Investigation of the electrocaloric effect in BaTiO₃ multilayers by pASC calorimetry

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Abstract. The electrocaloric heat production in BaTiO₃ - based multilayer ceramic capacitors with Y5V specification was measured in a direct way by means of an adiabatic calorimeter setup. Applying an electric field of 30 MV m⁻¹ is found to result in a heat release of 0.94 J g⁻¹ and an electrocaloric temperature change of 0.46 K, in good agreement with direct results in previous studies.

Keywords: Electrocaloric effect · Adiabatic scanning calorimetry · Multilayer · Ferroelectrics.

1 Introduction

The increasing exploration of novel electrocaloric materials with enhanced electrocaloric effect and their applications in electrocaloric cooling devices requires the development of practical measuring methods to investigate their electrocaloric properties [1–4]. Such characterization involves the measurement of the adiabatic temperature change and isothermal entropy production upon application of a certain electric field across a sample. In most studies, the electrocaloric effect has been estimated in an indirect way, using Maxwell’s relation and exploiting the reciprocity between the polarization or the pyroelectric coefficient and the electrocaloric effect [9, 11–13].

However, the reliability of this approach has long been a topic of discussion in the scientific community. For example, in the case of polyvinylidene fluoride and its derivatives, the accuracy of the extracted value for the electrocaloric energy production is controversial, due to non-ergodic behaviour[11]. As a consequence, direct characterization techniques are highly demanded in the field of electrocalorimetry.

Infrared sensing has been used for non-contact measurement of the direct temperature change [7, 11]. A thermal microscope, using a thermometer in direct contact with the sample [8, 9] has been employed as well. However, for direct determination of the electrocaloric heat production, adiabatic conditions are needed. These typically require a large sample volume (such as a bulk ceramic

or single crystal) in order to limit the fraction of heat flowing to or from the surroundings [4].

Efforts have been made to develop custom-made setups, among which a modified commercial differential scanning calorimeter, in which the heat flow was measured during application (or removal) of an electric field in isothermal conditions [10, 7].

Provided the sample is small, maintaining isothermal conditions is feasible. However, this comes at the price of a small amount of heat and thus a limited accuracy. In view of this, a complementary approach with a higher sensitivity, taking into account several crucial factors such as heat capacitance and thermal losses affecting the measurements, would be desirable.

The present study addresses this need, proposing a genuine adiabatic calorimeter design that is intended to yield reliable direct measurements on electrocaloric materials. The design is based on a Peltier element based adiabatic scanning calorimeter [15]. In its standard mode of operation, a constant power P is supplied to the sample platform, while the temperature evolution is continuously monitored. Meanwhile, by means of a proportional integrating control loop that nullifies the voltage over the Peltier element, which acts as a differential thermometer between the sample platform and the shield surrounding the sample platform, the temperature of the shield is maintained at the temperature of the sample platform, so that there is no heat exchange between the sample platform and the environment, guaranteeing adiabatic conditions. From the supplied power and the time evolution of the temperature, the temperature dependence of the heat capacity C_p and enthalpy H can then be deduced. In the following, a description is given of a modified version of an adiabatic scanning calorimeter, which allows to apply an electric field across the sample and measure the resulting heat production and temperature change. The performance of the device to quantify the electrocaloric heat production is demonstrated on a multilayer capacitor (MLC) based on barium titanate. The MLC geometry is attractive for use in applications, as the multiple electrodes provide both thermal and electrical access to a significant quantity electrocaloric (EC) material. This results in a large electrocaloric response for relatively small applied voltages (a few volts per μm). The results are compared with literature data on barium titanate based MLCs obtained by direct and indirect measurements [9, 16].

2 EXPERIMENTAL DETAILS

As mentioned above, Peltier-element-based adiabatic scanning calorimetry (pASC) is a well-established method for thermal analysis, in which a constant power is applied to a sample, in particular for studying the enthalpy evolution throughout a phase transition while maintaining thermodynamic equilibrium and yielding rate independent results. In this work, a standard pASC measurement setup [15] was modified in order to apply an electric field to the sample for direct electrocaloric measurements under isothermal conditions. Measurements were carried out on a multilayer capacitor containing barium titanate (Model Y5V)

purchased from AVX Company. The sample size was $3.3 \times 2.9 \times 2.56 \text{ mm}^3$ with mass 91.14 mg. The multilayer capacitor consisted of 200 doped Baryum Titanate layers of thickness $6.5 \mu\text{m}$ separated by interdigitated Ni electrodes of thickness $2 \mu\text{m}$. The terminals were covered with titanium nitride (TiN) for electrical contact. Ni electrodes were used for applying electric field, and also enhanced the conduction of electrocaloric heat between the baryum titanate layers and the terminals.

