The influence of the Zr/Ti content of the PZT ceramics obtained by sol-gel method on the electric conductivity

A. Zarycka, R. Zachariasz, M. Czerwiec, J. Ilczuk and J. Rymarczyk

Department of Material Science, Faculty of Computer Science and Material Science, University of Silesia, 3 Żeromskiego St., 41-200 Sosnowiec, Poland
azarycka@us.edu.pl; rzachari@us.edu.pl

Abstract. In this work, the results of investigations of the PZT ceramics, received on the base of two - component solid solutions $Pb(Zr_xTi_{1-x})O_3$ are presented. The samples were obtained by conventional ceramic sintering method with nanopowders received in the sol-gel method. The temperature dependencies of the electric conductivity σ for all samples, with different content Zr/Ti ($0.35 \leq x \leq 0.65$), in the range temperatures of 300÷750 K, were performed. On the base of the $\ln\sigma T = f(1/T)$ dependencies, the activation energy E_a was calculated. The determined values of the E_a were limited in the range 0.53÷0.71 eV for ferroelectric phase as well as 0.75÷0.80 eV for paraelectric phase.

1. INTRODUCTION

The electric conductivity of the PZT type ceramics has complex electron-ion character. The main contribution in conductivity has electron component but attendance and distribution of ion vacancies (quantity of defects in the structure) makes possible to flow of electrons, too [1]. In the case of polycrystalline and multiphase ceramic materials, electric properties can be changed, for example by the modification of their chemical composition. In the PZT type ceramic materials it take place by the change of Zr/Ti ratio and also by using various dopants in the basic chemical composition. The value of the electric conductivity σ of the ceramic materials is most frequently describes by obtaining the temperature dependencies of the density of current j or the intensity of current I with constant values of electric field. On the base of the values, the electric conductivity σ is calculated [2].

2. MATERIALS AND RESULTS

In the work, the temperature dependencies of electric conductivity σ for all ceramic samples in the range of temperatures 275÷750 K are obtained. The investigated material is the PZT type ceramics obtained by the sol-gel method with different Zr/Ti content, it means: from ferroelectric rhombohedral phase with content Zr/Ti=65/35 (PZT65/35), from morphotropic area with content Zr/Ti=48/52 (PZT48/52) and ferroelectric tetragonal phase with content Zr/Ti=35/65 (PZT35/65) [3]. Obtained dependencies are shown on **figure 1**.

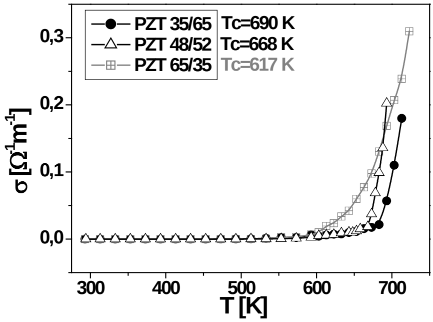

Figure 1. The temperature dependencies of the electric conductivity σ for investigated PZT type ceramic samples.

The temperature changes of the electric conductivity σ are the results of the changes in concentration of carriers of electric charge or their activity. The value of the electric conductivity in the room temperature takes place on the border between values typical for dielectrics and semiconductors. The temperature dependencies of the electric conductivity take a typical form for semiconductors [1]:

$$\sigma = \sigma_o \exp\left(-\frac{E_a}{k_B T} \right) \tag{1}$$

where: σ_o – electric conductivity for T → ∞, E_a – the activation energy of carriers of electric charge, k_B – Boltzman constant, T – absolute temperature.

The electric conductivity could be changed by the external factors which cause changes in sorts of the centers of dissipation. In the case of the PZT type ceramics the centers of dissipation are: dopants, thermal vibrations of lattice, point defects, domain boundaries. Considering the fact of the phase transition in Curie temperature (T_C), the role of the centers is different in both- ferroelectric and paraelectric phases. The characteristic changes of the electric conductivity are observed for all investigated samples after deep analyses of the dependencies σ = f(T) (**fig. 1**). In the range of low temperatures, till the point of phase transition (T_C), the value of electric conductivity σ is low and is limited in the range $10^{-7}÷10^{-3}$ $\Omega^{-1}m^{-1}$. So low value of the electric conductivity is connected with changes which take place in material structure such as: dissipation of energy on the domain boundaries and point defects which occur during technological process of obtaining investigated material. The rapid increase of the electric conductivity which is mainly connected with disappearance of domain structure (the centers of dissipation of energy) is observed in paraelectric phase (above T_C) for all obtained dependencies σ = f(T).The values of electric conductivity σ as a function of content Zr/Ti for this area are in the range $5\times10^{-3}\div3\times10^{-1}$ $\Omega^{-1}m^{-1}$. The shift of the phase transition point (T_C) towards higher temperatures with increasing of $PbTiO_3$ content, is observed too. This phenomenon takes place for all investigated chemical compositions, what is typical for PZT type ceramic materials [4].

