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Comparison study of macro and micro scale AC and DC conductivity measurements with Impedance Spectroscopy and Atomic Force Microscopy techniques applied in PBZT ceramics

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Abstract

Ferroelectric materials systematically enter into the structure of microelectronic devices. The ability to increase the packing density of the ferroelectric structures, and thus the piezoelectric coefficients of the final device, is primarily limited by the fact that such tiny ferroelectric structures may not preserve their microscopic properties at macroscopic scale. A problem of current interest in ferroelectric research is to get to know how to modify the domain structure and the piezoelectric properties of the material, if the polycrystalline material consists of grains and grain boundaries, in which electrical properties differ significantly. In this paper, we have combined the Impedance Spectroscopy (IS), as a method for detecting such inequality in the form of separated impedances, and Atomic Force Microscopy (AFM), as techniques for direct local engineering and investigation of grain and grain boundaries conductivity. We would like to present hitherto unreported connection between values of electrical parameters obtained by both methods.

Keywords: C. Dielectric properties; Relaxor ferroelectrics; Ceramics; Axial pressure; AFM: IS

1. Introduction

Lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) perovskite material has still its successful position not only due to its electric, pyroelectric and dielectric properties but also before all due to their piezoelectric and electromechanical behavior, in which deficiency leads to serious shrinkage in the area of applications. These materials are widely used for piezoelectric actuators and electromechanical transducers and PZT and are still candidates for use in the prospective nonvolatile ferroelectric memory FeRAMs [1]. These applications of PZT materials, in the bulk as well as in thin film form, were explored over wide range of compositions and controlled ion substitutions. In the literature, the role of La^{3+}, Nb^{5+}, and Ba^{2+} ion substitution on A and B site of perovskites structure is widely described [2–6].

Especially barium-doped PZT ceramics (PBZT) have emerged as a promising ferroelectric system due to their rich variety of interesting physical properties of fundamental importance [7,8]. Our early investigations, which have been carried out until now, were in relation to relaxor properties of this material. The electric properties of this system, particularly $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$, have not been investigated yet however they open a promising branch to explore.

A nondestructive way of determination of materials microstructural changes is AC Impedance Spectroscopy (IS) [9,10]. Consequently, we present the evaluation of our AC and DC conductivity measurements of this material using IS. This method enables to determine applications oriented temperature dependences of grain (R_g) and grain-boundary resistance (R_{gb}) and also evaluate their respective activation energies (E_a). The Local Conductivity Atomic Force Microscopy (LC-AFM) is the second method, previously used by Szot et al. to investigate the mechanism of resistance switching by local application of DC voltage [11], which in our case was a useful tool to obtain the grain and grain boundary resistance in microscale.

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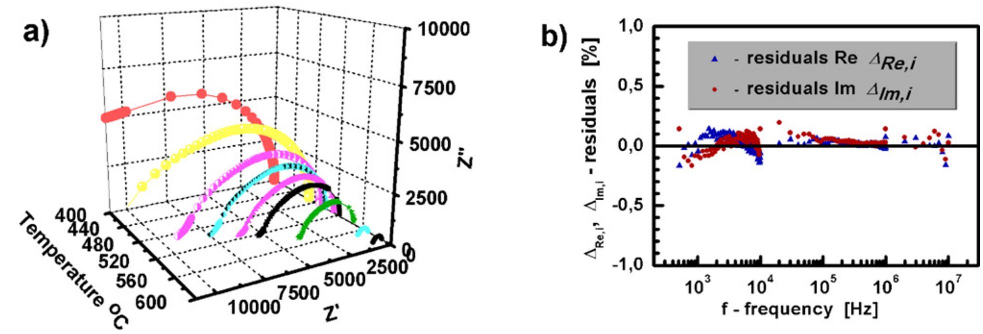

Fig. 1. Nyquist plot for PBZT 25/70/30 ceramics at different temperature (a). Display of the Kramers–Kronig test residuals for the measured IS data as example in temperature 873 K (b).

The main aim of this article is to compare between the macroscopic and microscopic methods of electrical investigations particularly oriented towards the values of grain resistance R_g obtained from IS method with these measured by Local Conductivity Atomic. What is worth mentioning is the fact that it is, according to the best knowledge of authors, the first attempt of comparing the results obtained by using the IS and LC-AFM methods.

