Methods for assessing pyroelectric current in ferroelectrics with first order phase transition by dielectric measurements

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Abstract. The creation of devices based on the electrocaloric effect requires the methods for assessing pyroelectric currents at the different external parameters. Two indirect methods for calculating pyroelectric currents in ferroelectrics are considered. The first one based on the temperature-field dependences of the dielectric hysteresis loops. The second one based on the temperature-field dependences of the dielectric constant. The original method for directly estimating the magnitude of the pyroelectric currents by the charge change with thermal flux of laser radiation pulses is proposed.

1. Introduction

Quantitative assessment of pyroelectric currents is necessary to characterize ferroelectrics (FE) and the development of a new generation of multifunctional devices [1], in particular, solid-state energy converters and solid-state cooling devices based on the electrocaloric effect (ECE) [2,3]. Thermodynamic analysis of ECE showed that it is necessary to consider the contribution of the pyroelectric current \(J_{pyr}\), which is determined by the value of pyroelectric coefficient \(p\) [2,4].

Measurements of pyroelectric currents are carried out with simultaneous influence of an electric field and temperature. Thus, conduction currents, thermally stimulated currents, as well as currents arising at the interface with metal electrodes can contribute to the measured pyroelectric current. Therefore, for each specific application of ferroelectric materials requires simultaneous influence of temperature and electric field, methods for measuring pyroelectric coefficients and pyro currents can be different.

In this paper, the methods for calculating pyro-currents from the experimental results of measuring the temperature-field dependences of the dielectric hysteresis loops and capacitance were considered. Also, an original method for measuring pyro-currents resulting from the thermal effect of laser pulses on samples of FE has been proposed.

Pyroelectric current appears when the temperature changes. Heating the sample by a small amount \(dT\) will lead to a change in the bound charge on the surface of the electrodes:

\[
\frac{dQ}{S} = \frac{dP}{dT} dT
\]  

(1)

where \(S\) is the electrode area, \(T\) is the temperature, \(P\) is the spontaneous polarization of the sample, since field-induced polarization can be neglected compared to spontaneous. Then the density of the pyroelectric current can be written as:
\[ J_{pyr} = \frac{dP}{dT} \frac{dT}{dt} \]  

(2)

where \( p = \frac{dP}{dT} \) is the pyroelectric coefficient. Usually, the pyroelectric properties of materials are compared in terms of pyroelectric coefficients.

2. Experimental

For the measurements, we used plane-parallel ceramic samples of barium titanate (BaTiO\(_3\) - BTO), a solid solution of barium strontium titanate (Ba\(_{0.55}\)Sr\(_{0.45}\)TiO\(_3\)) with addition of 12 mol.% Mg (BSTM) and a solid solution of barium strontium titanate - (Ba\(_{0.62}\)Sr\(_{0.38}\)TiO\(_3\) - BST). Curie temperatures are 407 K, 215 K and 277 K for BTO, BSTM and BST, respectively. The thickness of the capacitor structures was 0.25 mm for BTO and 0.50 mm for BSTM and BST. The diameter of the metal electrodes ranged from 6 mm to 10 mm.

Figure 1 shows the temperature dependences of polarization at different rates of temperature change, obtained from measurements of dielectric hysteresis loops.

Figure 2 shows the temperature dependences of the pyroelectric current, which were calculated from the dependences \( P(T) \). With an increase in the temperature change rate, the pyroelectric current increases in accordance with the change in the pyroelectric coefficient. Estimation of the pyroelectric coefficient in the paraphase gives the value \( \sim 5\times10^{-4} \text{C/m}^2\cdot\text{K} \), and in the ferrophase \( \sim 20\times10^{-4} \text{C/m}^2\cdot\text{K} \).

Despite direct measurements of polarization, the proposed method is indirect, since to build temperature dependences of pyroelectric currents requires intermediate calculations of spontaneous polarization from the dielectric hysteresis loops. The accuracy of the method is limited by the number of stabilized temperature points for measuring hysteresis loops at different field strengths.
Figure 2. Temperature dependence of the pyroelectric current of BTO samples at different heating rates at an amplitude of the electric field strength $E = 3\, \text{MV/m}$.