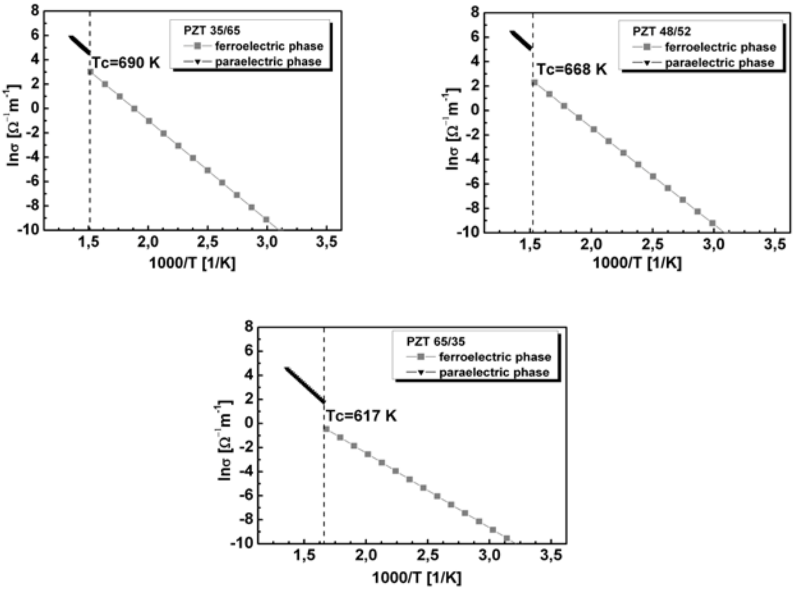

Figure 2. The temperature dependencies of the lnσ = f(1/T) for examined samples of the PZT ceramics.

The changes of the electric conductivity σ as function of temperature were obtained for both phases (ferroelectric and paraelectric). The results are shown as dependencies lnσ = f(1/T) (fig.2). On the base of this the energy of activation E_a was calculated for all investigated PZT type ceramics. The changes of gradient (inclination) of rectilinear parts on the dependencies lnσ = f(1/T) are observed. This phenomenon takes place near the point of phase transition ferroelectric ↔ paraelectric (T_C), as well as for both phases for all investigated samples. The values of the energy of activation are compared in the **table 1** and calculated on the base of analysis of angles of gradient (inclination) of particular straight lines in both phases. It is clearly shown that with increasing of $PbTiO_3$ content (ferroelectric hardness) the energy of activation E_a increases, too (0.53÷0.71 eV respectively for PZT65/35÷PZT35/65 – ferroelectric phase). In the paraelectric phase differences between calculated values of the activation energy are small (E_a = 0.75÷0.80 eV).

For samples PZT65/35, a clear growth in the values of activation energy (from 0.53 eV for ferroelectric phase to 0.80 eV for paraelectric phase) in comparison to PZT35/65 (from 0.71 eV to 0.75 eV).

Table 1. The values of activation energy E_a for investigated PZT type ceramics.

PZT	E_a [eV] ferroelectric phase	E_a [eV] paraelectric phase
PZT65/35	0.53±0.01	0.80±0.01
PZT48/52	0.68±0.01	0.77±0.01
PZT35/65	0.71±0.01	0.75±0.01

3. CONCLUSIONS

The interpretation of obtained results in investigation of the electric conductivity for polycrystalline PZT type ceramics is very important because of special properties of these materials. The investigations were obtained for wide range of content Zr/Ti in the same well known technological conditions. The authors proved, that the changes in Zr/Ti content in PZT type ceramics obtained by sol-gel method, have clear influence on the temperature dependencies of the electric conductivity. The electric conductivity increase with the growth of $PbTiO_3$ (ferroelectric hardness); it is caused by increase of grains size (increase of quantity of structural defects). The increase of quantity of structural defects caused the growth of carriers of electric charge. As a proof of this phenomenon the increase of energy of activation E_a from 0.53 eV for content Zr/Ti = 65/35 to 0.71 eV for content Zr/Ti = 35/65, was observed too. This fact is directly connected with appearance of additional centers of dissipation of energy.

Acknowledgments

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