2. Experiments

The $Pb_{0.75}Ba_{0.25}Zr_{0.70}Ti_{0.30}O_3$ ceramics were prepared by conventional mixed-oxide processing technique; those details were described on our previous paper [12]. The cylindrical shaped samples were cut, coated with gold electrodes and used in IS measurements. Impedance data as a function of frequency and temperature were obtained in the frequency range 5 Hz–13 MHz using an HP4192A impedance analyzer. The coherence of the obtained data was performed by using the K–K validation test [10,13]. Data fitting was carried out using the Z View equivalent circuit software produced by Scribner Associates [14]. The samples were polished and one of their surfaces was electroded by silver paste and glued to the AFM holder. The opposite surface without electrode was subjected to AFM tip scanning.The surface conductivity mapping was obtained using commercially available equipment (XE-100 PSIA). This device enables applying DC voltage between the conductive tip and bottom electrode, therefore it can be used for local current measurements. All scans were performed at room temperature with a doped silicon tip (NT MDT). Simultaneously, a sample topography was recorded, due to grain and grain boundary area and the surface morphology can be distinguished.

3. Results

Aiming at better understanding of the correlation between the microstructure and the electric properties the impedance analysis was carried out. This enables one to study the temperature dependence of grain resistance (R_g) and grain boundary resistances (R_{gb}) and to evaluate of their respective activation energies that allow to understandunequal ion and electron transfer phenomena. Fig. 1a shows the complex impedance spectrum of PBZT 25/70/30 ceramics measured at several different temperatures. According to the method described in literature [10,13] and with the help of Equivalent Circuit Computer program the Kramers–Kronig test was performed for investigated impedance data. Results of residuals for characteristics measured at 873 K, as an example, are given in Fig. 1b.

One can see, that distribution of the residuals around the frequency axis has a random form. The value of $\Delta_{Re,i}$ $\Delta_{Im,i}$ does not cross the 2% value. It indicates that impedance data are K–K complaint. What is worth mentioning, is the fact that for remaining characteristic the results of K–K test were similar. The change in temperature gives a distinct effect on impedance spectrum. At high temperatures dependence of $Z''(Z')$ consists with only one semicircle, but very detailed analysis of the data points that at high frequency range it shows a distinct deviation from a semicircle shape (Fig. 1a). As a consequence of this deviation, the diagram could be properly resolved using two semicircle models, one in a high frequency region and second in low one. Based on ZV program a careful deconvolution analysis of impedance spectra of investigated ceramics has been done. The data can be represented as an equivalent circuit shown in Fig. 2, which consists of two parallel *R–C* elements in series.

This is the one of most common interpretation for polycrystalline ferroelectric materials such as PBZT ceramics, which have electrical equivalents contribution of grain and grain boundary. The "Nyquist plot" (NP) visualization of the impedance characteristics, in which the imaginary part of impedance (Z'') is plotted as a function of the real part (Z'), was used for separation of the grain and grain-boundary effects. The graphical example of fitted results shows Fig. 3.

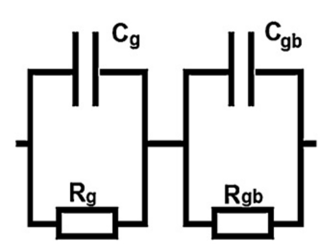

Fig. 2. Equivalent circuit used to represent the impedance response of PBZT 25/70/30 ceramic.

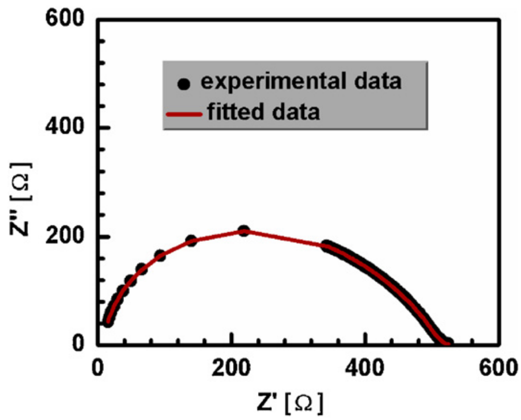

Fig. 3. Example of fitted and experimental impedance data, ''Nyquist Plot'' of PBZT ceramics.

