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Pyroelectric Properties of the Multi-component Ferroelectric Ceramic Materials

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Abstract

Five-component ferroelectric ceramic materials, on the basis of solid solutions of: $PbTiO_3$–$PbZrO_3$–$PbNb_{2/3}Zn_{1/3}O_3$–$PbSb_{2/3}Mn_{1/3}O_3$–$PbW_{1/2}Mg_{1/2}O_3$ *(system I) and* $PbTiO_3$–$PbZrO_3$–$PbNb_{2/3}Zn_{1/3}O_3$–$PbSb_{2/3}Mn_{1/3}O_3$–$PbNb_{2/3}Mn_{1/3}O_3$ *(system II), have been prepared by means of hot pressing technique. The pyroelectric properties of the above mentioned ceramic materials were investigated at room temperature for compositions from both tetragonal and rhombohedral phase areas, as well as from the morphotropic phase boundary region. The dependence of the pyroelectric coefficient on the concentration of* $PbTiO_3$ *is shown. Enhanced pyroelectric activity of the systems under investigation was found. The pyroelectric coefficient for the compositions from the morphotropic region worked out at* $\gamma_1 = 4\times10^{-4}Cm^{-2}K$ *and* $\gamma_2 = 5\times10^{4}Cm^{-2}K$ *for the system I and II, respectively. It was stated that the materials under investigation were characterised by high merit numbers, which made them prospective for pyroelectric detectors.* *© 1999 Elsevier Science Limited. All rights reserved*

Keywords: pyroelectric properties, hot pressing, dielectric properties, ferroelectric properties, PZT.

1 Introduction

It is a common knowledge that ferroelectric ceramics have a number of properties which make them very useful in a variety of applications. These include (i) a high dielectric constant, (ii) high piezoelectric constants, (iii) relatively low dielectric loss, (iv) high electrical resistivity, (v) low moisture sensitivity, (vi) high electromechanical coupling, (vii) medium hardness, (viii) fairy high pyroelectric coefficients, and in some special compositions, also (ix) high optical transparency and (x) high electrooptic coefficients. However, these properties do not always combine to produce an optimum effect in any one application. On the other hand, these properties in ceramics can be continuously modified over specified ranges because many ceramic compositions form solid solutions of one or more compounds in each other. This is particularly true when we consider ceramic materials based on lead-zirconate-titanate (PZT).[1]

On the phase diagram of the $PbZrO_3$–$PbTiO_3$ system one can see that the ferroelectric phase has tetragonal (T) or rhombohedral (R) symmetry. The boundary between the tetragonal and rhombohedral forms is called a morphotropic phase boundary (two phases are present in equal quantity) and the region of coexistence of these two phases is called a morphotropic region (M). As it results from the analysis of the literature data,[1–3] dielectric permittivity and piezoelectric parameters reach their maximum values near that morphotropic region. Unfortunately, there is no simple relation between pyroelectric and piezoelectric parameters in ferroelectric materials.[4]

It was our goal to show the results of investigations of electrophysical properties of the two five-component PZT—based systems of complex ferroelectric oxides for compositions from the rhombohedral phase, morphotropic phase transition region and tetragonal phase.

2 Experimental

Two PZT-based complex oxide systems were prepared for investigation. System I which consists of: $xPbTiO_3 + (1\text{-}x)(a_1PbZrO_3 + b_1PbNb_{2/3}Zn_{1/3}O_3 + c_1PbSb_{2/3}Mn_{1/3}O_3 + d_1PbW_{1/2}Mg_{1/2}O_3)$, and system II of the following chemical composition: $xPbTiO_3 + (1 - x)(a_2PbZrO_3 + b_2PbNb_{2/3}Zn_{1/3}O_3 +$

