

EFFECTS OF γ IRRADIATION ON THE ELECTRIC CONDUCTION OF PZT CERAMIC SYSTEM

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In the work, the results of investigations of the electric conduction σ of the PZT ceramics with the two following compositions: $\text{Pb}_{0.94}\text{Sr}_{0.06}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3 + 0.25\%$ wt. Cr_2O_3 (hard material) and $(\text{Pb}_{0.9}\text{Ba}_{0.1})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + 1.67\%$ wt. Nb_2O_5 (soft material), are presented. The “soft” ceramics are characterized by high electric values ($\varepsilon_{33}^T/\varepsilon_0 > 1300$ (in room temperature), $d_{31} = 120 \cdot 10^{-12}$ C/N) and electromechanical coupling coefficient ($k_p > 0.5$). Due to good parameters it is used in electromechanical transducers of low frequency. The “hard” PZT ceramics, which are used in resonators, filters and ultrasound transducers are characterized by the following parameters: $\varepsilon_{33}^T/\varepsilon_0 > 900$ (in room temperature), $d_{31} = 65 \cdot 10^{-12}$ C/N and electromechanical coupling coefficient $k_p > 0.35$. The temperature dependences of the electric conduction σ for all samples before and after γ irradiation with dose of 20 kGy were performed. The activation energy E_a was calculated on the basis of the $\ln \sigma = f(1/T)$ dependences.

Key words: electric conduction, PZT materials, γ radiation, activation energy.

1. Introduction

The band theory of a solid body provides a classification criterion as far as electrical properties for all materials are concerned. According to this theory when a conduction band overlaps with a basic band we deal with a conductor, when an energy break between the bands is of an order of several electron volts a material is a non-conductor. Materials with the energy break of order of a fraction of the electron volt show semi-conductor properties. In dielectrics (majority of ceramics and glass) electrons are bounded strongly with atoms and only their excitation e.g. thermal, optical or by an action of a strong magnetic field they can be moved to the conduction band and conduction can be induced.

Electric conduction of the PZT type ceramics shows a complex electron-ion character. The electron component contributes mainly to conduction, but presence and distribution of ion vacancies (structures with defects) create conditions for the flow of electrons [1]. In case of polycrystalline and multi-phase ceramic materials electric properties can be changed, among other things, by modifying a chemical composition. In the ce-

ramic of the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ type, having a structure of the ABO_3 perovskite type, it takes place by both changing Zr/Ti content and using different admixtures in the basic chemical composition. Traditional admixtures added to PZT can be divided into isovalence ones substituted for A ions and heterovalence ones placed in B positions [2, 3]. Isovalence doping does not lead to the formation of cation and anion vacancies. In case of isovalence modifiers general effects of doping cannot be given explicitly. Heterovalence admixtures however can be divided into two groups. In the first case the PZT type ceramic becomes ferroelectrically soft (SF – soft ferroelectrics), whereas in the second case – ferroelectrically hard (HF – hard ferroelectrics). Soft admixtures result in a decrease in electric conductivity of PZT of p type, because they are a source of electrons, which lower the concentration of positive holes. Atoms, among other things, of such elements as: Nb^{5+} , Ta^{5+} , W^{6+} , Sb^{5+} are included into such admixtures. Hard admixtures lead to an increase in a value of electric conduction of PZT of p type, due to an increase in the concentration of positive holes. The most often used hard admixtures are: Fe^{3+} , Al^{3+} , Cr^{3+} , Co^{2+} , and Mn^{2+} .

Investigation results of electric conduction for the PZT type ceramic with two different chemical compositions, in which a soft admixture of the Nb_2O_5 niobium oxide and hard one of the Cr_2O_3 chromium oxide were used, are presented in the work.

2. Material and experimental procedures

Temperature examinations of dependences of the σ electric conduction for the obtained ceramic specimens in the temperature range of $290 \div 700$ K, at the constant heating rate being 3 K/min, were made in the work.

The “soft” ceramics of the PZT type has the following chemical composition: $(\text{Pb}_{0.9}\text{Ba}_{0.1})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + 1.67\%$ wt. Nb_2O_5 and it has Nb^{5+} ions in positions B and Ba^{2+} ions occupying positions A in the perovskite structure. The material with the following chemical composition: $\text{Pb}_{0.94}\text{Sr}_{0.06}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3 + 0.25\%$ wt. Cr_2O_3 with Cr^{3+} ions in positions B and Sr^{2+} ions in positions A, is a “hard” ceramics of the PZT type.