The diagram of natural logarithm of obtained grain and grain boundary resistivity vs reciprocal absolute temperature is presented in Fig. 4.

The linear character of those dependences proves that the process can be described by the following formula:

$$R = R_o \exp\left(\frac{-E_a}{kT}\right) \tag{1}$$

The directional coefficient of linear equation allows to estimate not only the value of grain and grain boundary resistance at room temperature (which is equal $0.62 \times 10^{12}\ \Omega$ and $0.28 \times 10^{12}\ \Omega$, respectively), but also the conductivity activation energy equal to 0.98 eV (Fig. 4a) and 0.85 eV (Fig. 4b) for grain and grain boundary, respectively. The results allow us to suppose, that the path of conductivity leads mainly throughout the grain boundaries.

The Local Conductivity (LC) has been carefully researched using LC-AFM method by surface conductivity mapping. It has been mentioned that small DC voltage applied between the conductive tip and bottom electrode can be used for local current measurements in contact mode. Therefore, the lateral resolution depends mainly on the tip-sample contact area. The sample topography of the measurement area is presented in Fig. 5a. The map of point to point conductivity obtained by using LC-AFM method from the same area is presented in Fig. 5b.

The probing tip was positioned at the center of grain and the current signal was measured after applying a small reversal DC voltage to this conductive tip. Based on the map of current intensity obtained from LC-AFM method and the value of applied DC voltage the map of change of local resistivity was determined (Fig. 5). The average resistance value of investigated sample point measurements changes distinctly between grain and grain boundary (Fig. 5b) and is equal $0.8 \times 10^{12}\ \Omega$ and $0.4 \times 10^{12}\ \Omega$, respectively. Additionally, an apparent difference is visible in IV curves shape for grain and grain boundaries, that is indicator of local non-homogenous composition in nanoscale that can be revealed by electrical methods. Considering this fact more detailed, the grain boundaries show non-linear character indicating semiconductor local nature, that is shown in Fig. 5d, whereas linear behavior of grain areas should be associated with metallic conductivity areas which corresponds with local non-stoichiometry, that is presented in Fig. 5c.

4. Discussion

Our previous investigations proved that the PBZT ceramics 25/70/30 show relaxor behavior [13]. The temperature dependence of real and imaginary part of permittivity demonstrated strongly diffused dielectric peak, in which temperature position is shifting to higher values with increasing frequency. The dependency originates from diffused character of FE–PE phase transition, caused by compositional fluctuation (e.g. local differences in Pb/Ba and Zr/Ti ratios) and by various kinds of defects (for instance – vacancies in the Pb and O sublattices). The microregions of varying compositions or concentration of defects have different local FE–PE transition temperatures. The size distributions of these microregions give rise to a dielectric dispersion – a feature characteristic of the most typical relaxor ferroelectrics [16,17]. Due to differentiation in the local Curie temperatures (T_C) the part of domains with lower T_C disappeared quickly (which means in lower temperatures). When the temperature is approaching T_m values, disappearing process becomes more spontaneous. However in sample bulk, remain domains with T_C temperature, which is significantly higher than T_m. Such remaining domains (clusters) become surrounded by the PE phase. The depolarization field associated with P_s of such domains tends to the compensated

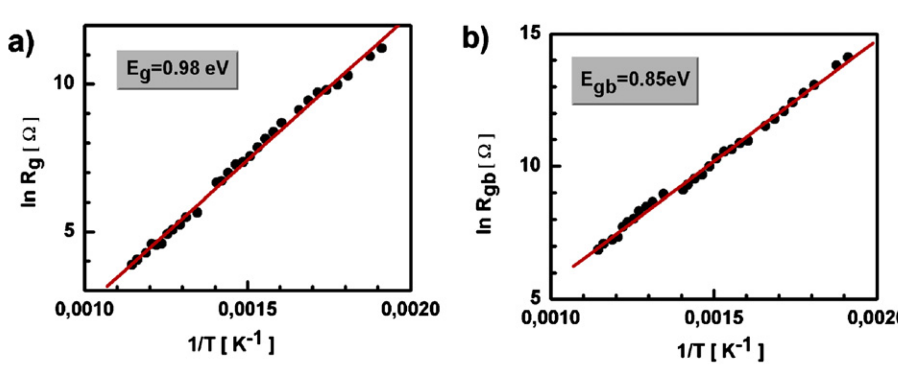

Fig. 4. Arrhenius plots for calculation of conduction activation energies of grain (a) and grain boundary (b).