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$c_2PbSb_{2/3}Mn_{1/3}O_3 + d_2PbNb_{2/3}Mn_{1/3}O_3)$, where a_i, b_i, c_i, d_i—are constants. The range of $PbTiO_3$ mole fraction 'x' was: $0{\cdot}35 \leq x \leq 0{\cdot}57$, and $0{\cdot}05 \leq x \leq 0{\cdot}95$ for compositions in system I, and system II, respectively. It should be noted that sets of constants (a_i, b_i, c_i, d_i) were selected on the basis of the phase diagram of the $PbTiO_3$–$PbZrO_3$–$PbNb_{2/3}Zn_{1/3}O_3$ ternary system[5] and the method of searching for the morphotropic phase region of the multi-component PZT–type systems.[5,6]

The ceramic samples were prepared by hot-pressing method. The optimal temperature of the process of sintering was chosen experimentally for every composition and was within the range $T_S = (1100–1200)$°C; time of sintering $t_S = 40$ min; pressure applied to the samples worked out at $P = 19{\cdot}6 \times 10^6$ Pa. Density of the as-made samples was within the range $\rho = (7{\cdot}9–8{\cdot}0) \times 10^3$ kg m^3, and porosity was from 0·2 to 0·3%. To polarise the samples a constant electric field of $E_c = 4 \times 10^6$ V m^{-1} was applied for 25 min at the temperature of $T_P = 140$°C. The samples were then cooled under the electric field to 90°C in 20 min.

Measurements of the dielectric permittivity was carried out by a bridge technique. X-ray diffraction method was used to confirm the compound formation and to determine the structural parameters of the elementary cell. As a measure of tetragonal and rhombohedral distortions of the elementary cell the homogeneous parameter of deformation[7] δ was used. For small tetragonal distortions (i.e. if $|\frac{c}{a} - 1| << 1$)), the homogeneous parameter of deformation is given by:

$$\delta = \frac{2(c-a)}{2a+c} \approx \frac{2}{3}\left(\frac{c}{a} - 1\right) \qquad (1)$$

where c, a are parameters of the tetragonal elementary cell. For small rhombohedral distortions (i.e. if $|\cos\alpha|1)$, the parameter of deformation is given by:

$$\delta = 1 + 2\cos\alpha - 1 \approx \cos\alpha, \qquad (2)$$

where α is the angle of the rhombohedral elementary cell.

Pyroelectric coefficient γ was measured by means of dynamic method[8,9] at room temperature. As the source of light an AP106-type light emitting diode, with wavelength $\lambda = 0{\cdot}98\ \mu$m, with amplitude modulation of the intensity of radiation was used. Frequency of the amplitude modulation was 5 Hz. Such a frequency made it possible to measure pyroelectric coefficient of samples with thickness up to 2 mm without increasing the measurement error (accuracy of the measurements was 5–7%).

3 Results

The measurements reveal high pyroelectric activity of the systems under investigation. When the amount of $PbTiO_3$ decreases, the system undergoes a morphotropic phase transition from tetragonal to rhombohedral phase. In Fig. 1 the dependence of the homogeneous deformation parameter δ and Curie temperature T_C versus $PbTiO_3$ mole fraction are shown. The dependence of the dielectric constant $\varepsilon^T_{33}/\varepsilon_0$ of the polarised sample and pyroelectric coefficient γ that characterise sensitivity of the pyroelectric detectors on the $PbTiO_3$ ratio is shown in Fig. 2. Both Figs 1 and 2 show results of investigations for the samples made from composition in the system I. The exact values of the constants are as follows: $a_1 = 0{\cdot}764, b_1 = 0{\cdot}127, c_1 = 0{\cdot}016, d_1 = 0{\cdot}093$.

In Figs 3 and 4 the dependencies of δ, T_c, $\varepsilon^T_{33}/\varepsilon_0$ and γ for one of the compositions of the system II are shown. In that case the values of the constants are: $a_2 = 0{\cdot}821$, $b_2 = 0{\cdot}116$, $c_2 = 0{\cdot}024$, $d_2 = 0{\cdot}039$.

