Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of the European Ceramic Society 24 (2004) 1905–1909
www.elsevier.com/locate/jeurceramsoc

Thermal dependence of pyroelectric parameters of PZT-based multi-component electroceramics

D. Czekaj[a,*], A. Lisińska-Czekaj[a], Z. Surowiak[a], J. Ilczuk[a], M.F. Kupriyanov[b], Yu.N. Zakharov[b]

[a]Department of Materials Science, Faculty of Engineering, University of Silesia, Katowice, 2, Sniezna St., 41-200 Sosnowiec, Poland
[b]Department of Physics, Rostov State University, 5, Zorge St., Rostov-on-Don, Russia

Abstract

Five-component electroceramics based on solid solution $PbTiO_3$–$PbZrO_3$–$PbNb_{2/3}Zn_{1/3}O_3$–$PbSb_{2/3}Mn_{1/3}O_3$–$PbNb_{2/3}Mn_{1/3}O_3$ was studied. The chemical composition of the solid solution varied with $PbTiO_3$ content. Thus samples exhibiting rhombohedral crystalline structure, tetragonal structure, as well as samples exhibiting compositions from the morphotropic phase boundary region (MBR) were under investigation. Conventional mixed oxide method was used for the powder preparation. Hot pressing technique was employed for fabrication of ceramic pellets. To produce pyroelectric activity the samples underwent high voltage poling (HVP) or low voltage poling (LVP). Thermal stability of the pyroelectric coefficient was measured according to both quasi-static $\gamma_{ST}(T)$ and dynamic method $\gamma_D(T)$. The customised measuring system was developed. Dependence of the dielectric permittivity $\varepsilon_{33}/\varepsilon_0$ of poled samples on temperature was also recorded. Results are reported and explanation of the observed temperature traces for $\gamma_{ST}(T)$, $\gamma_D(T)$, and $\varepsilon_{33}/\varepsilon_0(T)$ is given taking into consideration the two different methods of poling the multi-component samples.

Keywords: Dielectric properties; Hot pressing; Pyroelectric properties; PZT; X-ray methods

1. Introduction

It is a common knowledge that polar classes *6·m*, *4·m*, *3·m*, *2·m*, *m*, *6,4,3,2,1* describe symmetry of dielectric crystals exhibiting preferred direction of polarization without external electric field i.e., non-zero spontaneous polarization P_0 in the volume unit. Homogeneous heating can change the spontaneous polarization of a crystal and thus it conditions the pyroelectric effect. Pyroelectric activity is described by the pyroelectric coefficient $\gamma = \Delta P_0/\Delta T$ i.e., ratio of change in polarization ΔP_0 to ΔT at small changes of temperature T. It should be noted that interpretation of the pyroelectric effect is rather difficult because all pyroelectric materials exhibit piezoelectric effect. Change in temperature causes deformation of any material,[1] which generates secondary effect of the piezoelectric nature.

Lead–zirconate–titanate[1] (PZT) based ceramic materials exhibit a number of properties (e.g., high dielectric constant and low dielectric loss, high piezoelectric constants, electromechanical coupling, and pyroelectric coefficients) which can be continuously modified over specified ranges. It is due to the fact that PZT-based ceramics can form multi-component solid solutions.[3]

The purpose of this paper is to report thermal dependence of pyroelectric and dielectric parameters for the five-component PZT-based solid solution exhibiting different content of $PbTiO_3$ component. Influence of different poling conditions was also studied.

2. Experiment

PZT-based multi-component oxide system chosen for studies exhibited the following chemical composition $xPbTiO_3 + (1-x)(0.821PbZrO_3 + 0.116PbNb_{2/3}Zn_{1/3}O_3 + 0.024PbSb_{2/3}Mn_{1/3}O_3 + 0.039PbNb_{2/3}Mn_{1/3}O_3)$. The range of $PbTiO_3$ mole fraction x varied within the

* Corresponding author. Tel.: +48-32-291-8381x345; fax: +48-32-291-8243.
E-mail address: czekaj@us.edu.pl (D. Czekaj).

