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Application of the FITSC method for characterization of PZT-type ceramics with the diffuse phase transition

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ABSTRACT

In the present work the $(Pb_{0.84}Ba_{0.16})(Zr_{0.54}Ti_{0.46})O_3$ (PBZT 16/54/46) ceramics has been studied from the point of view of its electrical properties. Dielectric properties of PBZT were measured within the temperature range of the ferroelectric-paraelectric (FE-PE) phase transition region. The method of field-induced thermally stimulated currents (FITSC) was applied and thus the thermal relaxation effects were studied. The observed field dependence of thermally stimulated depolarization currents has revealed the existence of different frequency-dependent relaxation processes in the temperature range between 200 and 400 °C.

Our experiment demonstrates that modification of ferroelectric materials with isovalent ions, but bigger radii than the origin atom, significantly affect its properties, particularly the PBZT real part of electrical permittivity shows the phase transition character change from ferroelectric to relaxor and finally, that electrical examination can be effectively used for drawing decisive applications conclusions considering polarization parameters distribution.

1. Introduction

Modified lead zirconate titanate (PZT) – type ceramic materials are currently the leading materials for piezoelectric applications due to their unique properties such as higher accuracy, higher response speed, lower power requirements and by contrast to other ceramics both sensing and actuating functions can be realized in this material. It has been widely used for fabricating nonvolatile memory elements, pyroelectric detectors, photoelectric devices and piezoelectric actuators [1,2]. However, pure PZT-type materials are rarely applied in electronic devices. The doping process is usually used to enhance the piezoelectric coefficients of PZT-based materials or solid solutions and to create structures with properties unachievable in single component materials [3].

The $(Pb,Ba)(Zr,Ti)O_3$ ceramic system is generally thought as a solid solution of the subsystems $Pb(Zr,Ti)O_3$ and $Ba(Zr,Ti)O_3$. Early interest in the PBZT ceramic materials focused on implementation in piezoelectric transducers and actuator applications, due to the high electromechanical coefficients value [4]. The first systematic investigation of the PBZT system [5] enabled to determine the phase diagram and successive measurements of dielectric characteristics and electric field induced strain properties [4,5], not only confirmed the phase diagram, but also showed that properties of this particular ceramics are typical for relaxor ferroelectrics. These properties were revealed in the PBZT ceramics for ferroelectric phase with the rhombohedral symmetry [6,7] and partially also from the range close to the morphotropic boundary separating the rhombohedral and tetragonal phases [4].

The method of field-induced thermally stimulated current (FITSC) consists of measurements with a definite heating scheme: the currents generated by the buildup and/or the release of polarized state in a solid dielectric between two metal electrodes. During the past years the experimental and theoretical development of FITSC has reached a high level and recently the thermally stimulated depolarization currents technique (TSDC) has been recognized as a method for studying all the fundamental mechanism of charge storage and release in nonmetallic solids. The TSDC became a general method of investigating the electrical properties of high-resistivity solids via the study of thermal relaxation effects. It offers an attractive alternative to the conventional bridge methods or current–voltage–temperature measurements [8,9].

In the present study $(Pb_{0.84}Ba_{0.16})(Zr_{0.54}Ti_{0.46})O_3$ (PBZT 16/54/46) ceramics was fabricated by hot-pressing method and its dielectric properties as well as the behavior of the thermally stimulated depolarization current (TSDC) was studied.

2. Experimental

Ceramics with the chemical composition $(Pb_{0.84}Ba_{0.16})(Zr_{0.54}Ti_{0.46})O_3$ was prepared using the conventional mixed-oxide processing technique. Commercially available PbO, ZrO_2, TiO_2, $BaCO_3$ powders were used as starting materials. Stoichio-