From the dependence of the homogeneous deformation parameter δ on the $PbTiO_3$ ratio 'x',

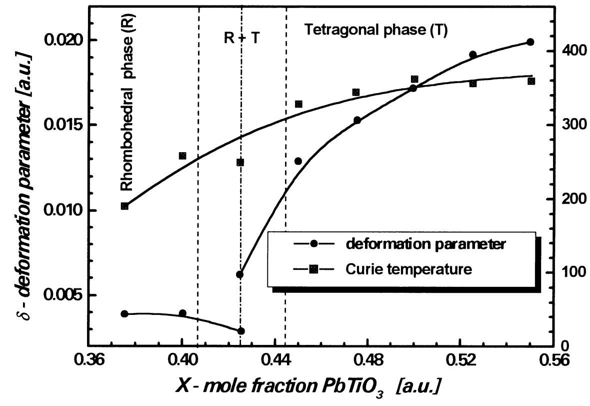

Fig. 1. Dependence of the deformation parameter δ of the elementary cell and Curie temperature T_C on the mole fraction x of $PbTiO_3$ component for the PZT ceramic system I.

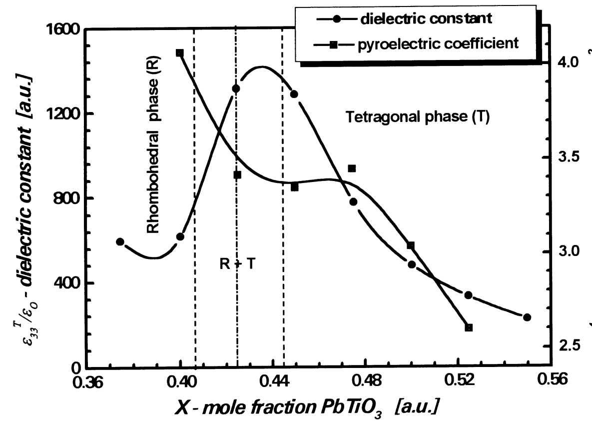

Fig. 2. Dependence of the dielectric constant of the poled samples $\varepsilon^T_{33}/\varepsilon_0$ and pyroelectric coefficient γ on the mole fraction x of $PbTiO_3$ component for the PZT ceramic system I.

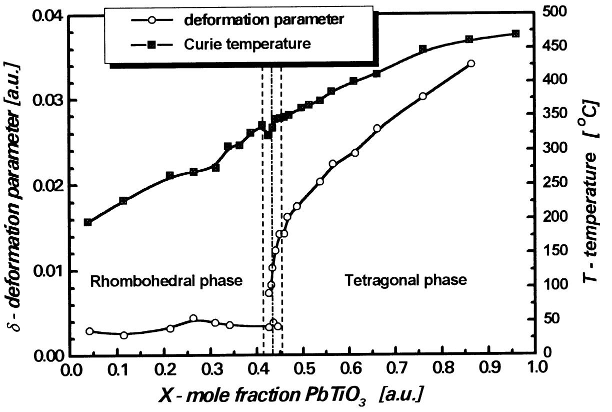

Fig. 3. Dependence of the deformation parameter δ of the elementary cell and Curie temperature T_C on the mole fraction x of $PbTiO_3$ component for the PZT ceramic system II.

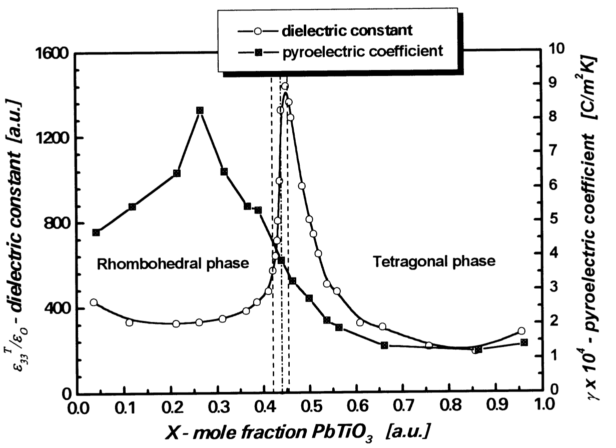

Fig. 4. Dependence of the dielectric constant of the poled samples $\varepsilon_{33}^{T}/\varepsilon_0$ and pyroelectric coefficient γ on the mole fraction x of $PbTiO_3$ component for the PZT ceramic system II.

the position of the two-phase compounds corresponding to the centre of the morphotropic phase region (dot-point line in Figs 1–4) was determined. It was found that the centre of the M-region was situated at $x_1 = 0{\cdot}425$, and $x_2 = 0{\cdot}436$ for composition in systems I and II, respectively. Boundaries of the morphotropic phase region correspond to the boundaries between mono- and di-phase compositions (dot-lines in Figs 1–4). The width of the M-region works out at (2–4)% mole $PbTiO_3$.