0955-2219/$ - see front matter
doi:10.1016/S0955-2219(03)00468-0

range $0.072 \leqslant x \leqslant 0.462$. Detailed description of the system used was published elsewhere.[4]

The ceramic samples were prepared by hot pressing method. Experiment was carried out for batches of samples. Each batch consisted of 8–10 pieces and it was divided into two equal parts. First of these parts underwent so-called high voltage poling (HVP), that is poling at $T = 50$ °C and an electric field strength $E = 4 \times 10^6$ V/m for 1 h. Second of these parts underwent so-called low-voltage poling (LVP), that is, the samples were first heated up to temperature, which exceeded the Curie point (T_C) by 10–15 °C, and then cooled down to room temperature (RT) under an electric field strength $E = 1 \times 10^6$ V/m.

Measurements of the dielectric permittivity of the poled samples ($\varepsilon_{33}/\varepsilon_0$) were carried out using a bridge technique. X-ray diffraction method was used to confirm the compound formation and to determine the structural parameters of the unit cell. As a measure of tetragonal distortions of the unit cell the homogeneous parameter of deformation[5] $\delta_T = 2(c_T - a_T)/(2a_T + c_T)$ was used where c_T and a_T are parameters of the tetragonal unit cell.

The customised measuring system was developed (Fig. 1) to carry out investigations into the temperature dependence of pyroelectric coefficient γ by quasi-static (γ_{ST}) and dynamic (γ_D) method.[6] The sample (3) placed in the heat chamber (4) was subjected to temperature increase according to two modes. The first mode consisted in uniform heating from RT to $T > T_C$ and it provided possibility of measuring the temperature dependence of γ_{ST} [through the circuit: sample, choking-coils L_1 and L_2, load resistor R_n, X–Y recorder (11), blocking resistor R_1]. The second mode lay in exposure to a periodic thermal radiation flux with frequency 20 Hz and thus made it possible to measure temperature variations of γ_D [through the circuit: L_1, L_2, capacitors C, C_3, narrow-band amplifier (6), synchronous detector (7), and X–Y recorder (8)].

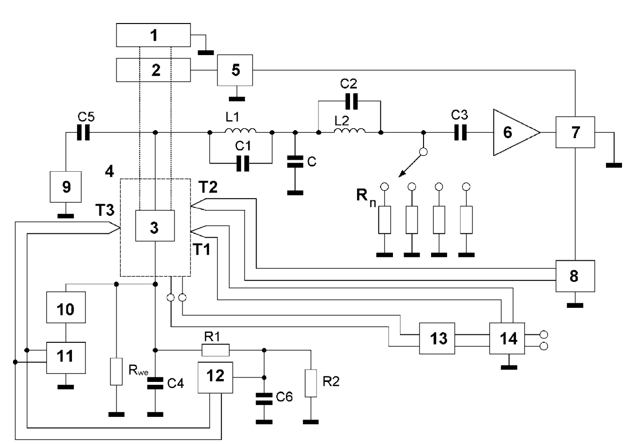

Fig. 1. Block diagram of the system for thermal investigations of ceramics. 1—source of thermal radiation, 2—modulator, 3—ceramic sample, 4—heat-chamber with transparent window, 5, 9— generators, 6—narrow-band amplifier, 7—synchronous detector, 8, 11, 12—X–Y recorders, 10—direct-current amplifier, 13, 14—thermoregulator, T1, T2, T3—thermocouples.

3. Results

Fig. 2 shows thermal dependence of relative permittivity ($\varepsilon_{33}/\varepsilon_0$) and pyroelectric coefficients (γ_D and γ_{ST}) for PZT-based ceramic samples exhibiting the rhombohedral symmetry (curves 1, $PbTiO_3$ content $x = 0.242$) and the tetragonal symmetry (curves 2, $x = 0.462$). Although runs of all the curves are similar the difference in the chemical composition as well as the method of poling is reflected in both absolute values of the measured parameters and temperatures corresponding to their peak values.

