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Electrocaloric properties of high dielectric constant ferroelectric ceramics

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Abstract

In the last two decades, the electrocaloric (EC) effect which is associated to the temperature (θ) dependence of the macroscopic polarization $P(E, \theta)$ under electric field E has been spasmodically studied in ferroelectric materials in order to find an alternative to the classical refrigeratory devices using freon. Basically, large electrocaloric temperature variation ΔT originates from electric field-induced phase transition at the Curie temperature, but temperature changes of the sample are difficult to measure and depend on the experimental conditions. In this paper, the electrocaloric effect has been quantified directly and precisely by measuring the thermal energy exchanged under isothermal conditions using a modified Differential Scanning Calorimetry (DSC) apparatus. The DSC technique allowed to compare the EC properties of high-dielectric-constant (ε) ceramics in the vicinity of ferroelectric–paraelectric phase transition. The measurements were also simulated starting from polarization versus electric field hysteresis loops for different temperatures. It is shown excellent agreement between simulations and direct DSC measurements, except in a limited temperature range where the hysteresis of the polarization versus temperature is high.

Keywords: Ferroelectric properties; Thermal properties; Perovskites; Electrocaloric

1. Introduction

The electrocaloric effect in a given material is the ability to convert electrical energy into heat in a reversible process. Previously studied bulk Pb(Zr,Ti)O_3 ceramics doped with Sn^{4+} and Ti^{4+}[1–3] or PLZT ceramics[4] exhibit some of the most impressive electrocaloric effect although recently studied $(1-x)$Pb(Mg,Nb)O_3–xPbTiO_3 ceramics[5,6] gave similar temperature controllable variations (1–2 °C) or exchanged heat (up to 0.5 J/g). More recently, outstanding advances[7] have been done in ferroelectric thin films (PZT) with a calculated reversible temperature drop of about 12 °C. These last results open several innovative applications in refrigeration devices. Experimental applications (for example, see Refs. 8 and 9) have already being tested, and we can conclude from these studies that only the lack of adequate materials refrains from offering effective applications for energy harvesting and refrigeration.

This study deals with the electrocaloric effect in $(1-x)$ Pb(Mg,Nb)O_3–xPbTiO_3 ceramics. The heat flow of a sample subjected to high electric fields step was measured using a Differential Scanning Calorimeter. The previously published results are in good agreement with ours. In order to understand the limitations of the electrocaloric effect, we used a direct integral approach to calculate expected electrocaloric effect from polarization versus electric field hysteresis loops measured at different temperatures. Upon the application of an electric field, the exchanged heat will be given by the integration of the pyroelectric coefficient on the electric field as denoted by Mischenko et al.[7] and Tuttle and Payne.[3]

We remind here the equations above-mentioned. Electrocaloric conversion is modelled using standard energetic considerations. First, the differential of the internal energy balance U of a ferroelectric material may be written:

$$dU = E\,dD + dQ \tag{1}$$

where $E\,dD$ and Q are the dielectric energy and the exchanged heat, respectively. In this case, dilatation and mechanical energy are not considered.

The electric induction is calculated as:

$$dD = \frac{\partial D}{\partial E}\,dE + \frac{\partial D}{\partial \theta}\,d\theta \tag{2}$$

where D, E and θ are, respectively, electric induction, electric field and temperature.

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We calculate the differential of the internal energy and replace the electric energy using Eq. (2):

$$\mathrm{d}Q = \left(\frac{\partial U}{\partial E} - E\frac{\partial D}{\partial E}\right)\mathrm{d}E + \left(\frac{\partial U}{\partial \theta} - E\frac{\partial D}{\partial \theta}\right)\mathrm{d}\theta \tag{3}$$

The entropy Γ is an exact differential and is given by

$$\mathrm{d}\Gamma = \frac{\mathrm{d}Q}{\theta} = \frac{1}{\theta}\left(\frac{\partial U}{\partial E} - E\frac{\partial D}{\partial E}\right)\mathrm{d}E + \frac{1}{\theta}\left(\frac{\partial U}{\partial \theta} - E\frac{\partial D}{\partial \theta}\right)\mathrm{d}\theta \tag{4}$$