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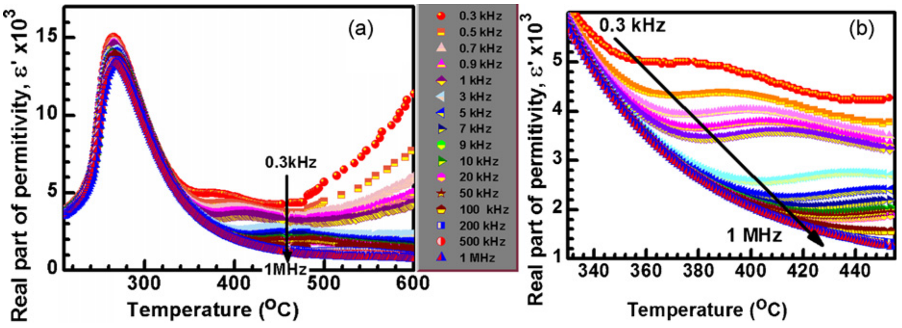

Fig. 1. Temperature dependence of the real (ε)part of permittivity for PBZT 16/54/46 ceramics.

metric amounts of the oxides were weighed and mixed in a ball mill for 16h with zirconia balls as the grinding media and ethanol as the solvent. After milling, the resultant slurry was dried in an oven and then the disk-shaped pellets were formed.

The thermal behavior of the PBZT 16/54/46 powders was studied by simultaneous thermal analysis (STA) with Netzsch 409 equipment in which both thermal (DTA) and mass change effects (TG and DTG) are concurrently measured on the same sample. On the base of STA measurements the calcination temperature ($T = 900\,^\circ$C) as well as the sintering temperature ($T = 1120\,^\circ$C) used during the hot pressing method was chosen. The ambient atmosphere was present in the furnace.

The crystalline structure of the ceramic powders was examined by X-ray diffraction (XRD) analysis, using the Philips PW 3710 X-ray diffractometer ($\Theta - 2\Theta$ method, Co$K_{\alpha1\alpha2}$ radiation) at room temperature. It was found that PBZT 16/54/46 can be described by the tetragonal structure P4 mm (space group No 99) with the following elementary cell parameters: $a = b = 4.0597$ Å; and $c = 4.1033$ Å ($c/a = 1.0107$).

Prior to electrical measurements the ceramic samples were subjected to thermal treatment at about $T = 450^\circ$C in order to cause partial recombination of defects frozen after the sintering process. The strains, caused by mechanical treatment during cutting and polishing, were also removed this way.

Disk shape samples of 0.6 mm in thickness and 10 mm in diameter, coated with silver electrodes, were used for dielectric measurements. Both temperature and frequency dependencies of dielectric permittivity (ε') and dielectric loss factor (tanδ) were measured and recorded with an automatic measuring system based on HP 4192A impedance analyzer.

The study of TSDC was carried out in sequential thermal cycles as follows: (1) the application of a dc bias $E_p = 1$–5 kV/cm at a starting temperature $T_p = 150$–$300\,^\circ$C; (2) cooling under this bias to temperature $T_0 = 50\,^\circ$C; (3) switching off the bias at T_0; and (4) heating the sample under zero electric field up to $T = 600\,^\circ$C. The current, called the thermally stimulated depolarization current, was measured as a function of temperature. A standard short circuit method was utilized and a temperature rate of about 5 °C/min was kept constant during measurements. The temperature dependence of the corresponding polarization was obtained by time integration of electrical current. The sample temperature was measured with accuracy better that 0.1 °C.

3. Results and discussion

Measurements of the real (ε') and imaginary (ε'') part of dielectric permittivity given in Fig. 1 and Fig. 2 were performed for several frequencies of the measuring electric field. However, the earlier investigations of PBZT 25/70/30 ceramics showed high concentration of defects frozen during the cooling step after the sintering process [6] and the runs of both $\varepsilon'(T)$ and $\varepsilon''\,(T)$ obtained from the first heating step usually differ considerably from those obtained during the subsequent heating – cooling cycles [7], at the constant rate of temperature changes equal 2 °C/min. Therefore, for the reason mentioned above, results of the dielectric measurements shown in Figs. 1 and 2 were recorded during the second heating step.

The temperature dependence of real and imaginary part of dielectric permittivity show a strong diffuse character of the phase transition probably caused by chemical disorder.