One can see diffuse maxima on the experimental curves of $\gamma_{ST}(T)$ and $\gamma_D(T)$ given in Fig. 2. Small peak values of γ_D and γ_{ST} for both rhombohedral (R) and tetragonal (T) phase samples subjected to the HVP-method of poling testify to lower effectiveness of the method as compared with the LVP-method. Except for the higher degree of poling the samples the LVP-method has caused a shift of maximum of γ_D and γ_{ST} towards higher temperatures. The observed phenomena indicate the higher thermal stability of the state of polarization produced by the LVP-method of poling for both R- and T-phase samples.

It is worth noting that in case of the R-phase samples poled according to HVP-method maximum of γ_D corresponds to temperature of rapid increase in relative

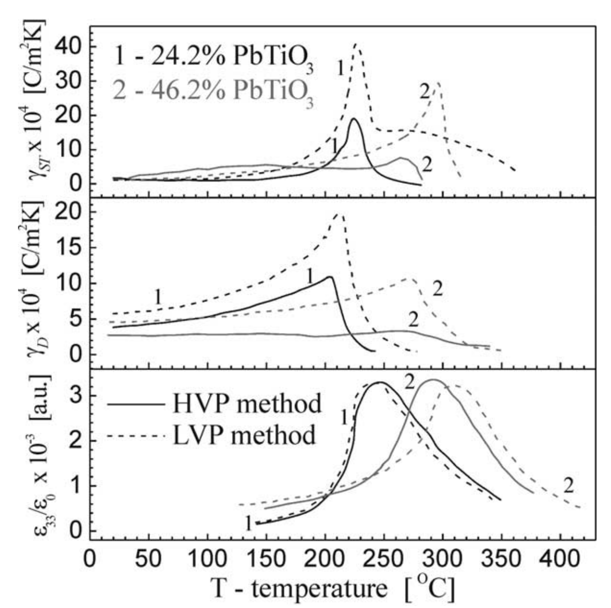

Fig. 2. Dependence of pyroelectric coefficient γ_{ST} and γ_D, and relative permittivity $\varepsilon_{33}/\varepsilon_0$ on temperature for PZT-based ceramics with $PbTiO_3$ content $x = 24.2\%$ (rhombohedral phase, curves 1) and $x = 46.2\%$ (tetragonal phase, curves 2).

permittivity ($\varepsilon_{33}/\varepsilon_0$). However, for LVP-method it corresponds to maximal value of $d(\varepsilon_{33}/\varepsilon_0)/dT$. In case of T-phase samples poled by HVP-method maximum of γ_D and γ_{ST} correspond to temperature of maximal increase in $\varepsilon_{33}/\varepsilon_0$. The LVP-method of poling caused a shift of maximum of $\varepsilon_{33}/\varepsilon_0$ towards higher temperatures by 20 °C (Fig. 2).

It is commonly known[1–3,5] that the relative permittivity and piezoelectric parameters of PZT-based solid solutions reach their maximal values near the MBR region. Therefore, we have studied the temperature dependence of $\varepsilon_{33}/\varepsilon_0(T)$, $\gamma_D(T)$ and $\gamma_{ST}(T)$ for the samples exhibiting compositions corresponding to MBR (Figs. 3 and 4, $x = 0.4245$).

It can be seen from Fig. 3 that $\varepsilon_{33}/\varepsilon_0(T)$ curves exhibit asymmetric profiles in relation to T_C. In this connection it should be noted that for the samples poled by the LVP-method a low-temperature peak appears on the $\varepsilon_{33}/\varepsilon_0(T)$ curve at $T = 168$ °C. However, the peak does not emerge on cooling the sample. It has been found that heating the samples up to temperature that exceeds temperature of the first maximum but is smaller than the Curie point and subsequent cooling to RT leads to disappearance of such a low-temperature peak on the $\varepsilon_{33}/\varepsilon_0(T)$ curve.

