielectric properties

The next stage of the research was to determine the temperature dependence of dielectric permittivity (ε). This dependencies for the pure $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics are presented in Fig. 3.

The obtained material at room temperature shows a low ε value, not exceeding 300. This value is almost completely frequency-independent and changes insignificantly up to 450 K. Nonetheless above that point a rapid increase of ε takes place. The maximum of dielectric permittivity (ε_{max}) is achieved at temperature T_c = 598 K and the value is frequency dependent. The observed anomaly is characteristic for ferroelectric-paraelectric phase transition. The comparison of presented results with results described by Chaimongkon *et al.* [16] shows that the $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics obtained with the conventional mixed oxide method exhibit a higher value of dielectric constant and the Curie temperature than the same ceramics obtained with the combustion technique [16].

The temperatures corresponding to the maximum of dielectric permittivity and the minimum of loss factor are consistent, which is a feature characteristic for the classic ferroelectric-paraelectric phase transition. The loss factor in the vicinity of the temperature of phase transition also strongly depends on the frequency of applied electric field (Fig. 3). Describing temperature de-

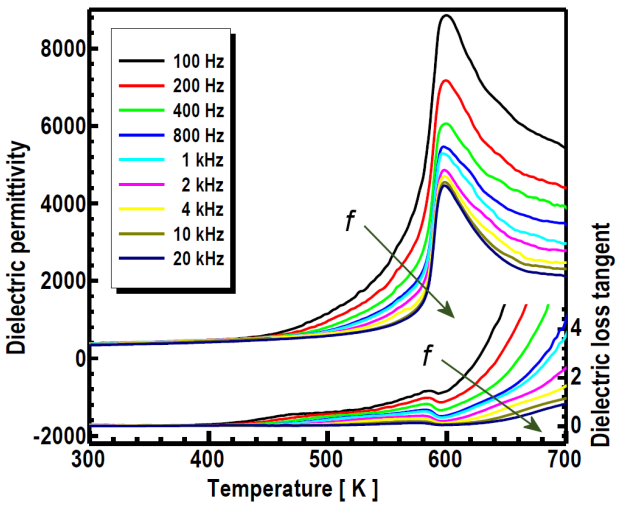

Figure 3. Dielectric constant and loss factor as a function of temperature, measured at various frequencies

Table 2. Characteristic data obtained from dielectric measurements

Sample	T_c [K]	ε at T_r	ε_{max} at T_c	$\tan\delta$ at T_r	$\tan\delta$ at T_c
PBT – 0% glass	598	276	5250	0.02	0.30
PBT – 2% glass	601	294	5990	0.02	0.23
PBT – 4% glass	600	584	17490	0.12	0.89
PBT – 6% glass	598	11600	41700	0.29	1.02
PBT – 8% glass	597	9085	32570	0.43	0.77

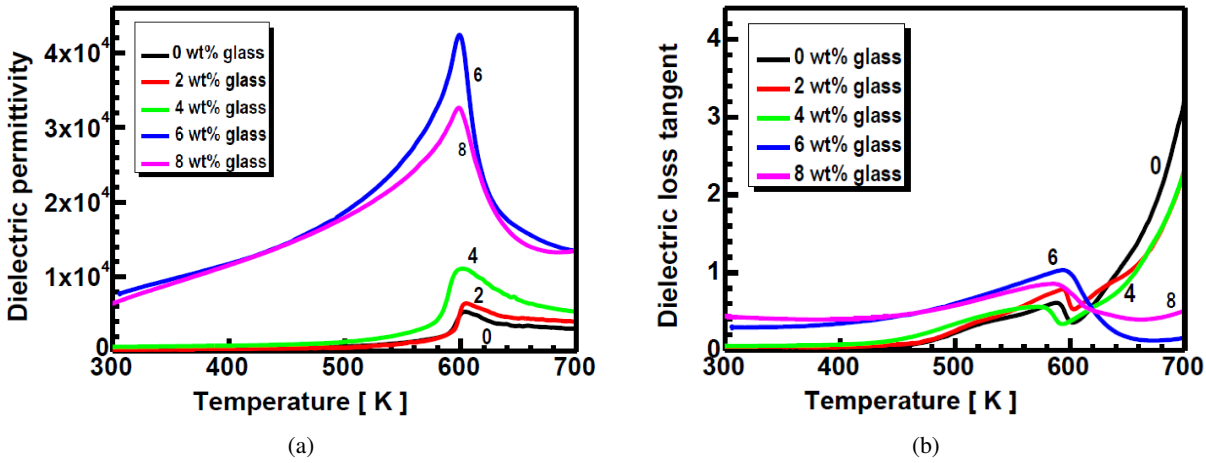

Figure 4. Dielectric permittivity (a) and loss factor (b) as a function of temperature, measured at frequency 1 kHz, for $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics with various glass contents

pendence of tan δ, extremely low value at room temperature should be emphasized (Table 2).