Martirena [10] and Uchino [11] suggested the variable power law, which is rewritten to Eq. (1). It describes the paraelectric side dielectric permittivity of ferroelectrics with diffuse phase transition.

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_{\mathrm{max}}} = \frac{(T - T_{\mathrm{m}})^{\gamma}}{C'} \qquad (1)$$

The ε' and $\varepsilon'_{\mathrm{max}}$ are the permittivity and its maximum, respectively, T is the temperature, T_{m} is the temperature of $\varepsilon'_{\mathrm{max}}$, γ is the diffuseness exponent of the phase transition, and C' is a constant. In Eq. (1), $\gamma = 1$ should represent "normal" Curie–Weiss behavior represents classical ferroelectrics, while $\gamma = 2$ corresponds to a "complete" diffuse phase transition [12] connected to ferroelectric relaxors. The value of $1 < \gamma < 2$ shows the degree of dielectric relaxation in the ferroelectric relaxors. In the present study the coefficient γ and C' were found equal to 1.85 and 167×10^5, respectively (what is in good correspondence with values presented in paper [12]).

Moreover, the temperature T_{m} of broadened maxima insignificantly increase, whereas the value of $\varepsilon'_{\mathrm{max}}$ decreased with the frequency of measuring field. The above mentioned facts indicate that the material in question exhibits a ferroelectric relaxor like behavior.

At temperature $T \geq 350\,^\circ$C (i.e. in PE phase) the additional broadened maxima arise in the $\varepsilon'(T)$ dependence. They are more distinct for lower frequencies and gradually disappear. When the frequency exceeds of about $f = 5 \times 10^4$ Hz (see figure inserted in Fig. 1) the mentioned maxima are practically invisible. It is worth noting that similar shape of temperature characteristic of dielectric permittivity was found in case of PBZT x/70/30 ceramics, however, in case of PBZT 16/54/46 ceramics the low frequency dispersion in PE phase is significantly lower (estimated at $T = 400\,^\circ$C) [6]. Generally this additional dispersion is often found in ferroelectric ceramics of perovskite structure [13,9] and originates from the non-homogeneous distribution of ion space charge participating in the screening process of polar regions [14].

In case of classical ferroelectrics the local minima in temperature dependence of loss factor permittivity correspond to the temperature of ferroelectric – paraelectric (FE-PE) phase transition. In our materials as well the minima of loss factor as the minima of imag-

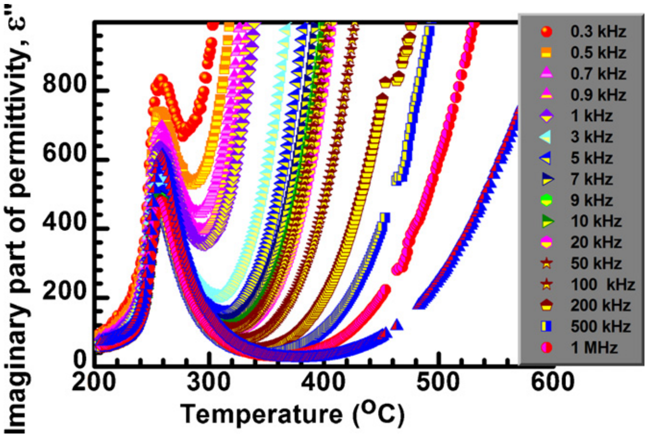

Fig. 2. Temperature dependence of the imaginary(ε'') part of permittivity for PBZT 16/54/46 ceramics.

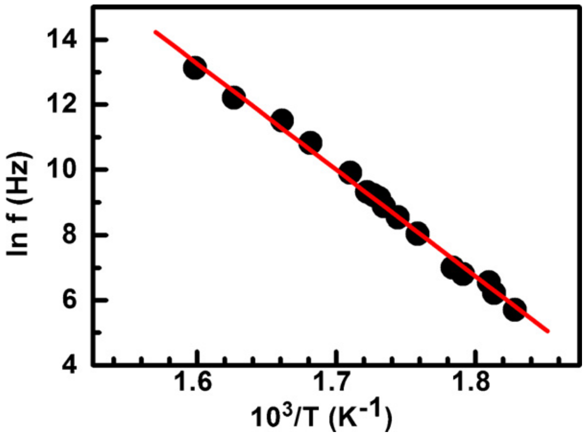

Fig. 3. Natural logarithm of the measuring frequency versus the reciprocal temperatures at which the minima in ε'' (T) occur for PBZT 16/54/46 ceramics.