The ceramics were obtained from adequately prepared ceramic powders of high homogeneity by the conventional ceramic sintering method (CCS). Ceramic blocks obtained in such a way were heated at the temperature of 1250 K for 2 h. Specimens in a shape of rectangular prism plates with dimensions $(30 \times 10 \times 0.9)$ mm³ were formed from the blocks obtained. Then, the specimens were ground and polished and silver paste electrodes were coated on their surfaces.

The “soft” ceramics are used in electromechanical transducers of low frequency. The “hard” PZT ceramics are used in resonators, filters and ultrasound transducers [4].

As it has been mentioned earlier, depending on a type of the material and admixtures in it electric conduction can have electron-ion or mixed character. It can change additionally under the influence of external factors, such as irradiation, which causes a change in a mechanism of scattering of carriers under an influence of a change in a type of dissipation centers. In case of the ferroelectric ceramics such scattering centers can include: admixtures, thermal lattice vibrations, dislocations, point defects, domain

boundaries. A role of such centers because of a phase change taking place at Curie temperature is different in the ferroelectric and paraelectric phase. In order to investigate those phenomena, some of the ceramic specimens were irradiated with the γ radiation. The radiation source was the Co^{60} cobalt isotope. The specimens after the irradiation were placed in the radiation chamber and by changing the exposure time the doses of energy absorbed by the specimens of the value of 20 kGy were obtained [5].

3. Results and discussion

Temperature changes in the σ electric conduction for the specimens of the “soft” and “hard” ceramics are presented in Figs. 1 and 2. They result from the change in the concentration of charge carriers or their mobility. If the concentration of carriers is constant, an increase in their mobility is the reason for an increase in conduction with the temperature. A value of electric conduction at room temperature is on the border line of the conduction value for dielectrics and semi-conductors, and the temperature dependence of electric conduction has a form typical for semi-conductors [1]:

$$\sigma = \sigma_o e^{-E_a/k_B T}, \quad (1)$$

where σ_o – electric conduction for $T \rightarrow \infty$, E_a – activation energy of a charge carrier, k_B – Boltzman’s constant, T – absolute temperature.

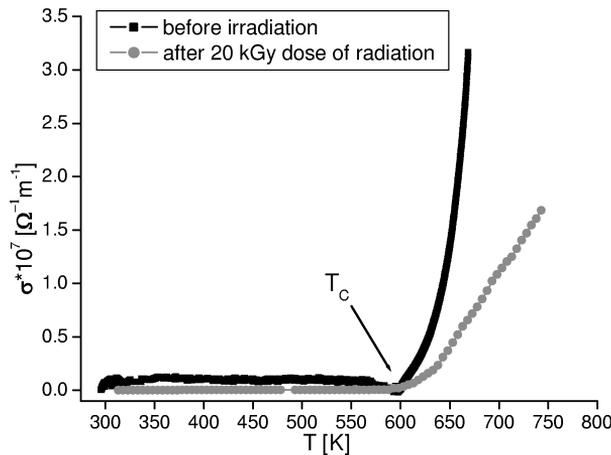


Fig. 1. Dependences $\sigma = f(T)$ obtained for the examined “soft” ceramics.

Analyzing the obtained $\sigma = f(T)$ dependences for both ceramics certain characteristic changes in conduction can be noticed for the specimens in question: in the low temperature range to the phase change point (Curie temperature – T_C) a value of electric conduction for both ceramics is low and it is: about $10^{-8} \Omega^{-1}\text{m}^{-1}$ in case of the “soft” ceramics and about $10^{-7} \Omega^{-1}\text{m}^{-1}$ in case of the “hard” ceramics, respectively. Such a low value of the electric conduction is connected, among other things, with the changes taking place in the material: dissipation of energy on the domain and point de-