Introduction of a small amount of special glass to the base material caused an increase of both dielectric permittivity and loss factor values, which can be attributed to the elimination of micropores in the ceramic bodies [15]. The changes of dielectric properties are particularly visible for the higher concentrations of modifier (6 and 8 wt.%), as can be seen in Fig. 4. Also, the temperatures of phase transitions shifted to the lower values (Table 2).

The described changes are caused by a partial substitution of titanium ions with tungsten ions in the sublattice B of perovskite structure, which is compliant with the results of XRD measurements. The special glass modifier was added to the pure BPT ceramics in order to create the PTCR effect. The results of XRD and dielectric measurements seem to confirm the assumed thesis about the role of liquid phase in the prevention of lead escape, as well as the partial exchange of titanium ions by tungsten ions, deriving from special glass.

Such scenario should be reflected in the changes of DC conductivity. Namely, the pure BPT ceramics is characterized by a significantly higher concentration of lead vacancies in comparison with the oxygen vacancies, resulting in a p-type conductivity. The introduction of W^{6+} ions to the lattice should change the type and value of conductivity. In order to finally confirm the thesis DC measurements were conducted in a wide range of temperatures. The results are presented as a graph of resistivity versus temperature in Fig. 5.

The obtained results indicate that the introduction of tungsten ions to crystalline lattice is a two-step process. The first step involves the insertion of a small concentration of W^{6+} ions, which exchange the titanium cations. The process is associated with the appearance of redundant electrons in order to keep the electric neutralit, Eq. 2. These electrons are responsible for decreasing the concentration of holes, which leads to a decrease in conductivity. The second step is connected with an increase of tungsten concentration and, consequently, an increase of the concentration of redundant electrons. The number of electrons is high enough not only to neutralize the holes, but also to create an additional donor level. As a result, the ceramics with high concentration of glass modifier reveals the n-type conductivity.

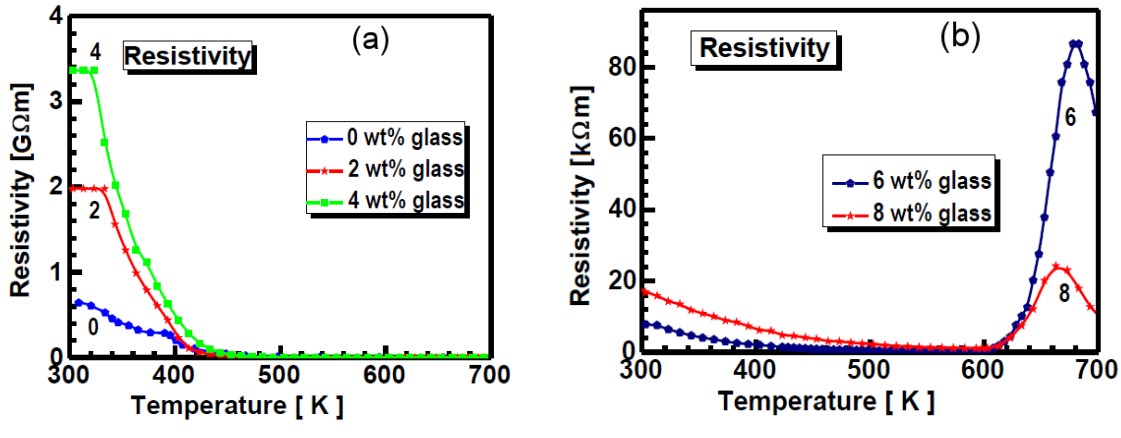

Figure 5. Electric resistivity vs temperature for $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics with various glass contents

