



Available online at www.sciencedirect.com



**CERAMICS** INTERNATIONAL

Ceramics International 42 (2016) 229-233

www.elsevier.com/locate/ceramint

# Direct and indirect analysis of the electrocaloric effect for lanthanum-modified lead zirconate titanate antiferroelectric ceramics

A. Peláiz-Barranco<sup>a,\*</sup>, Jinfei Wang<sup>b,c</sup>, Tongqing Yang<sup>b</sup>

<sup>a</sup>Facultad de Física-Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, San Lázaro y L, Vedado, La Habana 10400, Cuba <sup>b</sup>Functional Materials Research Laboratory, College for Materials Science and Engineering, Tongji University, 4800 Caoan, Shanghai 201804, China <sup>c</sup>Dwo Chemical (China) Investment, Ltd., Zhangheng Road 936, Pudong district, Shanghai 201203, China

> Received 29 May 2015; received in revised form 3 August 2015; accepted 20 August 2015 Available online 28 August 2015

### Abstract

The electrocaloric effect is studied in lanthanum-modified lead zirconate titanate antiferroelectric ceramics by using direct and indirect methods. A maximum value for the temperature change ( $\Delta T$ ) is obtained around a critical electric field (the electric field which forces the antiferroelectric–ferroelectric phase switching). An abrupt change in the polarization occurs at that critical field, which provides an adiabatic increasing in the temperature of the material. The temperature dependence for  $\Delta T$  shows a maximum value around 348 K, which could be related to the influence of the temperature on the relative stabilities for the ferroelectric and antiferroelectric phases. © 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Electrocaloric effect; Antiferroelectrics; Ceramics

## 1. Introduction

Ferroelectric materials have a net dipole moment, which provides the increasing of the polarization with the electric field. It also causes a decrease in the entropy and an adiabatic increase of the temperature for the system. The adiabatic temperature change, which is caused by the polarization change under an external electric field, is known as electrocaloric effect (ECE) [1–4]. As the pyroelectric effect, the ECE originates from the cross-coupling between polarization and temperature. It is restricted by the practical limitations of applying large voltages to avoid the dielectric breakdown and the leakage current.

The ECE can be studied by using the so called "direct methods" or "indirect methods" [1]. The formers correspond to the direct measurement of the temperature change ( $\Delta T$ ), which can be made by using differential scanning calorimeter, temperature sensors and scanning thermal microscopy [5]. By using

\*Corresponding author.

E-mail address: pelaiz@fisica.uh.cu (A. Peláiz-Barranco).

http://dx.doi.org/10.1016/j.ceramint.2015.08.097

0272-8842/© 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

"indirect methods",  $\Delta T$  can be calculated from the temperature dependence of the polarization.

Antiferroelectric materials are characterized by either a low dielectric permittivity with a field-induced phase transition to a ferroelectric state at a critical electric field, or a relatively high dielectric permittivity with decreasing electric field strength dependence [6]. Previous results have showed that a large ECE can be obtained in materials where both antiferroelectric (AFE) and ferroelectric (FE) phases coexist [7,8]. On the other hand, it has been reported a small ECE for compositions where an AFE–FE electric field-induced phase transition is observed [9].

It has been reported that the lanthanum addition enhances the stability range of the antiferroelectric orthorhombic phase in the Zrrich side of the phase diagram for lead zirconate titanate compounds (PZT) [6]. Previous studies in  $(Pb_{1-x}La_x)(Zr_{0.90}Ti_{0.10})_{1-x/4}O_3$  ceramics have showed the coexistence of two phases (ferroelectric-rhombohedral, R3m, and antiferroelectric-orthorhombic, Pbam) [10]. The AFE state was found to be stabilized, whereas the long-range FE state was disrupted by the lanthanum substitution on the lead sites. The FE state was shown to be stable over the AFE state for low lanthanum contents in a wide temperature range. The

increasing of the lanthanum concentration provided the suppression of the long-range coherency for the FE state, i.e. the temperature range for the FE state stability decreased, disappearing for lanthanum concentrations above 3 at%. The present paper shows the analysis for the ECE in  $(Pb_{1-x}La_x)(Zr_{0.90}Ti_{0.10})_{1-x/4}O_3$  anti-ferroelectric ceramic materials by using indirect and direct methods.