fects formed in the technological process of the material production. Still lower values of electric conduction are for both ceramics irradiated with 20 kGy dose of the γ radiation: in case of the “soft” ceramics about $10^{-10} \Omega^{-1}\text{m}^{-1}$, and for the “hard” ceramics about $10^{-8} \Omega^{-1}\text{m}^{-1}$. It is connected with the formation of additional dissipation centers as a result of the irradiation (point defects). In the paraelectric phase (above T_C) for all determined $\sigma = f(T)$ dependences a rapid growth of conduction, connected mainly with disappearance of the domain structure, what results in disappearance of centers of dissipation of energy, is observed. The σ values, depending on the samples, are: for the specimens before the irradiation: the “soft” ceramics – about $3 \times 10^{-7} \Omega^{-1}\text{m}^{-1}$, the “hard” – about $5 \times 10^{-4} \Omega^{-1}\text{m}^{-1}$; for the specimens after the irradiation: the “soft” ceramics – about $10^{-7} \Omega^{-1}\text{m}^{-1}$, the “hard” ceramics – about $10^{-4} \Omega^{-1}\text{m}^{-1}$, respectively.

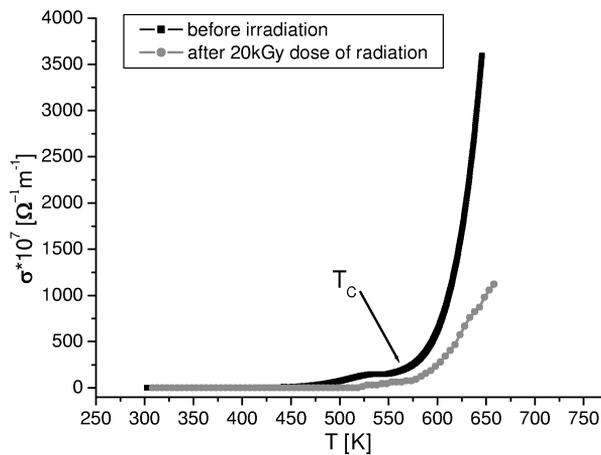


Fig. 2. Dependences $\sigma = f(T)$ obtained for the examined “hard” ceramics.

A characteristic parameter connected with the conduction of the PZT type materials, giving at the same time the information about the forbidden band width, is the activation energy of the E_a conduction process. In order to determine it for the PZT ceramic components in question the $\ln \sigma = f(1/T)$ dependences were made. The results for the “soft” ceramics are presented in Figs. 3 and 4 for the “hard” ceramics. A change in inclination of the rectilinear parts of those dependences near the phase change (T_C), and also for the ferroelectric and paraelectric phase, was observed. Those changes are a characteristic feature of materials showing ferroelectric properties, and they are connected, among other things, with the rebuilding of the crystalline structure at the transition from the low temperature to high temperature phase. Values of the activation energy, determined on the basis of an analysis of the inclination angles of particular straight lines in the phases: ferroelectric and paraelectric are presented in Table 1.

It is clearly visible that in case of the ferroelectric “soft” ceramics both in the ferroelectric phase (0.21 eV and 0.38 eV) and paraelectric phase (0.03 eV and 0.21 eV) activation energies determined for the specimens both before and after the irradiation show great differences among themselves. For a hard ceramic specimens those differ-

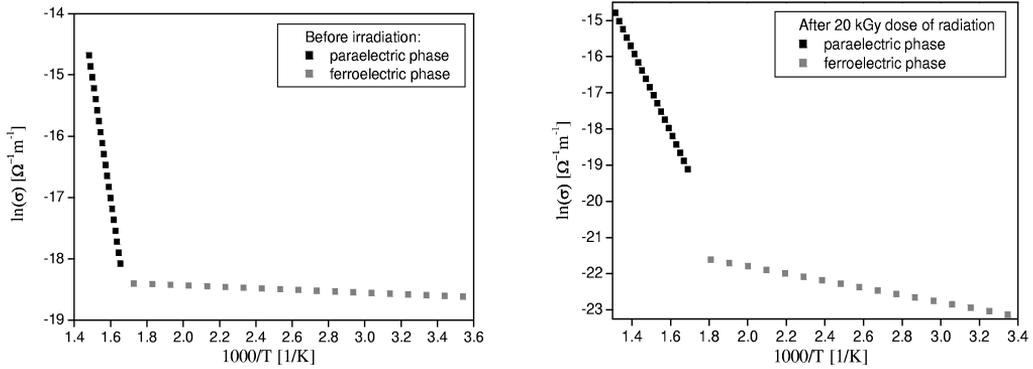


Fig. 3. The temperature dependences of the $\ln \sigma = f(1/T)$ for examined “soft” samples of the PZT ceramics.