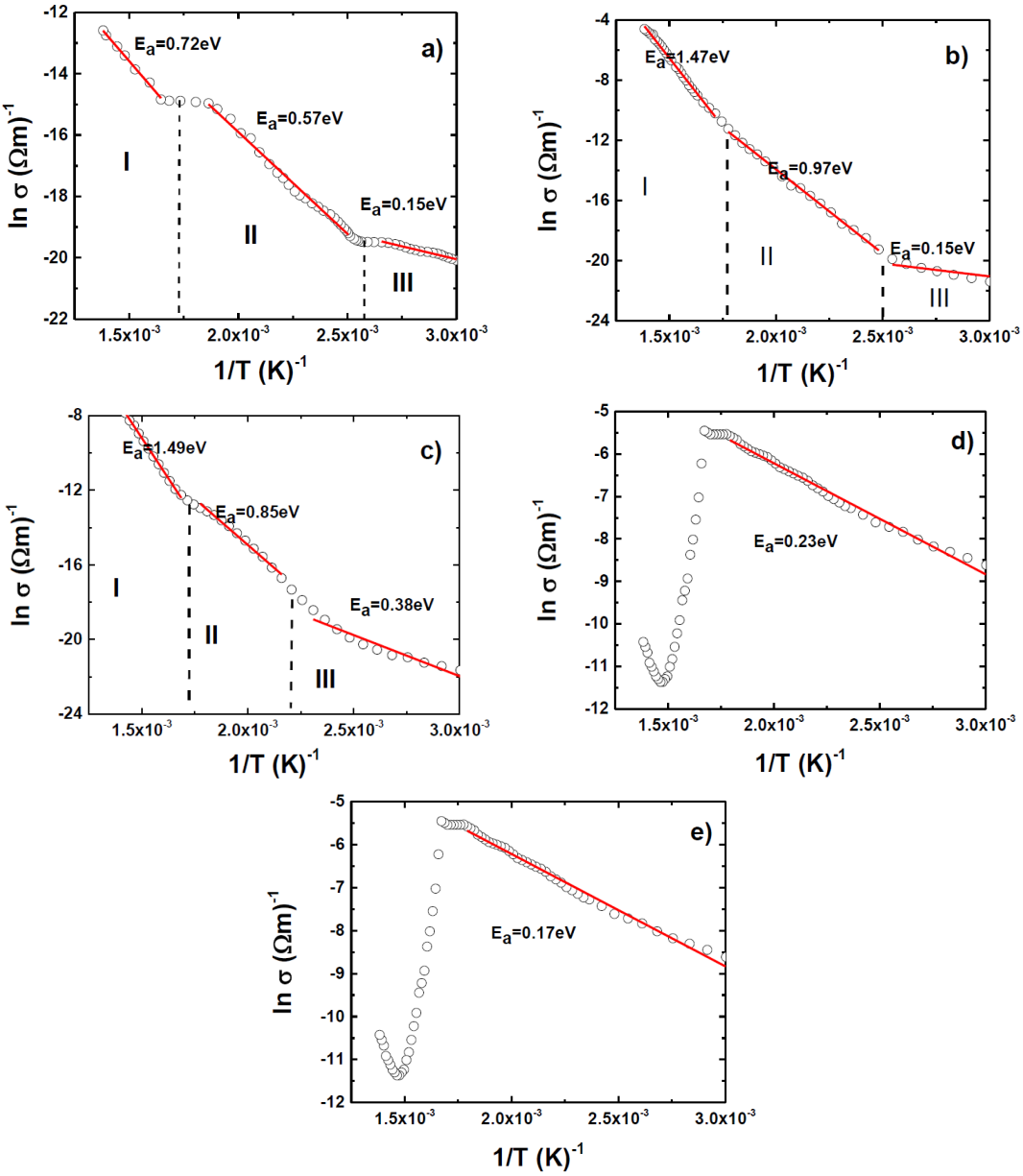

Figure 6. Natural logarithm of electric conductivity vs inverse temperature for $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics with: a) 0, b) 2, c) 4, d) 6 and e) 8 wt.% of glass

Electrons from ionized donors are trapped by acceptors at the grain boundary and the potential barrier is created [17]. The barrier makes the grain boundary more resistive than the grain interior. Heywand [1] attributed the resistivity jump, above the Curie temperature, to the change of dielectric permittivity in grain boundaries. Jonker [18] explains the low resistivity observed below T_c with the presence of spontaneous polarization, which effectively cancel out the barrier potential in regions along the grain boundary.

The dependences of $\ln\sigma$ vs $1/T$ for all discussed ceramic materials are shown in Fig. 6. In case of the pure $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics as well as ceramics modified by a small amount of glass (up to 4 wt.%) plots consist of three linear segments with different slopes. The linear shape of segments indicates the activation character of conductivity and allows to determine the activation energy of processes. The temperature of boundary between I and II is close to the Curie temperature. The value of activation energy of paraelectric phase is higher than ferroelectric phase, which is connected to the change of distance between atoms. The change of distance is responsible for a change of band gap width and the position of dopant levels. The second reason of such behaviour is the change of effective polarization value connected with disappearance of domain structure and spontaneous polarization. The second change of segments slopes (between area II and III) is probably related to the transition between free electron states in the conduction band (spontaneous conductivity in area II and the conductivity of dopant in area III).

The image of conductivity drastically changes in case of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics modified with 6 and 8 wt.% of special glass. Solely and exclusively one

change in the slope of linear segments in plots $\ln \sigma(1/T)$ is observed. It takes place at the temperature of phase transition. This change is related both to the transition between the ferroelectric and paraelectric phases, as well as to the transition to the region with a positive temperature coefficient of resistance.

IV. Conclusions

The technology described above allows to obtain the single-phase ceramics, which was confirmed by the XRD results. The admixture of special glass improved the quality of ceramics and had an influence on the dielectric behaviour and DC conductivity. The value of dielectric permittivity increases with an increasing concentration of glass additive. All investigated ceramics are characterized by fairly sharp transition from ferroelectric to paraelectric phase. The temperature of the transition shifts to lower values with an increasing glass concentration in the material. For ceramics containing a higher concentration of glass, the PTCR effect is observed in graphs presenting the temperature dependences of ceramics resistivity. The results are explained according to Heywang's and Jonker's models. The barrier formed at grain boundary regions acts as a trap for electrons available from ionized donors and provides a positive temperature resistivity coefficient.

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