One can see from Figs 2–4 that dielectric permittivity $\varepsilon_{33}^{T}/\varepsilon_0$ reaches its maximum value in the M-region near the T-phase boundary, and works out at $\varepsilon_1 = 1380$, and $\varepsilon_2 = 1440$ for compositions in systems I and II, respectively. The pyroelectric coefficient γ increases with the transition from T-phase to R-phase region (Figs 2 and 4). It undergoes small local maximum of about $\gamma_1 = 3{\cdot}45 \times 10^{-4}$ $Cm^{-2}K^{-1}$ in the T-phase region near the M-region (at $x = 0.475$ for composition in system I; see Fig. 2), and reaches a maximum of about $\gamma_2 = 8.3 \times 10^{-4}$ $Cm^{-2}K^{-1}$ in the R-region at a distance of 15% mole $PbTiO_3$ from the rhombohedral boundary of the morphotropic region (at $x = 0.26$ for composition in system II; see Fig. 4).

It has been also stated that in case of the system I increasing the amount of the 'hard' component 'c', $PbSb_{2/3}Mn_{1/3}O_3$, causes a shift in the maximum of the pyroelectric coefficient γ towards the boundary of the morphotropic region. Analysis of the dependencies of γ versus $PbTiO_3$ mole fraction x shows that the average value of the pyroelectric coefficient in the M-region of the system II works out at $\gamma_2 = 5 \times 10^{-4}$ $Cm^{-2}K^{-1}$ and for system I $\gamma_1 = 4 \times 10^{-4}$ $Cm^{-2}K^{-1}$.

The following explanation of the measured dependencies can be given. The increase in γ with the transition from the region of the tetragonal phase into the region of the rhombohedral phase and the formation of the peak value in the R-phase (Fig. 4) are caused by the monotonous decrease in the Curie temperature (Figs 1–3). The latter increases the rate of change of the remnant polarisation P_r with temperature. Also it should be noted that the remnant polarisation reaches its maximum value in the R-phase region.[2] The higher values of the pyroelectric coefficient γ in the system II as compared with system I, can be ascribed to the higher ferroelectric hardness of system II. The two multi-component ferroelectric systems differ in the fifth component, namely in the soft ferroelectric component $PbW_{1/2}Mg_{1/2}O_3$ in system I and in the hard ferroelectric component $PbNb_{2/3}Mn_{1/3}O_3$[2] in system II. On the basis of the mathematical equations[10] for remnant polarisation P_r in the R- and T-phases, one can show that when the ferroelectric hardness increases, the remnant polarisation of the solid solutions also increases as does the pyroelectric coefficient.

4 Conclusions

Solid solutions of the investigated systems exhibit higher pyroelectric activity as compared with pure PZT solid solutions due to the influence of the additional components. It has been found that increasing the amount of the hard ferroelectric component in the investigated PZT-type systems ($PbSb_{2/3}Mn_{1/3}O_3$ in system I and $PbSb_{2/3}Mn_{1/3}O_3 + PbNb_{2/3}Mn_{1/3}O_3$ in system II) causes an increase in the pyroelectric coefficient. Relatively small values of dielectric constant and high pyroelectric coefficient for the compositions from the rhombohedral phase, that is to say, for the range of $PbTiO_3$ mole fraction $0{\cdot}38 \leq x \leq 0.4$ for system I (Fig. 2) and $0{\cdot}2 \leq x \leq 0{\cdot}3$ for system II (Fig. 4), make them prospective for practical applications as materials for pyroelectric detectors.

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