Dependence of $\gamma_{ST}(T)$ for LVP-poled samples (Fig. 3) exhibits three maxima namely, at $T = 168$, 289 and 400 °C. Two of them have the ferroelectric nature, and correspond to temperatures of rapid change in γ_D. Strong diffuse of the low-temperature peak of γ_{ST} is a consequence of high stability of the state of polarization produced by the LVP-method of poling. The third maximum can be ascribed to the discharging current of the ferroelectric nature.

For the HVP-method of poling γ_D exhibits two maxima (Fig. 3) of the same value namely, a strongly diffuse low-temperature peak and the high-temperature peak corresponding to the flex point on the permittivity curve. Dependence of $\gamma_{ST}(T)$ exhibits two maxima at $T = 187$ °C and $T = 293$ °C. They correspond to maximum of $d\gamma_D/dT$ and they lie in the ferroelectric phase temperature region.

Family of the curves depicted on Fig. 4 describes influence of the regimes of poling on thermal stability of relative permittivity ($\varepsilon_{33}/\varepsilon_0$) and pyroelectric coefficients (γ_D and γ_{ST}) for samples with compositions corresponding to MBR. It has been found that an increase in poling temperature (HVP-method at $T = 140$ °C) as well as an increase in the electric field strength (LVP-method at $E = 210^6$ V/m) cause in increase in an amplitude of the low-temperature maximum on dependencies $\varepsilon_{33}/\varepsilon_0(T)$, $\gamma_D(T)$, $\gamma_{ST}(T)$. An increase in the poling field, however, can result in creation of the domain structure stable to heat.

These phenomena can be explained by the following facts: (1) action of the electric field brings to an increase in the rhombohedral distortion of the crystalline lattice. (2) It also induces phase transitions from the tetragonal phase to the rhombohedral phase in some microvolumes of the bulk material. Subsequent heating can cause reconstruction of the structure (i.e., rhombohedral-to-tetragonal phase transition occurs in microvolumes) followed by an intensive domain reconstruction towards more stable domain structure. Stabilization of the

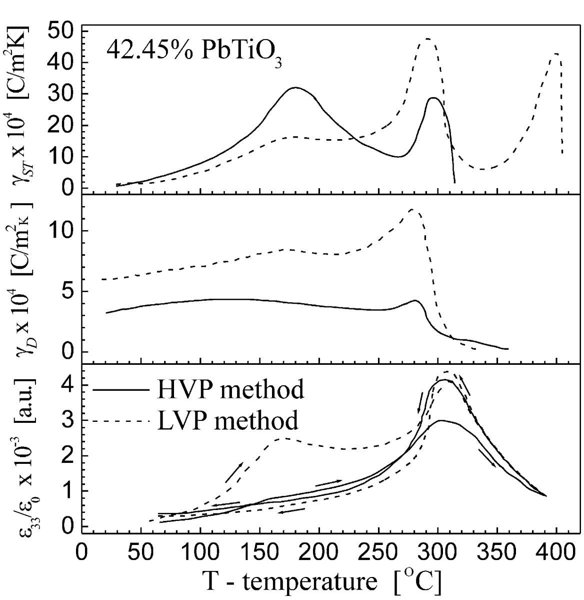

Fig. 3. Dependence of pyroelectric coefficient γ_{ST} and γ_D, and relative permittivity $\varepsilon_{33}/\varepsilon_0$ on temperature for PZT-based ceramics with $PbTiO_3$ content $x = 42.45\%$ (morphotropic phase transition region).