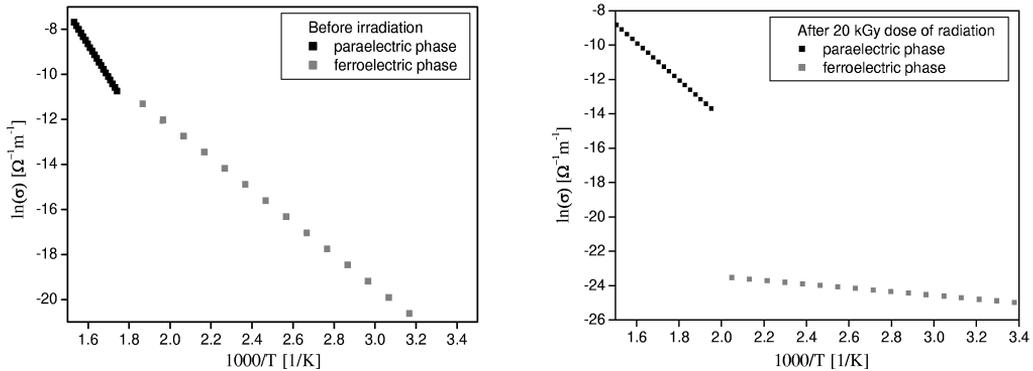


Fig. 4. The temperature dependences of the $\ln \sigma = f(1/T)$ for examined “hard” samples of the PZT ceramics.

Table 1. Values of activation energy E_a determined for the examined ceramics on the basis of the measurements of the σ electric conduction.

Dose [kGy]	“Soft” ceramics		“Hard” ceramics	
	E_a [eV] ferroelectric phase	E_a [eV] paraelectric phase	E_a [eV] ferroelectric phase	E_a [eV] paraelectric phase
0	0.21 ± 0.01	0.03 ± 0.01	0.14 ± 0.01	0.05 ± 0.01
20	0.38 ± 0.01	0.21 ± 0.01	0.19 ± 0.01	0.12 ± 0.01

ences are small (0.14 eV and 0.19 eV for the ferroelectric phase and 0.05 eV and 0.12 eV for the paraelectric phase).

It proves that irradiation had a little influence on a change of centers of dissipation of energy in case of the “hard” ceramics in comparison with the “soft” ceramics. An increase in activation energy of the E_a conduction process, what is followed by an increase in the width of the forbidden band, both in the ferroelectric and paraelectric for both ceramics subjected to tests after the irradiation is another effect observed. It proves the fact that under an influence of the γ radiation additional centers absorbing a greater

amount of energy (e.g. point defects) and hindering the transition of electrons from the basic band to the conduction band appeared in the structure.

Analyzing values of the E_a activation energy in the paraelectric phase in comparison with the ferroelectric phase for both “soft” and “hard” ceramic specimens a phenomenon of its clear decrease can be observed. Therefore, in the paraelectric phase thermally activated electric charge carriers are to cover a short distance of the forbidden band width to be in the conduction band. This change correlates closely with the changes observed on the $\sigma = f(T)$ dependences described earlier, on which a sharp increase in electric conduction above the phase change temperature (T_C) is clearly visible.

4. Conclusions

The results obtained in this work show that measurements of the σ electric conduction in the temperature function for the polycrystalline ceramics of the PZT type contribute a lot to know specific properties of those materials. In the measurements of the electric conduction, set of measurement devices to investigation of temperature changes of electric current in the constant voltage 1 V was used. The measurements of electric current was made with exactitude 10^{-12} A. The exactitude of activation energy (0.01 eV) is the result of the calculations in the analytical software obtained.

It has been also shown that influencing the structure of those materials by external factors such as the γ radiation can lead to visible changes in values of the parameters determined. So low value of the electric conduction 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 and after γ irradiation. The rapid increase of the electric conduction 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 $\sigma = f(T)$. The observed decrease in the values of the σ electric conduction in case of the specimens subjected to irradiation is advantageous from the point of view of practical applications. In case of the PZT ceramics electric materials with the optimum electric and mechanical properties and with the lowest conduction at the low temperature ferroelectric phase are sought.

Acknowledgments

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