Electrocaloric effect and freezing temperature in $(\text{Pb}_{0.8}\text{Ba}_{0.2})[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$ relaxor ferroelectric ceramic

A. Peláiz-Barranco*, F. Calderón-Piñar and Y. Méndez-González

Facultad de Física-IMRE, Universidad de La Habana.

San Lázaro y L, Vedado, La Habana 10400, Cuba

*pelaiz@fisica.uh.cu

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The electrocaloric effect (ECE) is studied in $(\text{Pb}_{0.8}\text{Ba}_{0.2})[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$ relaxor ferroelectric ceramic by using an “indirect method”. The electric dependence for the polarization (hysteresis loops) has been obtained for several temperatures showing typical relaxor characteristics. The temperature change ΔT , which is associated with the ECE, is calculated by using the temperature dependence for the polarization. A maximum value for ΔT is observed for temperatures close above the freezing temperature, showing an indirect evidence of that critical temperature. The results are discussed considering the contribution of the polar nanoregions to the polarization.

Keywords: Relaxors; ferroelectrics; electrocaloric effect; freezing temperature.

1. Introduction

It is known that ferroelectric materials have a net dipole moment, which provides that the corresponding polarization increases by the application of an external electric field. It provides a decrease in entropy and an adiabatic increase in the temperature of the material. The temperature change due to an adiabatic application of an electric field is known as electrocaloric effect (ECE).^{1–6} The ECE originates from the cross-coupling between polarization and temperature, as the pyroelectric effect, being restricted by the practical limitations of the high voltages application to avoid dielectric breakdown and leakage current.

The ECE can be studied by using the so-called “direct methods” or “indirect methods”.¹ The former corresponds to the direct measurement of the temperature change, by using differential scanning calorimeter or temperature sensors, when an external electric field is applied to a material. By using “indirect methods”, the temperature change is calculated from the temperature dependence of the polarization at a constant electric field.

Relaxor ferroelectric materials have been studied for years due to the different dielectric behavior concerning normal ferroelectric systems, whose nature has been associated with the existence of polar nanoregions (PNRs).^{7,8} These materials are also characterized for large saturated polarizations, small remnant polarizations and moderate breakdown fields. When an electric field is applied, a large change in the polarization can be induced by the PNRs, which provide high dielectric permittivity values in wide temperature ranges. It can also generate a large ECE.⁴

$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) belongs to the relaxor ferroelectrics family, receiving special attention for its technical

importance.⁹ However, its preparation usually needs the addition of BaTiO_3 (BT) to obtain pure phases because of the pyrochlore phase appears very easy.¹⁰ On the other hand, the addition of lead titanate (PT) to the PZN–BT system has shown a weak frequency dispersion of the dielectric response,¹¹ offering an interesting material (PZN–PT–BT). Previous studies in $(\text{Pb}_{0.8}\text{Ba}_{0.2})[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$ have shown the main characteristics of relaxor ferroelectrics.¹² The Volger–Fulcher relationship has been used to evaluate the dielectric behavior showing the typical relaxor behavior of a spin glass system. Considering the presence of local compositional fluctuation on a macroscopic scale, the relaxor behavior has been explained for this $\text{Pb}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ type pervoskite.

The present paper shows the analysis of the ECE in $(\text{Pb}_{0.8}\text{Ba}_{0.2})[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}]\text{O}_3$ relaxor ferroelectric ceramic by using an “indirect method”. The behavior around the freezing temperature is analyzed.

2. Experimental Procedure

The ceramic composition was prepared by using solid-state reaction method. The reagent powders were milled and calcined at 900°C during 2 h in air. The sintering process was carried out in a suitable atmosphere (PbO) at 1160°C during 1.5 h in a well-covered platinum crucible. High density samples were obtained ($\rho = 7.45 \text{ g/cm}^3$). X-ray diffraction patterns on powder samples were made by using a Siemens D500 X-ray diffractometer. Electrodes were deposited on the parallel faces of the ceramic disks by using Au strips and an organogold paste. A Sawyer–Tower circuit was used to

obtain the hysteresis loops at 1 Hz in a wide temperature range (50–350 K).

3. Results and Discussion

Figure 1 shows the electric field dependence for the polarization (P – E) at several temperatures. Figure 1(a) shows the hysteresis loops for temperatures until 230 K, where it can be seen that the polarization increases until 200 K and then decreases at 230 K. Figure 1(b) shows the following temperatures, beginning at 230 K for a better view of the obtained behavior. Slim linear hysteresis loops are observed above 230 K, which are typical of relaxor ferroelectric materials, indicating that the material was in the ergodic relaxor phase. For relaxor materials, on cooling from Burn's temperature (T_B), the system transforms from the paraelectric phase to the ergodic relaxor phase, where there are PNRs with randomly distributed dipoles.