inary part of dielectric permittivity are shifted upwards in relation to the temperature T_m, what is characteristic property of ferroelectric relaxor. The observed increase in both imaginary and real part of dielectric permittivity is probably attributed to the appearance of ionic conductivity. Moreover the mentioned minima are strongly frequency dependent. The plot of natural logarithm of the measuring frequency versus the reciprocal absolute temperature, corresponding to the local minima in the $\varepsilon''(T)$ curves is shown in Fig. 3.

The linear dependence shown in Fig. 3 proves that they obey the formula:

$$f = f_0 \exp\left(\frac{-E_a}{kT}\right) \qquad (2)$$

with calculated value of activation energy $E_a \approx 2.8$ eV, that is comparable with the one obtained by L. Pintilie using the optical method [15].

In order to better understand this unusual behavior of dielectric characteristics, especially interesting was low frequency dispersion that appears in paraelectric phase, the measurements of pyroelectric and thermally stimulated depolarization currents (TSDC) were carried out.

The occurrence of mentioned above polar regions and their interaction with free electron and ion space charges can be identified by TSDC [1,2,4]. The samples were first poled with dc electric field of 1 kV/cm strength applied at selected temperatures (T_p) during 10 min and subsequently cooled down to 50 °C under this field. After that, the samples were heated with a constant rate of 5 °C/min through the diffuse FE-PE phase transition to temperature as high as 600 °C. Density of the current (j) flowing in the circuit interconnecting electrodes of the samples, was recorded numerically as a function of temperature during heating and shown in Fig. 4. The current peaks are observed during the thermally activated transition from the polarized state to the equilibrium state.

The broad peaks of the pyroelectric current appear in the vicinity of temperature $T = 242 \div 247$ °C, i.e. at temperature of about 20 °C lower than T_m. It has been found that position of the temperature of maximum does not depend on the condition of poling. Moreover, for ceramics pre-poled at temperature $T_p = 300$ °C the observed current increases again and achieves the additional maximum at temperature of about $T = 310$ °C. Therefore this temperature was chosen as temperature of the next process of poling. The dc electric field intensity applied to the sample varied as follows $E_p = 1$, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 kV/cm. The recorded changes of the current density are shown in Fig. 5.

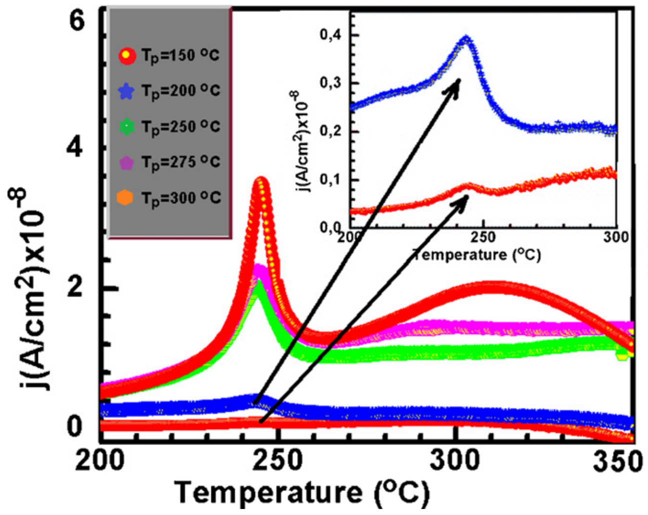

Fig. 4. The pyroelectric and thermally stimulated depolarization currents versus temperature, for the undoped PBZT 16/54/46 ceramics, pre-poled at constant electric field of strength $E_p = 1$ kV/cm, at various temperatures T_p.