2.1 Measurement setup

Figure 1 shows the schematic setup (a) and photos (b) of the modified pASC setup that was used for electrocaloric measurements. At the core of the pASC sits a sample platform that is equipped with an electrical heater and an NTC resistance thermometer. The sample holder is mounted on a miniature Peltier element (PE) acting as a differential thermometer between the sample holder and the surrounding shield. Heating of the shield is done electrically, while cooling is done by radiation to the Tamson bath TV4000, in which the calorimeter is immersed. Adiabatic operation can be achieved by controlling the heater of the shield with a proportional-integrating (PI) loop aimed at keeping the PE voltage at zero, so that there is no temperature difference between the sample and the shield, impeding exchange of heat. When an electric field is applied, due to the electrocaloric effect, the sample temperature abruptly increases.

Fig. 1. (a) Scheme of modified pASC cell for electrocaloric measurements under isothermal conditions. (b) Images of the inside chamber of the calorimeter

The pASC setup allows to measure the total enthalpy change, induced by the change of electric field, by integrating over time the heat flow from the sample to the shield or vice versa through the calibrated Peltier element yielded the total enthalpy change. This is done by monitoring the voltage over the Peltier element, which was calibrated as follows.

Starting from a temperature of interest, controlled by the shield, power was supplied to the sample by Joule heating of the heating resistor mounted on the sample platform. The power was kept till the sample temperature stabilized, indicating equality between the supplied power and the leak power. The Peltier voltage, V , was measured for different values of the supplied power. The resulting curve, shown in Figure 2 was then fitted with a linear curve, which was used as a calibration curve for the electrocaloric measurements. Fitting with $P = a \Delta V + b$ yielded $a = 6.13 \cdot 10^{-1} \mu\text{W} \mu\text{V}^{-1}$ and $b = 5 \cdot 10^{-4} \mu\text{W}$.

Fig. 2. Calibration measurements and the corresponding fitting curve of the Micro-Peltier sensor.

The main favorable feature of the employed calorimeter design is the highly precise measurement of the heat produced in the sample, by adequate control and measurement of the (typically zero) heat exchange with the environment [15, 17, 18]. In the used apparatus, the thermal contact with the environment is minimized by making use of long, thin coiled wires for the electrical connections to the platinum resistors and heating resistor on the measurement platform, and by maintaining vacuum in all compartments. Moreover, to ensure temperature uniformity between the different components, the water thermostat bath in which the calorimeter is immersed, is controlled to within $\pm 0.1^\circ\text{C}$. The device enables high temperature resolution measurements within an accuracy of 1 mK [19].

Prior to the electrocaloric measurements, the resistive thermometers were calibrated against the Tamson TV4000 thermal bath over the range of 30°C - 90°C . From the platinum resistor data, a calibration curve based on the Callendar-Van

Dusen equation [22], was fitted. For the NTC thermistor data, the resistivity versus temperature data were fitted to the Steinhart-Hart equation [23].

For different temperatures of interest, between 30 °C and 90 °C in steps of 5 °C, electrocaloric enthalpy changes were induced by applying a large DC electric field of 30 MV m⁻¹ during one hour and switching it off one hour. The voltage was supplied by a 400DI amplifier driven by an Agilent 33521A signal generator. Thermally conducting grease (WLP35, FISHER ELECTRONIK, thermal conductivity 0.61 W mK⁻¹) was used in order to have a uniform thermal contact between the sample, the Peltier element and the platinum temperature detector. Measurements of the Peltier voltage and of resistances values were performed by a Keithley 2700 multimeter. All instruments were computer controlled via LabVIEW software.

2.2 Modes of operation

In view of measuring the electrocaloric heat production, before applying a voltage across the sample, the temperature of the shield was stabilized to a value of choice (isothermal condition). Shortly before applying a voltage across the sample, the temperature equilibrium between the sample and the shield was insured by checking the null value of the Peltier voltage.

The applied electric field was 30 MV m⁻¹. The application of an electric field induced a step-like increase in temperature of the electrocaloric material, followed by a relaxation phase. Since the shield was not following the sample temperature, the heat was relaxed, i.e it was flowing through the Peltier to the shield. The relaxation phase was monitored following two different schemes: in quasi-adiabatic temperature jump and heat flow measurement.

Heat-flow measurement

In this mode of operation, the heat flux crossing the Peltier element from the sample to the shield or vice versa, which started to flow as soon as a temperature jump was electrocalorically induced in the sample, was recorded via the calibrated Peltier voltage till the sample temperature was back at the shield temperature (Figure 3). The total heat exchange value Q was then evaluated by integration of the area under the peak as follows:

$$Q = \int_0^t P \, dt \quad (1)$$

Quasi-adiabatic temperature jump

In Quasi-adiabatic temperature jump, the temperature of the shield was maintained at the initial value and the temperature of the sample was recorded as function of time. The value of the electrocaloric temperature change ΔT was determined as the difference between the average of initial values and the maximum temperature measured shortly after switching the electric field, which were

Fig. 3. Operating principle of a pASC by heat flow mode.

not yet affected by heat flow through the Peltier element. Nevertheless, given the short time span, too short for heat to flow to the shield, the determined temperature jump can be considered as a quasi-adiabatic value.

On a longer time scale, due to diffusion of heat through the Peltier element the temperature of the sample slowly decayed, to finally reach the shield temperature again, i.e. its value before the application of the voltage. The evolution of the temperature is depicted in figure 4.