The derivatives of the terms before dE and dθ must be the same to fulfil the exact differential condition

$$-\frac{1}{\theta^2}\left(\frac{\partial U}{\partial E} - E\frac{\partial D}{\partial E}\right) + \frac{1}{\theta}\left(\frac{\partial^2 U}{\partial E\partial \theta} - E\frac{\partial^2 D}{\partial E\partial \theta}\right) = \frac{1}{\theta}\left(\frac{\partial^2 U}{\partial E\partial \theta} - E\frac{\partial^2 D}{\partial E\partial \theta} - \frac{\partial D}{\partial \theta}\right) \tag{5}$$

This leads to the expression of $\partial U/\partial E$ and then to the simplified expression of dQ

$$\mathrm{d}Q = \theta\frac{\partial D}{\partial \theta}\mathrm{d}E + c_\mathrm{E}\,\mathrm{d}\theta \tag{6}$$

In this last equation, we assumed that in any case

$$\frac{\partial U}{\partial \theta} = c_\mathrm{E} \gg E\frac{\partial D}{\partial \theta} \tag{7}$$

where c_E is the thermal capacitance (J °C^{-1} m^{-3}).

In fact, there are experimentally three orders of magnitude between the two terms using constants close to experimental ones ($c_\mathrm{E} \sim 2.5 \times 10^6$ J °C^{-1} m^{-3}, and $E\partial D/\partial \theta \sim 2.5 \times 10^3$ maximum for $E = 2.5 \times 10^6$ V/m and $\partial D/\partial \theta = 1000 \times 10^{-6}$ C m^{-2} °C^{-1}, see Ref. 10).

As a consequence, for isothermal conditions (constant temperature θ_0), the heat variation δQ for a given electric field increase from 0 to E_max is given by:

$$\delta Q = \theta_0 \int_0^{E_\mathrm{max}} \frac{\partial D}{\partial \theta}(E, \theta)\,\mathrm{d}E \tag{8}$$

2. Experimental procedure

Ceramics of composition $0.75\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$0.25\mathrm{PbTiO_3}$ were prepared using a two-stage synthesis process in air. At the first stage, the columbite-like $\mathrm{MgNb_2O_6}$, precursor phase was produced from $\mathrm{Nb_2O_5}$ and MgO powders prepared with stoichiometric proportions. The powders were mixed in a ball mill for 2 h and then calcined for 6 h at 1100 °C. At the second stage, the precursor phase constituent was crushed and mixed with PbO and $\mathrm{TiO_2}$. The mixture was calcined at 850 °C for 4 h, milled for 3 h, sieved and then pressed with organic binder at 50 MPa with a shape of pellets (diameter of 15 mm and a thickness of 15 mm). After the burning of the organic binder (600 °C, 10 h), the sintering of final compound, $0.75\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$0.25\mathrm{PbTiO_3}$, was carried out in $\mathrm{PbZrO_3}$ atmosphere at 1250 °C for 10 h. Samples were then sliced in thin plates of 12 mm × 4 mm × 1 mm.

A ferroelectric material exchanges heat with the outer medium when subjected to an electric field under isothermal conditions. The quantification of that heat is performed in this study with a Differential Scanning Calorimetry apparatus (MHTC96, Setaram, France). Temperature stabilization is first obtained. Then the electric field is applied using two thin wires reaching the heart of the apparatus where the sample is put. The sample is of 12 mm × 4 mm × 1 mm and electrodes are deposited with silver paste. To avoid electric arcs, the sample is immersed in silicone oil. The ceramic is submitted to a voltage step. The corresponding electric field, taken from 500 to 3000 V/mm, is applied during 500 s. The electric field is then decreased to zero. Due to the thermal conduction of the apparatus, such a long time is required to ensure that the initial temperature of the sample is recovered before decreasing the electric field (isothermal conditions). Heat flow as a function of time exhibits two peaks. The first one is always exothermic whereas the second is always endothermic. The integration of the peaks gives the exchanged heat, and both peaks gives very close values of heat. This observation proves the perfect reversibility of the phenomenon.