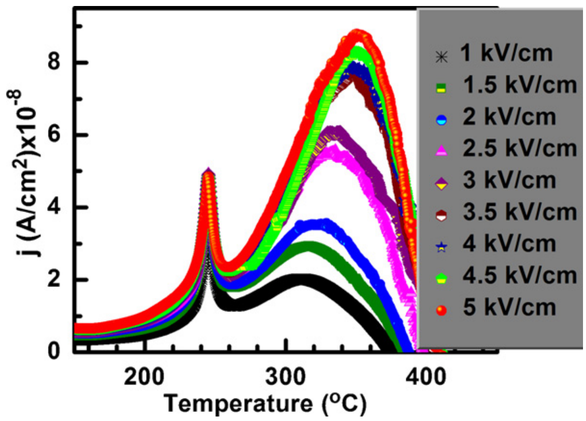

Fig. 5. The pyroelectric and thermally stimulated depolarization currents versus temperature, for PBZT 16/54/46 ceramics pre-polarized at constant temperature $T_p = 300$ °C and electric field of various strength shown in the figure.

On can see that temperature of the pyroelectric current peak remains unchanged and its value increases from 3.5×10^{-8} A/cm^2 to 4.8×10^{-8} A/cm^2 with increasing E_p. Temperature of the second large maximum gradually shifts to higher value for $E_p = 1 \div 4$ kV/cm and than stops shifting. Additionally, the value of the peak changes significantly with the increase the strength of electric field (see Fig. 6).

From temperature characteristic of current density measured for sample polarized applied 5 kV/cm at 300 °C the piroelectric cur-

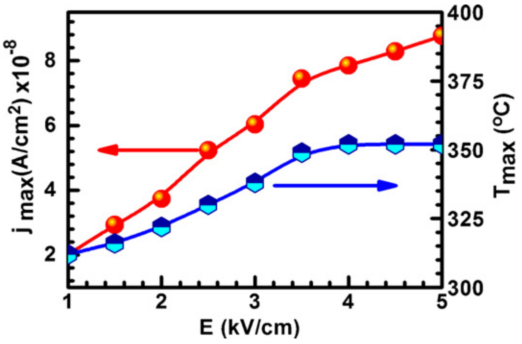

Fig. 6. Maxima in the $j(T)$ curves, connected with the thermally stimulated depolarization currents versus temperature, and corresponding temperatures as a function of strength of the polarizing field.

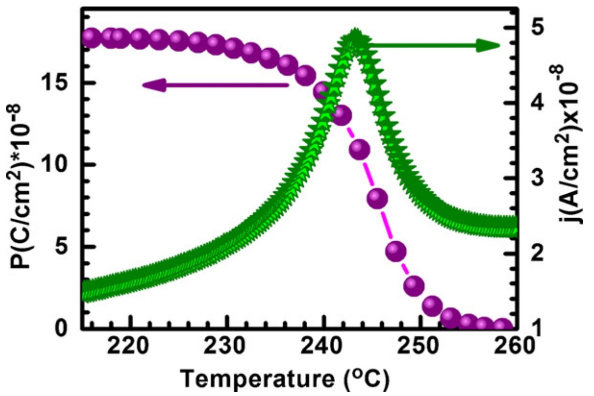

Fig. 7. The $P(T)$ dependence determined by back integration of the pyroelectric peak vs time for PBZT 16/54/46 ceramics.

rent was separating. Backward integration of the current versus time made it possible to determine the $P(T)$ dependence shown in Fig. 7.

It should be noticed that the maximum of macroscopic polarization appears at temperatures far below T_m, which is a typical behavior observed for ferroelectric relaxor. In aim of verification the temperature dependence of remanent polarization the histeresis loop measurements were made. These measurements were carried out in a field of frequency 50 Hz and strength 10 kV/cm. The maximum values of P obtained through both ways are very similar. Maximum value of remanent polarization determined from the pyroelectric measurements is equal 17.7 $\mu C/cm^2$, the same value calculated from histeresis loop experiment is equal 18.5 $\mu C/cm^2$, which suggested the weak dynamic nature of macro states.