A freezing temperature (T_F) around 229 K has been previously reported for the studied system.¹² The present results have shown a change in the polarization around that temperature.

Fig. 1. Hysteresis loops for several temperatures.

Figure 2 shows the temperature dependence of the polarization $P(T)$, which has been obtained from the P – E dependence in the studied temperature range. A maximum value for the polarization can be observed around the freezing temperature (T_F), which has been previously estimated by using the Vogel–Fulcher relationship.¹² The studied system¹² has also showed closer T_C and T_F values (T_C — Curie temperature). Thus, the polarization does not vanish above the peak due to the persistence of nanopolar domains interacting with each other at temperatures between T_C and T_B .

It is known that the size and the interaction between PNRs increase on cooling from the high temperature region and its contribution to the polarization becomes negligible below the freezing temperature.¹³ For $T < T_F$, there is a frustration of the cooperative effect, i.e., the applied electric field is not strong enough to break such interactions and only the smallest regions can switch with the electric field. For $T > T_F$, the macroscopic polarization decreases upon heating due to fluctuations between equivalent polarization states.¹⁴

From the $P(T)$ dependence, $(\delta P/\delta T)_E$ was obtained in order to calculate the temperature change (ΔT) by using Eq. (1), where ρ is the density of the material and C_E the heat capacity (68 J/Kmol), respectively. ΔT is associated with the ECE.¹

$$\Delta T = - \int_{E_1}^{E_2} \frac{T}{\rho C_E} \left(\frac{\partial P}{\partial T} \right)_E dE. \quad (1)$$

Figure 3 shows the temperature dependence of ΔT for the studied material, showing good results concerning other ceramic materials.¹ A maximum value is obtained close above T_F showing that the ECE study could give indirect evidence of the freezing temperature for ferroelectric relaxor materials. As it has been pointed previously, for $T < T_F$ there is a frustration of the cooperative effect, which is the responsible for the ferroelectricity; above T_F , the applied electric field cannot reorient the ferroelectric dipoles because of the thermal agitation (the macroscopic polarization decreases on

Fig. 2. Temperature dependence of the polarization.

Fig. 3. Temperature dependence for ΔT .

heating). The contribution to the polarization (and dielectric permittivity) is due to the PNRs, which can switch with the applied electric field. For temperatures close above T_F , the PNRs could contribute to the polarization, showing a maximum value for the dielectric permittivity. Thus, a maximum value of ΔT could be expected. From this point of view, the ECE analysis could offer an indirect evidence of that critical temperature (T_F).

It can be also observed from Fig. 3 a region with negative ΔT values below 200 K. ΔT decreases 50–180 K showing negative values.

Fig. 4. (Color online) X-ray diffraction pattern at room temperature. The experimental data are represented by red circles and the calculated profiles by continuous black line, respectively. The short lines below the diffraction pattern correspond to the calculated Bragg reflections for both phases. The difference between the experimental and the theoretical patterns are presented below.

Table 1. Refined atomic data for the studied system.

Phase	Tetragonal (P4mm)
a (Å)	4.028(2)
b (Å)	4.028(2)
c (Å)	4.054(7)
V (Å ³)	65.79(3)
Phase	Rombohedral (R3c)
a (Å)	5.707(5)
b (Å)	5.707(5)
c (Å)	14.020(5)
V (Å ³)	395.53(6)
χ^2	1.2
R_p	14.3
R_{wp}	17.8

The studied system exhibits a mixture of rhombohedral and tetragonal phases at room temperature. Figure 4 shows the X-ray diffraction pattern and the corresponding calculated profiles, which has been carried out by using the FullProf Suite software. The experimental data are represented by red circles and the calculated profiles by continuous black line, respectively. The short lines below the diffraction pattern correspond to the calculated Bragg reflections for both phases. The difference between the experimental and the theoretical patterns is presented below. Table 1 shows the results for both phases.

Previous studies on ECE have shown negative ΔT values in PMN-PT and Na_{0.5}Bi_{0.5}TiO₃ systems,^{15,16} which have been associated with induced-phase transitions. In the present system, no previous reports have been found concerning phase transitions below room temperature. The ECE results could be an evidence of possible induced-phase transitions for PZN-PT-BT systems for very low temperatures. Further researches are in progress.

4. Summary

The ECE has been studied in (Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O₃ relaxor ferroelectric ceramic by using an “indirect method”. The temperature dependence of ΔT has shown a maximum value closed above T_F , which has suggested that the ECE analysis could offer an indirect evidence of that critical temperature for ferroelectric relaxor materials. Further researches are in progress.

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