In order to predict the heat measured as previously described, polarization versus electric field (*P*–*E*) loops were determined for different temperatures. The ceramic sample is immersed in a thermostatic oil bath. Current and electric field are recorded while applying cyclic electric fields (current amplifier Keithley 428 and high voltage amplifier TREK Model 20/20C). When reaching temperatures close to the Curie transition, the conduction becomes quite high, and an optimal frequency must be chosen to minimize losses effect on the hysteresis loops. The working frequency was fixed to 1 Hz. Finally, dielectric permittivity measurement was conducted using a HP4194A impedance analyzer in a temperature controlled oven with an accuracy of ±1 °C.

3. Results and discussion

In Fig. 1 is shown the polarization versus electric field for different temperatures. Those curves were taken from decreasing electric field portion of the curve, where the polarization decreases from saturation polarization down to remnant polarization. It is noticeable that when the temperature increases, the remnant polarization (P_r for $E = 0$) decreases fastly whereas the saturation polarization decreases slowly (P_sat for $E = E_\mathrm{max}$). As a consequence, it is expected to have a pyroelectric coefficient decreasing with the electric field. As explained in the introduction, integrating pyroelectric coefficient versus electric field – see Eq. (8) – gives the exchanged heat. It is thus expected that the heat will exhibit saturation versus electric field. We could also remark that even at 175 °C – far from the Curie temperature expected to be around 125 °C – the hysteresis cycles still exhibit a small remnant polarization. This is characteristic of the relaxor nature of that composition of ceramics for which the structural ferroelectric–paraelectric phase transition shows a pronounced diffused behavior.

In Fig. 2 is shown the simulated and experimental heat as a function of electric field for different temperatures 90, 110 and

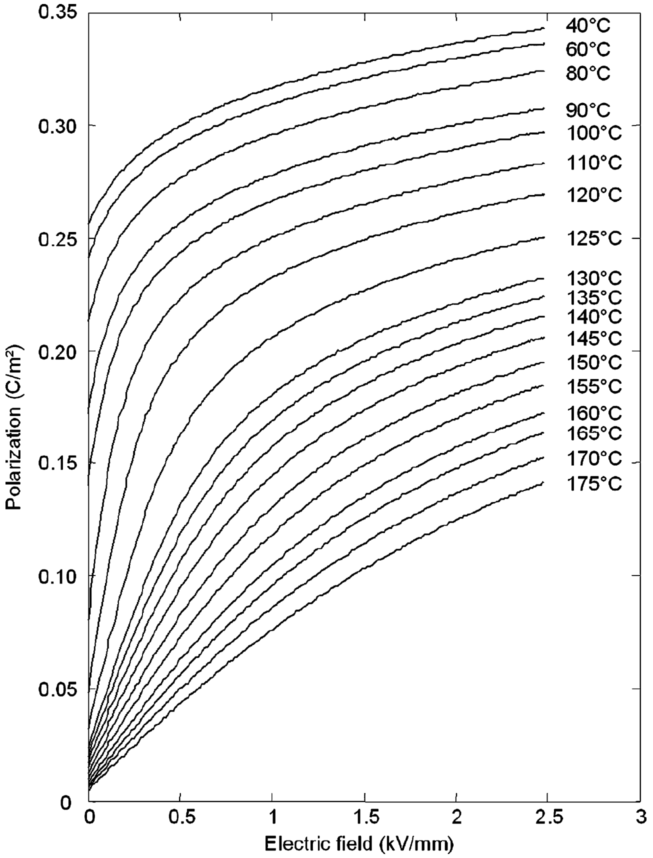

Fig. 1. Polarization vs. electric field for different temperatures on a 0.75Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.25$PbTiO_3$ ceramic. The Curie transition temperature is around 125 °C.

130 °C. Both results are in excellent agreement showing a maximum electrocaloric activity in the vicinity of the Curie transition (110 and 130 °C). The heat is found to be 0.2 J/g for an electric field of 2.5 kV/mm. The largest discrepancy appears at 130 °C where the hysteresis of the polarization versus temperature is mostly important (main depolarization of the ceramic).

Due to such hysteretic behaviour, it is impossible to associate a polarization to a given electric field since the polarization also depends on the history of the material (memory effect). In other words, the polarization of a ferroelectric material cannot be known from the only electric field information. The previous polarization state (so-called history of the material) is also necessary. In the same manner, the calculation of $\partial D/\partial \theta$ will depend whether we start from a polarized state, from a zero poling state, and whether the field is increasing or decreasing.

