Measurements of pyroelectric coefficients of BT and BST ceramics

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Abstract. In the work, the field and temperature dependencies on the pyroelectric coefficients of ceramic capacitor structures were measured. Barium titanate (BT) and solid solutions of barium-strontium titanate (BST) were investigated. At temperatures range from 20 ℃ to 30 ℃, the values of the pyroelectric coefficients of the BST ceramics \( p \approx 10^{-5} - 10^{-4} \text{C/m}^2\text{K} \) exceeded \( p \) for the BT ceramics by an order. The developed measurement technique made it possible to carry out direct pyroelectric coefficients measurements and determine the polarization initial state of the samples, regardless of their phase state.

1. Introduction

Ferroelectric ceramics based on barium titanate and its solid solutions with other perovskites, for example strontium titanate, have been intensively studied for more than half a century. These materials have great ferroelectric, dielectric, pyroelectric and piezoelectric properties [1-4]. BT and BST ceramics used in multilayer ceramic capacitors, microwave devices [5,6], and communication systems in modern microelectronics [1-3, 7-11]. Currently, one of the most interesting effects for practical use is the electrocaloric effect [12,13]. For these applications, BT and BST are being investigated as alternatives to toxic and environmentally harmful lead-containing ceramics [14].

The electrocaloric effect (ECE) is a phenomenon in which a material shows a reversible temperature change under an applied electric field. A new generation of solid-state cooling devices based on electrocaloric effect can be manufactured [12,13,15,16]. Low values of electrocaloric temperature change (\( \Delta T \)) are the main obstacle to using the electrocaloric effect in technology. Generally, information of the ECE value is obtained by indirect methods [17]. To determine the electrocaloric temperature change, it is necessary to calculate the integral of the pyroelectric coefficient over the applied field. [15].

The pyroelectric coefficient \( p \) includes primary, secondary, tertiary and field-induced pyroelectric effects. It is calculated as [15]:

\[
p = \frac{\partial P}{\partial T},
\]

where \( P \) is the polarization and \( T \) is the temperature.

This equation can be represented as follows:
\[ p = \frac{\partial P}{\partial t} \frac{\partial t}{\partial T} , \]  
where \( t \) is time. At a uniform distribution of charges over the surface with area \( S \), the modulus of the polarization vector can be written as \( P = Q / S \). Substituting \( P \) in (2):

\[ p = \frac{\partial q}{\partial S} \frac{\partial t}{\partial T} = \frac{S \cdot \partial U}{S \cdot \partial t} = \frac{C_0 \partial U}{S \cdot \partial T} , \]  
where the pyroelectric current density \( j = (dq / dt) / S \), capacitance \( C_0 \), pyroresponse voltage \( U \).

The purpose of the work is to develop and refinement the technique for measuring the pyroelectric coefficients in the ferroelectric ceramics based on solid solutions of barium-strontium titanate.

2. Methods and materials

The model of the measurement equipment for investigations pyroelectric response was developed. The temperature modulation (the rate of temperature change \( dT / dt \)) was carried out by laser pulses.

Figure 1 shows the flowchart of the measuring equipment. The ferroelectric sample \( C_x \) is placed in the measuring cell (MC). The initial temperature is controlled by a Peltier element. Using the laser (L) the sample is irradiated with thermal pulses of laser radiation with wavelength of 460 nm, maximum power of 1 W, the rise and drop of intensity ~ 1 ns and frequency of 0.1-0.5 Hz. The pulses are set by the signal generator (SG).

A modulated heat flow of the laser heats up the plane-parallel ferroelectric capacitor \( C_x \) and changes its polarization. The charge changes on the capacitor plates due to the polarization change. The charges on the plates of the capacitor \( C_x \) and the capacitor \( C_0 \) are equal since the capacitors are connected in series. The charge change of the capacitor \( C_x \) leads to a similar charge change of the capacitor \( C_0 \). The voltage change \( U \) is proportional to the charge change of the capacitor \( C_0 \), and, accordingly, charge change of \( C_x \). In the work, the voltage change \( U(t) \) will be called a pyroelectric response, which is measured by the signal detector (SD – Digital Multimeter Keysight 34461A, (Keysight Technologies, USA)).
The $C_x$ temperature at the point of heating is measured by the thermal radiation receiver (TRR – Testo 885-2, Germany) and transmitted to the personal computer (PC). The temperature measurement accuracy is 0.1 °C.

Thus, using the formula (3), the values of $p$ are calculated with measurements of the pyroelectric response $U(t)$. The area $S$, which should be used in the formula (3), is not equal to the area of the metal electrodes of the capacitor $C_x$, since the polarization changes only in the small heated area. The experimental determination of the effective area $S$ for calculating the pyroelectric coefficient is given below.

The measurements of the capacitance vs temperature were carried out by the Agilent E4980A precision LCR meter (Keysight Technologies, USA). A sample was fixed in the special holder placed in the climatic chamber. The measurements were carried out in the temperature range from -60 °C to 250 °C. The temperature change rate was 1 K / min. The capacitance measurement accuracy was 0.05 %.