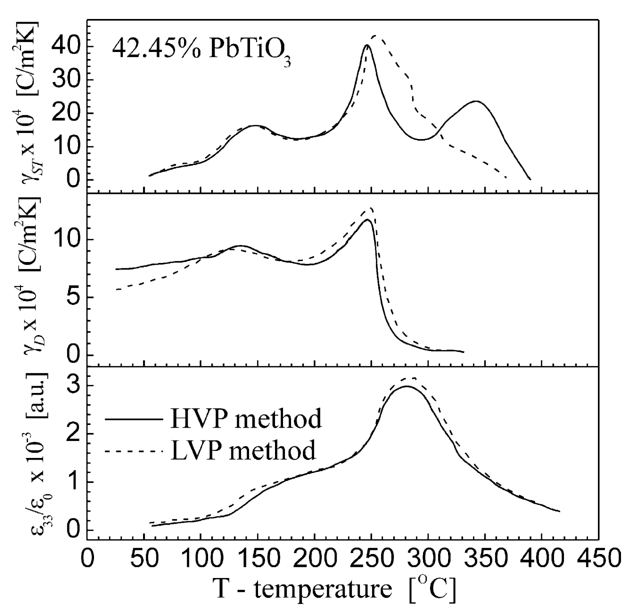

Fig. 4. Influence of increased temperature of poling (HVP at $T = 140$ °C) and electric field strength (LVP at $E = 2 \times 10^6$ V/m) on pyroelectric coefficient γ_{ST} and γ_D, and relative permittivity $\varepsilon_{33}/\varepsilon_0$ for PZT-based ceramics from MBR ($PbTiO_3$ content $x = 42.45\%$).

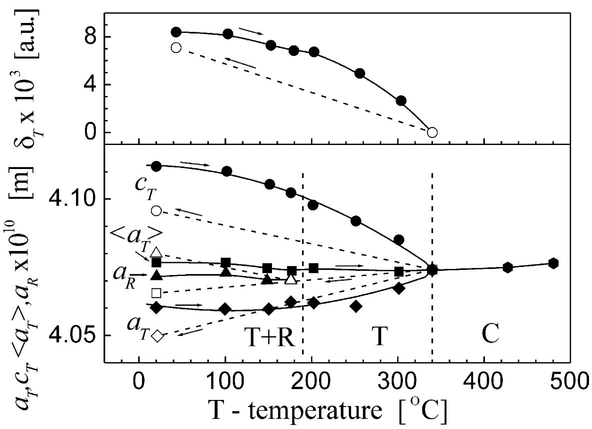

Fig. 5. Dependence of the elementary cell parameters (a_T, $<a_T>$, a_R, c_T) and homogeneous parameter of deformation (δ_T) on temperature for poled PZT-based ceramic sample.

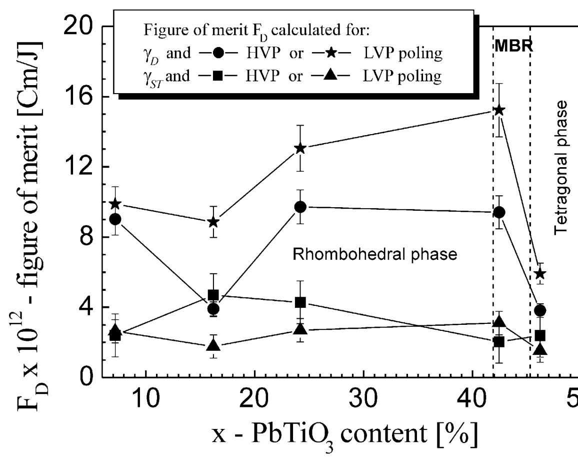

Fig. 6. Calculations of figure of merit (F_D) for PZT-based ceramics exhibiting different content x of $PbTiO_3$ component.

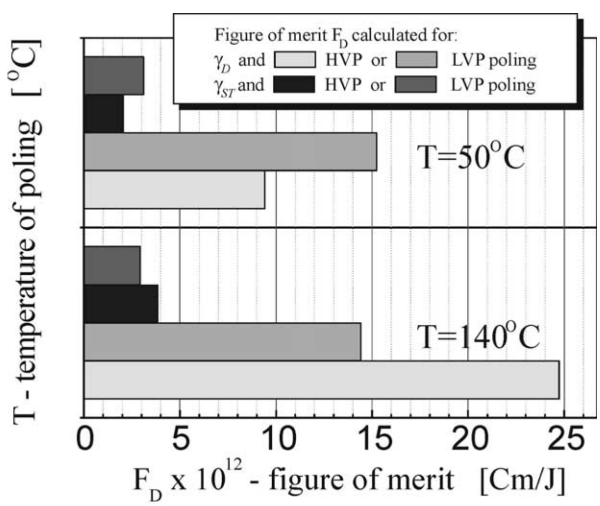

Fig. 7. Influence of regimes of poling on figure of merit for PZT-based ceramics from MBR ($PbTiO_3$ content $x = 42.45\%$).

domain structure results in disappearing of the low-temperature peak on $\varepsilon_{33}/\varepsilon_0(T)$ dependence, whereas possibility of R- to T-phase transition conditions the low-temperature peaks on $\gamma_D(T)$, $\gamma_{ST}(T)$ dependencies.

