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Ferroelectric and electrocaloric effect in lead-free $(Ba_{1-x}Ca_x)_{1-3y/2}Bi_yTiO_3$ ceramics

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ABSTRACT

Polycrystalline lead-free calcium bismuth titanate $(Ba_{1-x}Ca_x)_{1-3y/2}Bi_yTiO_3$ (BCBT) ferroelectric ceramics were synthesized by conventional solid state reaction process. The dielectric permittivity and ferroelectric hysteresis loops were measured. The electrocaloric (EC) temperature change (ΔT) was investigated from the Maxwell relation, using *P-E* hysteresis characteristics, in a wide temperature range and externally applied electric fields. It was found that it is possible to achieve a large ΔT around 0.81K under an electric field of ΔE = 39.5 kV/cm observed for specimen 0.05BCBT-7.5%. The temperature change per unit of applied electric field, called as EC responsivity ($\xi = \Delta T/\Delta E$), was 0.0207 Kcm/kV. This value promises this compound for applications of solid-state cooling devices.

1. Introduction

Over the past decades, usual refrigerators with a compressor present a noisy mechanical part and the liquid refrigerants deplete the ozone layer. Thanks to the great electrocaloric (EC) effect found in thin films and which provided solid-state cooling technology without polluting liquid refrigerants [1–4], a thin refrigerator has lately attracted attention because this EC refrigerator is compact, light and can be made-up from low-cost materials that respecting the environment. To produce EC cooling devices, materials with giant EC effect are necessary.

The phenomena known as the EC effect is the change in adiabatic temperature and/or entropy of a dielectric material induced by electrical energy upon the application or removal of an electric field. The entropy change was related to the polarization states [5,6]. EC effect was first discovered on Rochelle salt in 1930 [7,8]. However, the temperature change found is small for practical refrigeration applications [9,10].

During the previous years, EC materials have been the topic of several publications. Since 2006, Mischenko et al. demonstrated a giant EC effect, ΔT_{max} = 12 K in $PbZr_{0.95}Ti_{0.05}O_3$ (PZT) thin films [11]. Therefore, a large EC effect was successively reported for lead based ferroelectric materials like PMN-PT [2,12–14], PZN-PT [15] and the relaxor $Pb_{0.8}Ba_{0.2}ZrO_3$ thin films prepared by the Sol–Gel method and which has a giant EC effect (ΔT = 45.3 K and ΔS = 46.9 $Jkg^{-1}K^{-1}$ at 598 kV/cm) [16]. However, the toxicity of lead-based ceramics to both the human body and the environment limits its use. Moreover, the reproducibility of these compounds is difficult due to the modification of the structure caused by the volatilization of PbO at a temperature above 1000 °C. Hence, lead-free ferroelectric materials were developed as alternatives to lead-containing compositions. However EC strengths of the reported lead-free ceramics are drastically inferior to those of the lead-based systems, consequently the exploration of lead-free materials with a large EC strength is still a defy. Among these compounds may be mentioned the ferroelectric polymer of P(VDF–TrFE–chlorofluoroethylene) [17] and $BaTiO_3$ (BT) matrix which are considered as a better candidate-material for cooling microelectronic devices. In fact, Akcay et al. established that an adiabatic temperature variation of 7.8 K was reached in bulk BT at high applied electric field in an EC experiment [18]. Nevertheless, to use the lead-free BT matrix as a material in refrigeration devices, T_C must be shifted much lower than its value (near 120 °C) in pure BT.

Currently, $BaTiO_3$ (BT) – based materials are being developed [19]. Hence, various doping elements were tried in order to improve the properties of BT by replacing Ba with Sn, Ca, Sr, Mg etc and Ti with Zr, Nb etc. We can cite for example : $BaZr_xTi_{1-x}O_3$ (BZT) [4], $BaSn_xTi_{1-x}O_3$ [3], $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-BCT) [20,21] and $Na_{0.5}Ba_{0.5}TiO_3$-based systems [22]. A significant temperature change of 1.04 K at 411 K with an applied electric field of 30 kV/cm was given by Han et al. [23] in $Ba_{0.94}Dy_{0.04}TiO_3$. Recently Srikanth et al. [24] reported large EC responsivity coefficient ($\Delta T/\Delta E$) of 0.035 Kcm/kV in $BaCe_xTi_{1-x}O_3$ with x = 0.12 at 351 K near the phase transition temperature (349 K). Lately, Li et al. [25] noted that the addition of 17% of Hf element to $BaTiO_3$ decreases the phase transition temperature (T_C) toward room temperature (305 K) with high

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EC coefficient of 0.035 Kcm/kV at 343 K.