Moreover, almost no saturation on both experimental and simulated results is observed. Indeed, after a first increase of the exchanged heat, one can notice an almost linear increase of heat versus electric field. This result can be interpreted using the polarization versus electric fields measurements in Fig. 1. The polarization difference for two different temperatures is almost constant when increasing the electric field. The polarization saturates with the electric field, but the saturation values for two temperatures are different. As a consequence, although the polarization saturates, the pyroelectric coefficient does not saturate with increasing electric field. However, electric fields above 3 kV/mm on bulk materials usually results in sample breakage due to electric arcs. Most probably electrocaloric effect on PMN-PT thin films should bring very high energy density capability because it can be possible to apply quite high electric fields.

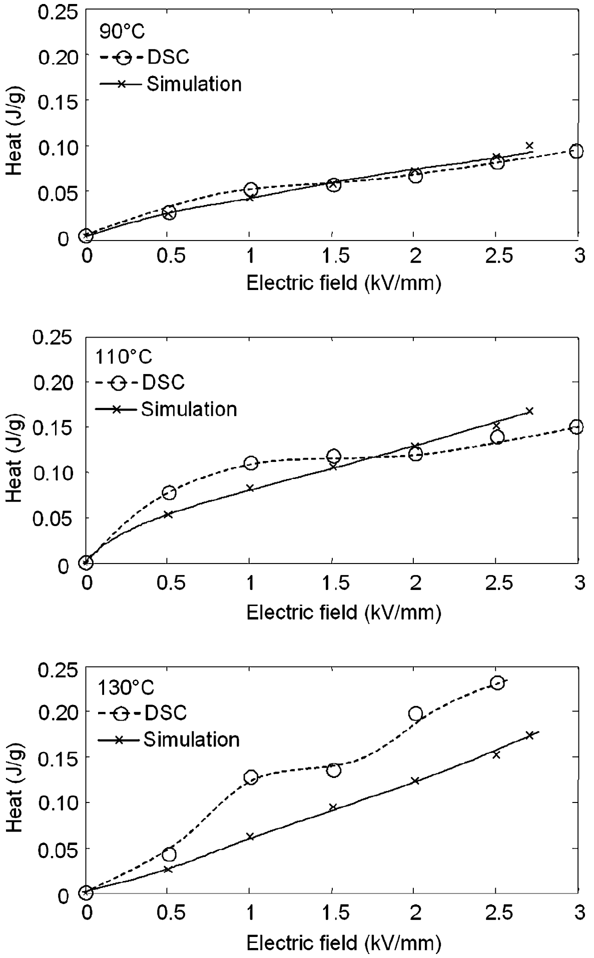

Fig. 2. Heat vs. electric field for three different temperatures. The heat is exchanged by the material with the outer medium when the electric field is released from a maximum value down to zero. The simulation and the DSC measurements are, respectively, in solid and dotted line.

4. Conclusion

Electrocaloric conversion in 0.75($PbMg_{1/3}Nb_{2/3}$)–0.25(Pb TiO_3) was investigated and large activity has been measured. The exchanged heat when applying a 2.5 kV/mm voltage reaches 0.2 J/g. We studied the dependence of this activity on the temperature and electric field. Relatively low saturation has been observed as a function of electric field. The direct integration of the pyroelectric coefficient $\partial D/\partial \theta$ (derivative of the electric induction on the temperature) along the applied electric field provides fine predictions of the exchanged heat. Further work should deal with PMN-PT single crystals where the polarization should be much higher than that of ceramics. In case of PMN-32PT composition, pyroelectric coefficient is larger for crystals ($p = 979 \times 10^{-6}\,\mathrm{C\,m^{-2}\,{}^\circ C^{-1}}$, after Ref. 10) than for ceramics ($p = 300 \times 10^{-6}\,\mathrm{C\,m^{-2}\,{}^\circ C^{-1}}$, after Ref. 11). Indeed, a larger pyroelectric coefficient should be associated with a larger electrocaloric conversion.

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