The leakage currents were measured by the Keysight B2987A Electrometer / High Resistance Meter (Keysight Technologies, USA). The resistance of the samples was not less than $10^{11}$ Ohm.

Both ceramics were produced using conventional mixed oxide route followed by sintering in air atmosphere. The temperature of BT synthesis was 1325 °C, the temperature of BST synthesis was 1350 °C. The synthesis was carried out in two stages with intermediate grinding and granulation of samples. Ceramic samples BT and BST had the value of relative densities 90 - 95%. For measurements, we used plane-parallel ceramic samples of barium titanate (BaTiO$_3$ - BT) and the solid solution of barium-strontium titanate (Ba$_{0.62}$Sr$_{0.38}$TiO$_3$ - BST). The Sr content was chosen so that the sample was in the paraphase at room temperature. The thicknesses of capacitor structures were 1.32 mm for BT and 0.48 mm for BST. The diameter of metal electrodes was 10 mm.

3. Experimental results
The temperature dependencies on the dielectric permittivity of studied samples are shown in Fig. 2. The temperatures of ferroelectric phase transitions were 5 °C and 124 °C for BST and BT, accordingly. Thus, the BT samples remained in the ferroelectric phase, while the BST samples remained in the paraphase during the measurements.

![Figure 2. Temperature dependencies on the dielectric permittivity of ceramic structures based on: 1) BT; 2) BST.](image-url)
Figure 3 shows the results of four measurements of pyroelectric responses $U$ for the same BT sample with a decrease in its area with no bias voltage applied. Reducing the area of the sample by 5 times decreased the pyroelectric response by 1.5 times. Thus, the value of the effective area of the electrodes $S$ used for calculating the values of the pyroelectric coefficients according to the formula (3), equaled the area of the laser beam which was 3 mm$^2$. Figure 3 also shows $T$ vs $t$ dependencies of the samples, synchronized with the $U(t)$ dependencies.

Figure 4 shows the dependencies on the pyroelectric responses $U(t)$ for the BST ceramics at different bias voltages and the fixed initial sample temperature $T = 26$ °C. It can be noted that in the absence of the bias voltage ($U_{BV} = 0$), the pyroresponse values for BT (Fig. 3) and BST (Fig. 4) have the same order. The increase in $U_{BV}$ leads to the increase in the pyroelectric responses, since the external field-induced polarization increases in accordance with the $P(E)$ dependence [18]. Similar dependencies $U(t)$ with the change in $U_{BV}$ were observed for the BT samples, although the values of the pyroelectric responses differed several times in accordance with their different phase states at $T = 26$ °C (Fig. 2).

![Figure 3. Dependencies of pyroelectric characteristics and temperature changes on time for different areas of the BT sample at $U_{BV} = 0$ V.](image)

![Figure 4. Pyroresponses of BST samples at different bias voltages $U_{BV}$.](image)

In accordance with the equation (3), the dependencies of the pyroelectric coefficients vs the field strength $p(E_{BV})$ (Fig. 5) and the temperature $p(T)$ (Fig. 6) were calculated using the experimental dependencies of the pyroelectric responses measured at different temperatures and field strengths.

Comparison of curve 1 and curve 2 in Figure 5 shows that the pyroelectric coefficient for BT is significantly lower than for BST. The linear dependence $p(E_{BV})$ of the BT samples (curve 1) at low field strengths ($\leq 1.2 \cdot 10^5$ V/m) corresponds to the linear section $P(E)$. The decrease in the pyroelectric coefficients for the BST samples with the increase in the initial temperature (curves 3, 4, 5) is associated with the sharp decrease in the nonlinearity of the samples at $T > 40$ °C temperatures (Fig. 2).

To compare the temperature dependencies on the pyrocoefficients of BT and BST the $p(T)$ plots are presented on the semilog scale (Fig. 6). The temperature dependencies on the pyrocoefficients shift upward with the increase in the bias voltage, since the polarization increases. In this case, the pyroelectric coefficient for the BT samples increases with increasing the temperature (curves 1, 2). For the BST samples, the pyroelectric coefficient decreases with increasing the temperature (curves 3-6). The difference in the behavior of the $p(T)$ dependencies is due to the fact that the BT samples were in the ferroelectric phase and the BST samples were in the paraelectric phase over the entire temperature range (Fig. 2).
4. Conclusion
The developed technique allows to obtain the pyroelectric coefficients from $U(t)$ dependencies without direct measurements of the pyroelectric current. The advantage of this technique is that it allows to measure pyroelectric coefficients due only to the spontaneous polarization, without the polarization induced by the external field for samples in the ferroelectric phase. For samples in the paraelectric phase, the technique is the means of reading the initial polarization state.

The nature of dependencies of the pyroelectric coefficients vs the bias voltage and temperature correspond to the temperature-field dependencies on the polarization, measured according to the standard measurement procedure $P(E)$.

It is shown that the ceramics based on BST solid solution have better pyroelectric properties compared to the BT ceramics at a temperature of 26 – 40 °C. It is more suitable for applications as a material for solid state cooling devices operating at room temperature.

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