In order to separate the temperature and time dependence the second experiment was done [7]. The investigated sample was again polarized in a dc field of strength 5 kV/cm applied at constant temperature 300 °C during 10 min. After discharging by short-circuiting the sample the time dependence of the depolarization current was recorded at this constant temperature (Fig. 8).

The recorded depolarization current disappeared with different time of relaxation τ. The determination of this time constant was evaluated from the data shown in Fig. 8: $\tau_1 = 130$ s; $\tau_2 = 600$ s; $\tau_3 = 1435$ s; and $\tau_4 = 2100$ s. In our opinion in higher temperature range space-charge polarization and also electrochemical processes played the essential role. The short time of relaxation could be explained by migration polarization, because phenomenon of space-charge polarization or reorientation dynamics of dipoles is relatively quick, whereas longer time constant is connected with electrochemical processes [9].

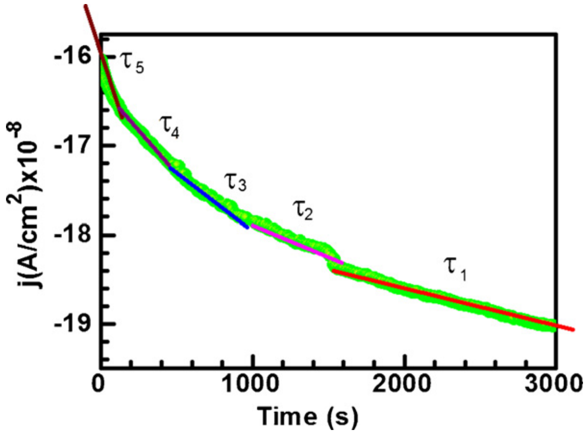

Fig. 8. Thermally stimulated depolarization current as a function of time for PBZT 16/54/46 ceramics.

4. Discussion

Evidential correlation was ascertained between the temperature variations in the dielectric properties (ε', ε'' and P_r) on the one hand and temperature changes of pyroelectric and thermal stimulated depolarization currents on the other hand. Similar correlation in these characteristic was observed in some PLZT ceramics [14] and in PBZT ceramics containing about 25% of Ba and have Zr/Ti ratio equal 70/30^7. The explanation of the huge thermal depolarization currents appearing in the sample at temperature considerably higher than T_m is connected with the existing in widely range of temperatures polar clusters, that was widely described in paper [14]. Namely due to local fluctuation in sample compositions a distribution of Curie temperatures in the whole volume of the ceramics and the process of spontaneous polarization disappearance begins even at temperature significantly lower than T_m. Above T_m remaining domains (clusters) are surrounded by the paraelectric cubic matrix. The depolarization field associated with spontaneous polarization of such domains tends to form locally compensated polydomain structure, smaller domains can have sizes of several hundred angstroms [16]. These domains may thus give rise to relaxor-like behavior, in particular to frequency dielectric dispersion. The other mechanism is connected with spontaneous polarization screening by the electrons and ion space charges. Even after disappearance of the spontaneous polarization in side the screened clusters at enough high temperature, the “traces” of nonrandomly distributed space charges remain in the PE matrix, that is connected with theirs long relaxation time. The resultant dipole moment must be compensated by trapping of electric carriers from the surrounding space again. These “traces”, with local concentration polarization vanishing very slowly and this fact is most probably responsible for low-frequency dielectric dispersion observed in PE phase [14]. The similar process is observed in some other perovskites ferroelectric materials [17,18]. In these materials, when the temperature increase, the process of the gradual disappearance of FE domains and also the mentioned above “traces” starts, that cause releasing carriers, which together with the additional carriers injected from the electrodes are responsible for the huge thermal stimulated depolarization currents.

5. Conclusions

In the present work the $(Pb_{0.84}Ba_{0.16})(Zr_{0.54}Ti_{0.46})O_3$ (PBZT 16/54/46) ceramics has been studied from the point of view of its electrical properties. The correlation between the variations in the dielectric properties on one hand and the pyroelectric and thermal stimulated depolarization currents on the other was observed and described in a light of existing of polar regions and their interaction with free electron and ion space charges.

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