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Intensive electrocaloric effect in the multilayer capacitor under equilibrium and nonequilibrium thermal conditions

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ABSTRACT

Precise direct measurements of the intensive electrocaloric effect (ECE) in commercial multilayer capacitor based on doped $BaTiO_3$ were performed using an adiabatic calorimeter. High reversibility of ECE studied under equilibrium thermal conditions was observed. The nonequilibrium thermal conditions caused by fixing the temperature of one of the ends of the linear EC element lead to the predominance of ECE when the electric field is turned off. The heat flow through the EC element appearing under the influence of a periodic electric field and depending on its frequency makes it possible to create a cooling cycle without thermal keys.

Electrocaloric effect (ECE) in ferroelectric materials has a great potential in realizing solid-state cooling devices with compact size and high efficiency which are highly desirable for a wide range of applications such as on-chip cooling and temperature controlling for sensors, electronic devices, and medical instruments. ECE is associated with the reversible change in the temperature, ΔT_{AD}, or entropy, ΔS_{ECE}, under electric field variation under adiabatic and isothermal conditions, respectively. According to interrelations between the extensive and intensive ECE and polarization, $\Delta S_{ECE} = \int(\partial P/\partial T)_E dE$, $\Delta T_{AD} = -(T/C_p)\Delta S_{ECE}$, the largest values of both effects can be obtained near the ferroelectric phase transition point, where the derivative $(\partial P/\partial T)_E$ reaches the maximum magnitude [1]. Recent development in the design of the electrocaloric (EC) components and cooling systems has indicated that the intensive ECE equal to ΔT_{AD}=3 K would be enough to construct an EC solid–state refrigeration system with refrigeration costs comparable to today's vapor–compression systems [2]. Theoretical estimations have shown that in order to realize ΔT_{AD} ≈6 K in $Ba_{0.5}Sr_{0.5}TiO_3$, rather high electric field E ≈300 kV/cm is needed [3]. However, the breakdown field for bulk ferroelectric materials does not usually exceed 60 kV/cm. On the other hand, thin ferroelectric films can support higher fields E ≈1000–2000 kV/cm which can be obtained at low voltage due to small thickness of films [4]. This is the reason why gigantic intensive ECE was observed in such kind of ferroelectric materials [5]. The largest ECE ΔT_{AD} ≈ 40 K under an electric field amplitude of 1.2 MV/cm was measured in thin films of the relaxor-ferroelectric lead lanthanum zirconate titanate [6]. Unfortunately, thin films have a small thermal mass which brings about small EC heat. Multilayer ceramic capacitors (MLCCs) have been suggested [4,7,8] as an alternative design for EC coolers since they combine high breakdown field due to rather thin layers (<10 μm) as well as large thermal mass and as a result high cooling power. Investigations of ECE in the multilayer structures based on lead-based relaxor ferroelectrics PMN-PT [9] and on $BaTiO_3$ [7,10-15] have demonstrated temperature changes of 2.26 K at 100 kV/cm and ~1 K at E=300 kV/cm, respectively.

However, refrigerators with solid working body operating on the classic ECE associated with the applying/removal of a constant

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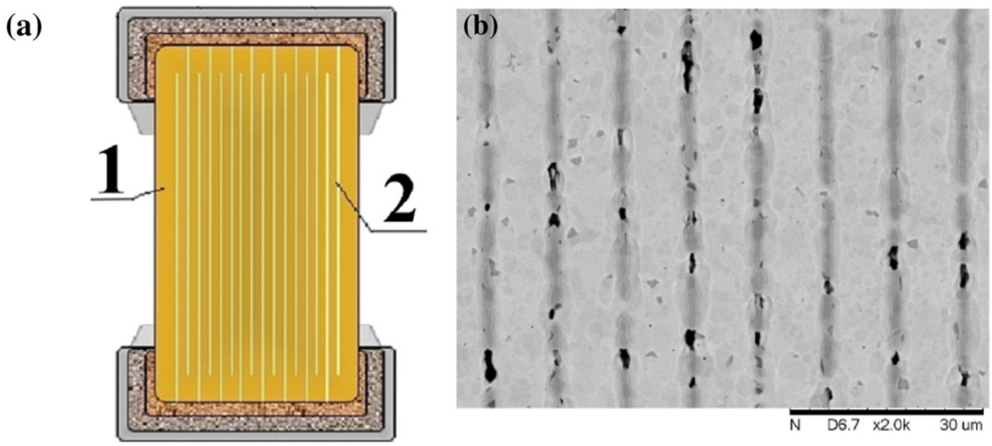

Fig. 1. (a) MLCBT cross-sectional schematic (1 – doped $BaTiO_3$; 2 – Ni electrodes). (b) SEM image of the cut perpendicular to the $BaTiO_3$ and Ni layers.

electric field to/from the ECE element have a serious disadvantage: heat switches are needed to provide thermal contact of solid refrigerant in turn with cooled object and environment [14,16,17].

