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Energy storage and relaxor behavior in $(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$ ferroelectric ceramic

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$(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$ relaxor-type ferroelectric ceramics was obtained via classical solid-state reaction. The hysteresis loop results were discussed in the frame of ergodicity criterium around the characteristic ferroelectric relaxor freezing temperature. Slimer hysteresis loops were observed below the freezing temperature reflecting an ergodic relaxor behavior. Above this temperature, estimated around 223 K for the studied system, larger and unsaturated like ferroelectric hysteresis loops were observed. This temperature also coincides with the slope change on maximum polarization and inflection point of remnant polarization curves. Energy storage, energy loss and efficiency values were determined in a wide temperature range. While the recoverable energy density shows relatively low values (0.23 J/cm^3), there are interesting behaviors for this parameter and for the efficiency, since the two physical quantities increase versus temperature and the efficiency even reaches the value of 97%.

Keywords: Relaxors; ferroelectrics; energy storage; freezing temperature.

1. Introduction

Relaxor ferroelectrics have emerged as a promising material for energy storage applications due to their high recoverable energy density and low dielectric loss, compared to canonical/classical ferroelectric systems.[1] In relaxors, the lack of macroscopic polar domain structure due to the stabilization of short-range interactions leads to the establishment of a local polarization thermally fluctuating between equivalent polar states in a wide temperature range below and above the maximum of dielectric permittivity.[2,3] This means that they present a broad temperature range over which their dielectric permittivity is maximum and the remnant polarization is minimum, making them attractive for high-temperature energy storage applications.[4,5] The energy storage mechanism is based on the polarization of the material under an applied electric field. When an electric field is applied, the dipoles in the material align along the field direction, resulting in a net polarization that can be maintained even after the electric field is removed. The high- energy density of relaxor ferroelectrics is due to the combination of their high dielectric constant, which allows for more charge to be stored per unit volume, and their low dielectric loss, which reduces energy dissipation during charge/discharge cycles. Additionally, these materials have a high breakdown strength, which makes them suitable for high-voltage applications where the stored energy needs to be released quickly without damaging the material.[1] Research on relaxor ferroelectrics for energy storage applications is ongoing, with a focus on optimizing their properties and developing practical applications.[1,6]

Lead-containing perovskite solid solutions such as $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ and some lanthanum-doping $Pb(Zr,Ti)O_3$ compositions are known for their relaxor characteristics.[7–9] Although lead-based ceramics are studied and used as ferroelectric and piezoelectric devices, these have seldom been studied for energy storage applications. Almost all of these studies, in the literature so far, have been dedicated to the typical perovskite system based on $Pb(Zr,Ti)O_3$ (PZT), and particularly on thin films.[10–13] Unfortunately, the studies carried out on polycrystalline ceramics, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ and PLZT 8/60/40 have not showed high-energy density values.[7,8,14] Nevertheless, relaxor ferroelectrics hold great potential for energy storage applications due to their unique properties. Further research on bulk ceramics could lead to the development of more efficient and sustainable energy storage solutions. On the other hand, the study of their behavior around the freezing temperature (T_F), a critical temperature for relaxors, could be interesting from the scientific and technological points of view.

In this way, $(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$, PZN–PT–BT, ferroelectric ceramic has been previously reported as a typical relaxor ferroelectric,[15] showing a strong deviation

from the Curie–Weiss law, which was only followed at temperatures much higher than T_m (the temperature which corresponds to the maximum of the real part of the dielectric permittivity). The results were analyzed by using the Volger–Fulcher relationship, showing the typical relaxor characteristics of a spin glass system with $T_F = 229\,\text{K}$.[15] The dielectric behavior was explained considering local compositional fluctuations on a macroscopic scale for $Pb(B'_{1/3}B''_{2/3})O_3$ type perovskite.[16] On the other hand, the dielectric and pyroelectric parameters have suggested the studied PZN–PT–BT composition as a suitable material to be used in pyroelectric applications and multilayer ceramic capacitors.[17] Finally, the study of the electrocaloric effect on this ceramic material has shown some interesting results, i.e., conventional (positive) ($\Delta T > 0$) and anomalous (negative) ($\Delta T < 0$) effects, a maximum ΔT value closed above T_F.[18] Considering the previous results, from the technological point of view, the study of the PZN–PT–BT relaxor ferroelectric system appears to be interesting for the development of dielectric, pyroelectric and electrocaloric devices near the room temperature and also around T_F. In this context, the aim of this work is to investigate the energy-storage properties in the $(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$ relaxor ferroelectric ceramic in a wide temperature range, in particular around the freezing temperature.