In this mode, the temperature evolution was measured using two platinum thermometers one which was placed on the platform on which the sample was resting, and one attached to the material's surface.

3 ELECTROCALORIC RESULTS

Heat-flow measurements

Figure 5 and 6 shows the time evolution of the measured power flow through the Peltier element, calculated from the Peltier voltage, and resulting from the application of electric field steps of 30 MV m^{-1} across the multilayer capacitor.

First, upon switching on the field, an exothermic peak occurs, corresponding to the flow of electrocalorically produced heat from the sample, through the Peltier element, to the shield, till the sample reaches the shield temperature, which is also initial temperature. Next, upon switching off the electric field, the heat power signal shows an endothermic peak, corresponding to electrocaloric

Fig. 4. Operating principle of a pASC by relaxation mode.

Fig. 5. Evolution with time of the power flow through the Peltier upon application and removal of applied electric field measured at 35 °C.

cooling of the sample, due to which heat flows back from the shield to the sample, till the sample is again at the shield temperature and its initial value. The exothermic and endothermic peaks are equal in magnitude within experimental uncertainty, indicating that the electrocaloric effect is reversible, and that the effect of Joule heating is negligible. The latter is also implied by the heat flow

asymptotically reaching zero at long times. The maximum reached heat flow magnitude was about 2 mW, similar to a value reported in the literature for the same type of sample [20].

Fig. 6. Heat flow from or to the MLC sample measured across a Peltier element throughout the application and removal of an electric field of 30 MV m^{-1} , for temperatures between 30 and 90°C in steps of 5°C .

As explained in section 2.2, the exchanged heat was computed from Eq.1, by integrating over time the power signal P from the switch moment till the full decay of the power flow. Figure 7 shows the temperature dependence of the totally produced heat. The error bars indicate the standard deviation determined from five consecutive electric field switching cycles. The value of Q at $T=90^\circ\text{C}$ and for a constant field of 30 MV m^{-1} , 0.95 J g^{-1} is consistent with direct DSC experimental results for BaTiO_3 MLC (0.91 J g^{-1} at $T=80^\circ\text{C}$ under 17.6 MV m^{-1}) [16]. As the measurements were carried out in a temperature range far below the Curie temperature (T_c of barium titanate is about 130°C), the temperature dependence of the electrocaloric enthalpy change is quite linear. Electrocaloric heat (polarization) and cold (depolarization) production values are equal within experimental uncertainty.

Quasi-adiabatic temperature jump

Quasi-adiabatic electrocaloric temperature changes have also been determined by subjecting the sample to subsequent polarization/depolarization cycles under the same applied field. Figure 8 and 9 present the electrocaloric temper-

Fig. 7. Temperature dependence of the heat flow obtained when applying (blue) and removing (red) an electric field of 30 MV m^{-1}

ature change ΔT as a function of time for an electric field jump of 30 MV m^{-1} , respectively for an initial sample temperature of 35°C , and for initial sample temperatures between 30°C and 90°C .

Fig. 8. Evolution with time of the sample temperature upon application or removal of an electric field (30 MV/m) measured at 35°C .

Fig. 9. Relaxation of the electrocaloric temperature change for MLC sample by applying and removing an electric field of 30 MV m^{-1} for temperatures between 30 and 90°C in steps of 5°C .

In figure 10, the electrocaloric temperature jump ΔT resulting from an electric field change of 30 MV m^{-1} is plotted versus the initial sample temperature. The presented values are averages over five successive measurements.

The value of the maximum temperature jump of $\Delta T = 0.46 \text{ K}$, measured at $T = 90^\circ\text{C}$ is consistent with the value of 0.5 K reported in Ref. [9, 21]. The found temperature jump magnitudes for polarization are about 5% higher when switching the electric field on compared to when switching it off. This small discrepancy is of the order of the absolute uncertainty on the thermometers, and could be related to residuals of heat flow after the polarization step during the measurement of depolarization step.

4 Conclusion

In this paper, we used an adapted Peltier based adiabatic scanning calorimeter for direct and accurate measurements of the heat and cold produced due to the electrocaloric effect in a multilayer capacitor of barium titanate. In addition, the adiabatic value of the electrocaloric temperature jump was determined. A maximal temperature change $\Delta T = 0.46 \text{ K}$ was achieved at $T = 90^\circ\text{C}$ starting temperature, which is consistent to a value that has been previously observed by Kar Narnyan et al. for the same material [9, 21]. The maximum heat flux generated by MLC was found to be 0.95 J g^{-1} , which is similar to a value found by Bai et al. [16].

While the MLC geometry is attractive for EC application in refrigeration or air-conditioning because the interdigitated electrodes allow to have access to

Fig. 10. Dependence of the electrocaloric temperature jump of MLC sample generated by switching on (blue) and off (red) an electric field of 30 MV m^{-1} across the MLC sample.

both a higher electrical field and a larger electrocaloric effect, studies of a thin electrocaloric film requires high sensitivity device for the characterization of the electrocaloric heat exchange of such system, due to the very small amount of material involved. Allowing the detection of microwatts of heat power, the results show that this calorimeter can be efficiently used to study thin film oxides by a direct approach.

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