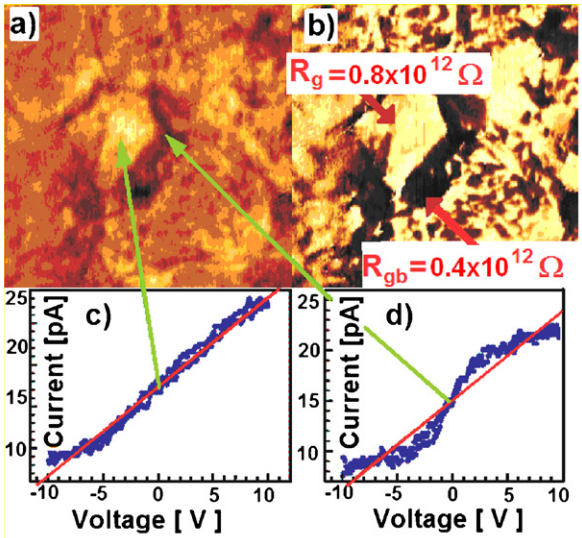

Fig. 5. AFM topography (a) and conductivity map (b) images and local IV plots (c) and (d) illustrating local conductivity in different regions of PBZT ceramics. Displayed measurement charts were acquired at the place marked by the arrows: in the middle of grain center – the c-oriented region (c) and in the grain boundary (d). The image size of (a) and (b) is 20 μm × 20 μm.

state by two possible ways, widely described in our previous papers [12,15]. One of the ways relies on a formation of locally compensated polydomain structure. The second way relies on the P_s screening by electron and ion space charges from surrounding medium. Our previous investigations showed that the second way is more likely in the case of PBZT 25/70/30 ceramics, because the materials are characterized by the huge participation of local space charges, which is confirmed by the presence of thermal stimulated depolarization currents (TSDC). In connection with participation of space charge in those materials very interesting things seem to be their electric properties. Hitherto investigations focused on the temperature characteristic of DC conductivity and thermal studies [15]. The linear character of the ln σ vs $1/T$ dependence made it possible to determine the activation energy (E_a). The value of this energy was equal 1.07 eV. Additionally the thermoelectric studies revealed that this ceramics were characterized by p type of electric conductivity. But the investigations could not confirm our assumptions connected with space charge. If really the space charge plays such an important role into these materials, the main conductivity path should take place not by the grain but by the grain boundary, where the agglomeration of ions and free electrons exists. We were seeking confirmation of our presumption in the results of Impedance Spectroscopy. This technique allowed us to determine the contribution of various microscopic elements such as grain and grain boundary to total electric conductivity. The complex plot between the real and imaginary parts of impedance had been done in chosen temperatures range between 400 and 580 °C. The careful analysis of impedance spectra of the investigated ceramics allowed us to determine both the grain and grain boundary resistance at the individual temperatures as well as determine the value of the activation energy of the grain and grain boundary conductivity. The comparison between the mentioned value of activation energy with the one obtained from temperature dependence of conductivity led us to the suspected conclusion that path of conductivity is mainly conducted by grain boundaries. Moreover the knowledge of linear relationship $\ln(R_{gb})(T)$ and $\ln(R_g)(T)$ parameters let to determine the value of R_{gb} and R_g at room temperature. These values stayed in good agreement with the ones determined from AFM-LC method, which confirms the correctness of our method and applied model of equivalent circuit.

5. Conclusions

In this paper, for the first time, we have compared macroscopic results obtained by Impedance Spectroscopy and direct local LC-AFM conductivity measurements. We confirmed that the impedance values obtained by the second method – LC-AFM, are in consistency with IS. The insignificant differences between the resistance obtained by both methods refrain from manner of measuring. We have to keep in mind that the results gained by Impedance Spectroscopy method reflect the whole volume immittance response, whereas AFM method is affecting only surface layer. Additionally the conductivity activation energy calculated for grain boundary had smaller value than the one obtained for grain. This fact allows us to state that in this ceramics at higher temperature the current flows in higher degree by grain boundaries than by grain interiors. The knowledge of grain and grain boundary resistance as well as the activation energy can be used in the future for drawing decisive applications conclusions.

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