Recently, an original way was suggested to avoid such a serious problem [18–21]. The idea was to create a heat flux through the EC element. Theoretical modelling has shown that such an effect can be obtained realizing ECE under the periodic E in the bulk EC element under nonequilibrium thermal conditions. The top of the linear element was thermally isolated and the bottom was kept at T_{bot}=const. As a result, in a certain temperature range, applying and removal of the electric field will be accompanied by the different values of $\Delta T_{AD}\left(|\Delta T|_{AD}^{ON} < |\Delta T|_{AD}^{OFF}\right)$. Periodic variations in the field, $E = 0 \rightarrow E \neq 0 \rightarrow E = 0$, will lead to fluctuations in the temperature of the top of the EC element, T_{top}. The gradual decrease of its average value down to $T_{top} < T_{bot}$ will appear due to the nonequivalence of the heat fluxes when the field is turned on and off.

Experimental studies of ECE under nonequilibrium thermal conditions were performed on the multilayer capacitor based on $BaTiO_3$ [7,14] and the bulk triglycine sulphate crystal (TGS) [22,23]. In the former case, in the temperature range investigated they have found $|\Delta T|_{AD}^{ON} \geq |\Delta T|_{AD}^{OFF}$ and as a result the heating of the sample under periodic E [14]. However, in the latter case, a decrease in the temperature T_{top} compared to T_{bot} of the TGS element was detected in accordance with previous predictions [18,21]. Thus, despite a small difference $T_{top} - T_{bot} = -0.012$ K at rather low E=2.8 kV/cm a cooling effect was observed.

We assume that failure of the cooling observation in MLCC [7,14] is due to at least two reasons. First, experiments were performed at high field E=300 kV/cm which necessarily leads to the release of Joule heat. Second, to avoid the destruction of the capacitor under high voltage, the discharge process was carried out through an additional resistor which led to different rates of switching on/off the electric field, $(dE/dt)_{OFF} < (dE/dt)_{ON}$. Both reasons contribute to the observed interrelation $|\Delta T|_{AD}^{ON} > |\Delta T|_{AD}^{OFF}$. At the same time, measurements of the ECE in TGS were carried out at equal rates of switching on/off the electric field [22,23].

In the present paper, we performed precise direct measurements of the intensive ECE in multilayer capacitor based on $BaTiO_3$ (MLCBT) by means of a homemade adiabatic calorimeter which is characterized by very high sensitivity to the small temperature change [22–24]. A commercially available MLCBT (100 μF) consisting of 200 interdigitated layers of $BaTiO_3$ and Ni electrodes was used. The nominal thickness of the layers is 6.5 μm for $BaTiO_3$ and 2.0 μm for Ni (Fig. 1 (a)). To obtain correct information on ECE and the temperature gradient $\Delta T = T_{top} - T_{bot}$, the study was carried out with the equal values of $(dE/dt)_{OFF}$ and $(dE/dt)_{ON}$ under voltage of 10 V, i.e. E=15.4 kV/cm, which is close to 15 kV/cm recommended by the manufacturer in order to avoid a deterioration in the functional properties of the capacitor.

The structural morphology of the cut perpendicular to the $BaTiO_3$ and Ni layers was examined using a scanning electron microscope (SEM) Hitachi TM3000 (Hitachi High - Technologies Co., Ltd., Tokyo, Japan) and is presented in Fig. 1 (b). The SEM image clearly demonstrates that the surface consists of alternating layers of ferroelectric (light broad stripes) and metal (dark narrow stripes) components contacting closely each other.

The X-ray powder diffraction data were collected at room temperature with a PANalytical X'Pert PRO diffractometer equipped with a PIXcel solid state detector and a secondary graphite monochromator (Cu-Kα radiation). Rietveld refinement shows the presence of Ni and $BaTiO_3$ doped with Sn^{4+} which gives the following chemical formula: $BaTi_{0.86}Sn_{0.14}O_3$ (BTSO).

Fig. 2 (a) represents the behaviour of the permittivity measured at 1 kHz using an E7-20 immittance meter. One broad smeared peak with a maximum at about 302 K was found which is characteristic for relaxors and coincides with manufacturer's information about anomalous behaviour of ε of MLCBT in wide temperature range [25].

Direct measurements of the intensive ECE were performed on the MLCBT + heater system by means of adiabatic calorimeter at the pressure of about 10^{-5} mm Hg. A dc power homemade supply was used to apply the electric field on the sample. To minimize the thermal losses, contact wires with small diameters ~0.05 mm were used. To obtain information on ΔT_{AD} only in MLCBT, the heat capacity of the heater was measured in a separate experiment. Since the real masses of Ni-electrodes, plastic coating, etc., are unknown, the values ΔT_{AD} relating to BTSO were obtained using the coefficient $\Delta T_{AD}^{BTSO}/\Delta T_{AD}^{MLCBT}$=1.47 evaluated for the similar capacitor [7].

Experiments were carried out under two different thermal conditions used by us studying TGS [23]: 1) at S=const under applying/removal of an electric field with subsequent exposure E=const for 5–10 min.; 2) the same procedure under nonequilibrium thermal conditions at T_{bot}=const. Hereinafter, these variants will be labelled as Var 1 and Var 2, respectively.

In Var 1, the temperature drift of the MLCBT + heater system at different temperatures was chosen within $dT/dt \approx \pm(1\text{–}5)10^{-4}$ K/min. Applying and removal of a constant electric field to/from electrodes of MLCBT resulted in a rapid increase/decrease in temperature of the system due to ECE in BTSO (Fig. 2 (b)). It is also seen that the rate of the temperature change, dT/dt, in the process of E=const is greater than before the applying of the electric field and becomes equal to it after the field is switched off. This experimental fact unequivocally indicates