$(Ba_{1-x}Ca_x)_{1-3y/2}Bi_yTiO_3$ (BCBT) system are among of the most promising lead-free ferroelectric materials. In fact, besides their interesting dielectric [26,27], piezoelectric [28], pyroelectric [28] and ferroelectric [29] properties, BCBT can improve the EC properties. Firstly, doping with Bi in BCBT solid solution favors the relaxor character [26]. Bi doping can be fully incorporated into the perovskite lattice of $(Ba_{1-x}Ca_x)TiO_3$. The nonequivalent substitution of the A-site bivalent ions (Ba^{2+} and Ca^{2+}) by Bi^{3+} ions (ionic radius of Ba^{2+}, Ca^{2+} and Bi^{3+} are 1.42 Å, 1.12 Å and 1.03 Å respectively) [30] in BCBT give rise to a larger off-centering of the cation (Bi^{3+} ion) and induce the distortion [26,27,31]. The relaxor behavior is accentuated by the fact that the Bi element has a particular electronic structure characterized by the presence of an electron doublet of the valence layer 6 s not participating in the bond and thus forming an isolated pair. This highly polarizable pair can induce additional dipole interactions favoring the relaxing character [26,27]. Secondly, doping with Ca in BT favors the first-order phase transition. As an example, a large EC responsivity ξ, $\Delta T/\Delta E = 0.015$ Kcm/kV, was found in $Ba_{0.8}Ca_{0.2}TiO_3$ ceramic which exhibit a first order ferroelectric phase transition . Wang et al. [21] obtained the maximum of the $\Delta T/\Delta E$ of 0.015 Kcm/kV in the BCZT lead-free ceramics. Singh et al. [32] reported recently a large EC responsivity of 0.0253 Kcm/kV in $(Ba_{1-x}Ca_x)(Zr_{0.05}Ti_{0.95})O_3$ with $x = 0.08$.

It was assumed that the existence of the polar nanoregions (PNRs) in relaxor ferroelectrics, which are distributed randomly throughout the volume of the material inducing many possible orientations of the polar domains, can improve the EC performance. On the other hand, the first-order phase transition or diffuse phase transition are contributed in the EC effect of ferroelectrics under low electric fields [25]. Indeed, since the EC effect has a maximum close to the ferroelectric-paraelectric phase transition, fundamental EC research was focused essentially on materials with a first-order phase transition [33–36].

In this work, emphasis was located on $(Ba_{1-x}Ca_x)_{1-3y/2}Bi_yTiO_3$ (BCBT) solid solution. Throughout the paper, we use also the following abbreviations: 0.05BCBT-7.5% ($x = 0.05$, $y = 0.075$), 0.3BCBT-5% ($x = 0.3$, $y = 0.05$) and 0.3BCBT-7.5% ($x = 0.3$, $y = 0.075$). The ferroelectric hysteresis measurements of lead-free BCBT bulk ceramic systems were inspected. A detailed EC effect study on BCBT ceramics using the thermo-dynamical Maxwell relations was carried out. A great EC effect was revealed in BCBT under relatively low applied fields.

2. Experimental details

BCBT bulk ceramics with various compositions were synthesized via the conventional powder processing technique. The detailed experimental system was described in Refs. [26,28]. Dielectric measurements were performed on ceramic discs, which their faces were electrode using gold sputtering deposition. The dielectric permittivity of samples was measured as a function of both temperature and frequency using an Agilent 4284A (20 Hz-1 MHz) impedance analyzer. (*P–E*) loops were resolute for diverse temperatures. Ceramic samples was immersed in a thermostatic oil bath. Current and electric field were noted while applying cyclic electric fields (current amplifier Keithley 428 and high voltage amplifier TREK Model 20/20C). The employed frequency was fixed to 1 Hz.