The second method is illustrated by the solid solution of barium strontium titanate (BSTM). This method allows to calculate the temperature dependences of $P(T, E)$ (Figure 3) from the measurement of the temperature-field dependences of the capacitance.

Figure 3. Temperature dependences of polarization for BST samples with 12 mol.% Mg at field strengths of 1 - 0.2 MV/m, 2 - 0.8 MV/m, 3 - 1.6 MV/m. Inset shows capacitance vs. temperature curves at different voltages.
The method is based on a nonlinear relationship between the electric field strength and polarization [5]. To calculate the polarization, measurements in the paraelectric phase [6] of a ferroelectric \( (P_s=0) \) are used:

\[
P = S \int_0^L c \, dU + \frac{\varepsilon_0}{d} U + \text{const}
\]

(3)

The pyroelectric current was calculated from the dependences \( P(T, E) \) (Figure 4). The estimation of the pyroelectric coefficient in this method is \( \sim (2-8) \times 10^{-4} \) C/m²·K. The second method of measuring pyroelectric currents is also indirect as the first method. Its main advantage is that measurements of the temperature-field dependences of the capacitance used in the calculations are one of the simplest methods for studying the dielectric properties of ferroelectrics. However, the computational part of the method, which uses numerical integration of large arrays of experimental data to obtain the \( P(T, E) \) dependence, is much more complicated than in the first method.

![Figure 4. Temperature dependences of the pyroelectric current at field strengths of 1 - 0.2 MV/m, 2 - 0.8 MV/m, 3 - 1.6 MV/m for BST samples with 12 mol.% Mg.](image)

We have proposed a method for directly estimating the magnitude of pyroelectric currents from the change in charge modulated by heat flux. The experimental setup is shown in Figure 5.

A DC bias is applied to create an induced polarization in the sample and accumulate the initial charge on the plates of capacitors \( C_x \) (the sample) and \( C_{\text{ref}} \). All voltage is applied to the capacitor \( C_x \). Difficulties in direct measurement arise because measuring devices have an input voltage limit. Therefore, the change in signal level is measured on a reference capacitor using a high-precision oscilloscope.

Peltier element is used to select a specific operating point. The range of temperature variation is from \(-30 \) °C to \(+130 \) °C.

The radiation power, the period and duration of the laser pulse are regulated by the generator and are selected separately for each experiment, based on the geometry of the sample and the ferroelectric material. The ferroelectric is heated under a modulated laser radiation. The polarization changes, the charge on the capacitor electrodes changes accordingly.
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Figure 5. Schematic laser pulse setup with simulated voltage and temperature signal for BST sample.

As a consequence, the potential changes at the point between the capacitors \( U_0 \). This change is detected and saved. The temperature change is recorded by the thermal imager and, together with the data of the potential change, is transmitted to a computer for further processing.

The change in the charge of the ferroelectric capacitor \( C_x \) due to a change in its polarization is defined as:

\[
dq = C_x(T) dU
\]  

(4)

Since the change in charge is associated with a change in temperature, the density of the pyroelectric current can be written as:

\[
J_{pyr} = \frac{C_x(T)}{S} \frac{dU}{dT} \frac{dT}{dt}
\]  

(5)

In accordance with the expression (5), it is necessary to synchronize the measurements of the capacitance \( C_x(T) \) with the measurements of \( U(T) \) and \( T(t) \). Experimental implementation of the proposed measurement method requires further careful study.

3. Conclusion
This paper shows that it is possible to carry out estimates of the amount of pyroelectric currents from field measurements using indirect methods. The temperature dependences of the pyroelectric currents for ferroelectric samples based on BTO and BSTM ceramics are obtained. Estimates of pyroelectric coefficients are given. Values are consistent in order of magnitude with the results of measurements by other authors [7]. However, the modes of external influences (\( E, T \)) in these methods differ from the modes of influence for solid-state coolers based on ECE. In the proposed method, the modes of temperature and field effects are close to the conditions used in the study of ECE. An experimental setup to measure pyroelectric currents was created. The response of the pyroelectric current to the short laser pulses was obtained.

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