#### 2. Experimental procedure

The ceramic samples were prepared by using the standard solid-state reaction method [6,10] from nominal composition  $(Pb_{1-x}La_x)(Zr_{0.90}Ti_{0.10})_{1-x/4}O_3$ , where *x*=4, 5, and 6 at% La. The stoichiometric mixture of high purity oxides (PbO, ZrO<sub>2</sub>, TiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>) was ball-milled and then was prefired at 800 °C in air for 1 h. The calcined powders were ball-milled again. The powders were pressed uniaxially as thick discs by using 200 MPa. Finally, the sintering was carried out in air at 1250 °C for 1 h, in a well-covered platinum crucible in order to minimize the evaporation of reagents. The densities of the samples were 7.3, 6.9 and 7.1 g/cm<sup>3</sup> for *x*=4, 5 and 6 at%, respectively. These results were above 92% of the theoretical density values. The diameter and thickness of the samples were 14.7 mm and 0.1 mm, respectively. The samples are hereafter labeled as PLZT *x*/90/10.

Electrodes were deposited on the parallel faces of the ceramic disks by using Au strips and an organogold paste. The hysteresis loops at 1 Hz were obtained by using a Sawyer-Tower circuit for several temperatures in order to evaluate the ECE (indirect method).

A computer recorded ECE system was established for direct measurements with pulsed and sine wave electric field (Fig. 1), which includes an Agilent 33220A (20 MHz Function/Waveform Generator), a Tektronic TDS1012B-SC (Two Channel Digital Oscilloscope), a Keithley 2000 (Multimeter) and a Trek Model 609A (Voltage Amplifier). A Pt-100 thin film thermometer was used to measure the temperature change  $\Delta T$  (resolution of 0.01 K). It was attached to the sample surface by a pinchcock. The samples were put into silicon oil to avoid the breakdown.

#### 3. Results and discussion

#### 3.1. Direct method

Fig. 2 shows the time dependence for the temperature and the applied sine wave electric field for PLZT 6/90/10, as example of the studied samples. The temperature change  $\Delta T$  follows the applied sine wave electric field.

Fig. 3 shows the electric field dependence for  $\Delta T$  at room temperature for the studied compositions. For each measurement cycle, the electric field was applied and then removed during 20 s. The data was selected during a state of heat balance in a cycle. The maximum  $\Delta T$  values were 0.078, 0.040 and 0.037 K, respectively for 4, 5 and 6 at% of lanthanum.

In the figure it has been also included the polarization– electric field (P-E) dependence at room temperature. Higher electric fields were not applied to avoid the breakdown of the



Fig. 1. Experimental setup for the analysis of the ECE by using the direct method.



Fig. 2. Time dependence for the temperature and the applied sine wave electric field for PLZT 6/90/10 composition.

samples. Typical antiferroelectric loops were obtained. It can be observed that the lanthanum concentration influences on the backward switching electric field ( $E_{\text{FE}-\text{AFE}}$ ) and the forward switching electric field ( $E_{\text{AFE}-\text{FE}}$ ) values.  $E_{\text{FE}-\text{AFE}}$  is the electric field at which the reverse ferroelectric (FE) to antiferroelectric (AFE) phase transition takes place.  $E_{\text{AFE}-\text{FE}}$ is the electric field, which forces the AFE to FE phase transition. For 5 and 6 at% of lanthanum concentration, a higher electric field must be applied in order to obtain true switching electric field values. Nevertheless, it could be concluded that the increasing of the lanthanum concentration provides higher values for both parameters.

For PLZT 4/90/10, it can be seen that  $\Delta T$  appears to jump for a critical electric field, which is around the forward switching electric field value ( $E_{AFE-FE}$ ). It suggests an important influence of  $E_{AFE-FE}$  on the ECE.

It is known that the antiferroelectric systems do not allow any macroscopic polarization due to the offsetting antiparallel alignment of the electric dipoles. However, an electric field-induced ferroelectric phase can be stabilized under the application of high electric field [11–12]. As a result, an abrupt change in the polarization takes place at  $E_{AFE-FE}$ . Also, the AFE–FE phase switching is accompanied by a high strain because of the difference between the molar volumes for both phases [13]. The enhancement of the polarization provides an adiabatic increasing

Download English Version:

# https://daneshyari.com/en/article/1459424

Download Persian Version:

https://daneshyari.com/article/1459424

Daneshyari.com