3. Results and discussion

3.1. Dielectric measurement

Fig. 1 displays the real and imaginary parts of dielectric permittivity dependence on various temperatures and the frequencies of BCBT ceramics. Only one dielectric anomaly was detected for all investigated specimens. The phase transition temperature T_C was identified in the vicinity of 367 K, 409 K and 380 K for 0.05BCBT-7.5%, 0.3BCBT-5% and 0.3BCBT-7.5% compositions respectively. Ceramics exhibited

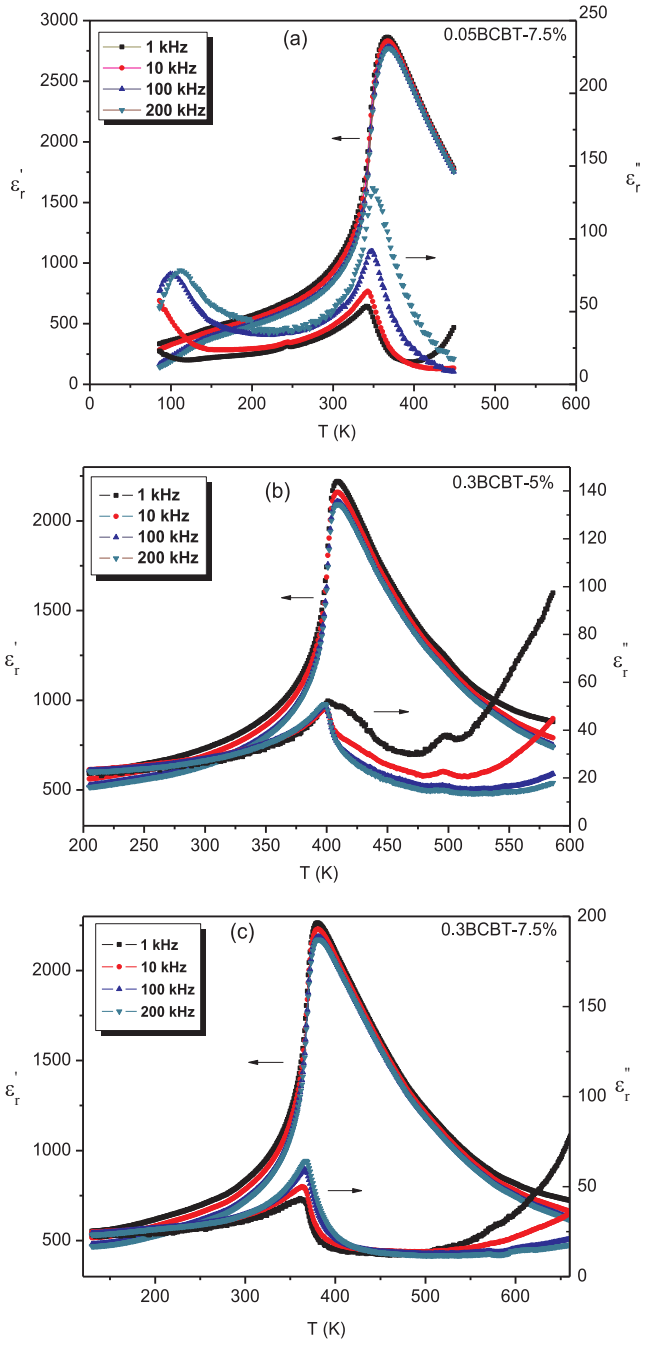

Fig. 1. The dielectric properties as a function of temperature for BCBT ceramics: (a) 0.05BCBT-7.5%, (b) 0.3BCBT-5% and (c) 0.3BCBT-7.5%.

classical ferroelectric behavior with an abrupt phase transition from the polar phase to the nonpolar phase at T_C whose value is independent of the frequency. The maximum value of the real dielectric permittivity for compositions with $x = 0.3$ and $y = 0.05$ or 0.075 increases when Bi percent increases from ~2220 up to ~2263 for 1 kHz [37] while T_C decreases from 409 K up to 380 K [26,38]. In contrast, with the increasing incorporation of Ca ions for compositions with $y = 0.075$ and $x = 0.05$ or 0.3, ε'_{rmax} decreases from ~2864 up to ~2263 for 1 kHz even T_C increases from 367 K up to 380 K [26,27,39,40].

The variation of the imaginary part of the permittivity as a function of the temperature and the frequency gives rise to a maximum (ε''_{rmax}) which is located at a temperature slightly less than T_C, then this curve gradually decreased and finally risen again with increasing temperature. In the Fig. 1b, as an example, we noted a small peak observed in