To prove the above assumptions X-ray investigations have been carried and dependence of the elementary cell parameters on temperature was studied. One can see in Fig. 5 that the rhombohedral unit cell parameter a_R is smaller than the average parameter of the tetragonal unit cell $<a_T> = \left(a_T^2 c_T\right)^{1/3}$ until the rhombohedral phase disappears at $T \approx 190$ °C. Heating through the Curie point up to $T = 600$ °C and subsequent cooling to RT results in a decrease in $<a_T>$ down to $<a_T> = 4.067$ Å (a_T and c_T parameters also decrease). At the same time, however, parameter a_R increases to $a_R = 4.08$ Å. As a result of such thermal treatment spontaneous deformation described by homogeneous parameter of deformation (δ_T) decreases. It has been found that secondary poling of the sample do not reconstruct the initial structural state.

Usually, the evaluation of pyroelectric material is carried out using the figure of merit $F_V = \gamma/c_V\varepsilon_r$ for voltage responsivity and $F_D = \gamma/c_V\sqrt{\varepsilon_r}$ for relative detectivity, where c_V is volume specific heat and ε_r is relative permittivity. Fig. 6 shows F_D as a function of $PbTiO_3$ content x for compositions from tetragonal and rhombohedral phase as well as MBR. It is worth noting that large figure of merit (i.e., $F_D > 8\times10^{-12}$ Cm J^{-1}) was obtained in case of a dynamic mode of measurement of the pyroelectric coefficient. It results from Fig. 6 that the compositions from MBR are the most prospective for practical applications.

Influence of regimes of poling on F_D for PZT-based ceramics from MBR is given in Fig. 7. In this connection it should be noted that an increase in poling temperature from 50 to 140 °C caused an increase in F_D by 2.5 times (i.e., up to $F_D = 25\times10^{-12}$ Cm J^{-1}).

4. Conclusions

New five-component PZT-based solid solution system was investigated. Comprehensive study of pyroelectric, dielectric and structural parameters was performed and compositions were found exhibiting large pyroelectric coefficient and small dielectric constant along the polarization axis.

Two methods of poling were used and it was found that the poling process conditions phenomena on thermal dependencies of pyroelectric coefficients due to structural changes induced during poling. It has been stated that the higher thermal stability of the state of polarization was produced by the LVP-method of poling.

Consideration of figure of merit for pyroelectric IR detection shows that investigated PZT-based solid solution system is a prospective material for pyroelectric infrared detectors as well as other practical applications.

References

1. Moulson, A. J. and Herbert, J. M., *Electroceramics. Materials, Properties, Applications*. Chapman and Hall, London, 1997.
2. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London and New York, 1971.
3. Fesenko, E. G., Danciger, A.Ia. and Razumovskaia, O. N., *Novyie Piezokieramicheskie Materially*. Izd.RGU, Rostov na Donu, 1983.
4. Czekaj, D., Lisiñska-Czekaj, A., Kuprianov, M. F. and Zakharov, Yu.N., Pyroelectric properties of the multi-component ferroelectric ceramic materials. *J. Eur. Ceram. Soc.*, 1999, **19**, 1149–1152.
5. Fesenko, E. G., *Semeistvo Perovskita i Segnetoelektrichestvo*. Atomizdat, Moskva, 1972.
6. Chynoweth, A. G., Dynamic method for measuring the pyroelectric effect with special reference to barium titanate. *J. Appl. Phys.*, 1956, **27**, 78–84.