2. Experimental Procedure

$(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$, PZN–PT–BT, ferroelectric ceramic system was prepared by using the standard solid-state reaction method. The reagent powders were milled for 2 h and then calcined at 900°C for 2 h in air atmosphere. The powders were milled again for 2 h and thick disks were obtained by cold-pressing. The sintering process was made in a PbO atmosphere at 1160°C for 1.5 h in a well-covered platinum crucible. X-ray diffraction patterns on powder samples were made by using a Siemens D500 X-ray diffractometer and Cu–K radiation, showing a mixture of rhombohedral and tetragonal phases.[18] Gold electrodes were deposited on the parallel faces of the disks by using Au strips and an organogold paste. The ferroelectric response and the energy storage behavior were evaluated from the hysteresis loops, at 1 Hz in a wide temperature range, by using a Sawyer–Tower circuit.

3. Result and Discussion

The electric field dependence for the polarization (P-E), at several temperatures chosen in the studied temperature range, is shown in Fig. 1. It can be seen as a trend, typical of relaxors, to the narrowing of the hysteresis loops with increasing temperature. The trend can be clearly seen as a continuous decrement in the coercive electric field (E_C) and remnant polarization (P_R) from Fig. 2. For both polarization

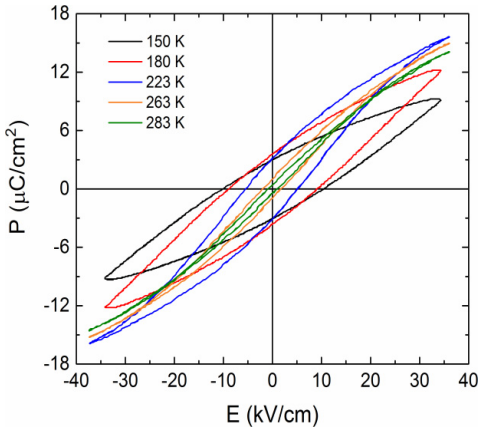

Fig. 1. Hysteresis loops, at several temperatures, recorded on the PZN–PT–BT ceramic.

parameters P_R and Maximum polarization (P_{MAX}) there is a critical temperature around 223 K, where P_{MAX} shows a maximum and P_R a change on its dependence showing the beginning of a clear decreasing trend with heating. Around the same temperature, a change in the hysteretic behavior can be observed in Fig. 1, going from a well-defined wide loop to a slim nonlinear loop. Note that for relaxor materials, on cooling from Burn's temperature (T_B), the system transforms from the paraelectric phase to the ergodic relaxor phase, where polar nanometric regions (PNRs) with a randomly distributed orientation of its dipoles begin to form. At those high temperatures, each PNR behaves like an electric single dipole that thermally fluctuates between equivalent polar states. On further cooling, for a temperature below T_m, the thermal energy is not enough to switch the polarization state so the PNRs get 'frozen'. The onset temperature of this freezing process is known as the freezing temperature of the system (T_F). Hence, below T_F, the system becomes nonergodic in nature due to the slowing down in the dynamics of PNRs, leading to a ferroelectric-like behavior with

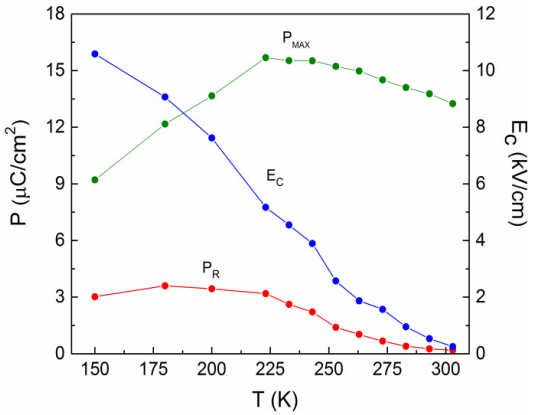

Fig. 2. Temperature dependence of the maximum polarization (P_{MAX}), the remnant polarization (P_R) and the coercive field (E_C), for the studied PZN–PT–BT ceramic.

larger hysteresis loop. On the contrary, for temperatures above T_F, the dynamics of the PNRs increases, so the aligned dipoles under an external electric field thermally return to the initial random polarization state once the electric field is removed, leading to a relaxor-like slim nonlinear loop. A freezing temperature (T_F) around 229 K has been previously reported for the studied system by using the Volger–Fulcher relationship.[15]

The energy storage properties were analyzed from the hysteresis loops in the first quadrant, which is associated to the discharge process. In this way, the recoverable energy density (J_R), can be obtained by numerical integration using Eq. (1), the loss energy density (J_L) is given by the area inside the loop, and the corresponding energy efficiency (η) can be obtained by Eq. (2).

$$J_R = \int_{P_R}^{P_{MAX}} \mathrm{EdP}, \tag{1}$$

$$\eta = \frac{J_R}{J_R + J_L}. \tag{2}$$

Figure 3 shows the temperature dependence for those parameters. While the recoverable energy density shows relatively low values,[19] but for lower applied electric fields, there are interesting behaviors for this parameter and also for the efficiency, since the two physical quantities increase versus temperature and the efficiency even reaches the value of 97%. J_R describes a monotonous increase in heating until around T_F and then there is certain stability for its values, which is an important result from the technological point of view. On the other hand, η increases too, reaching very high values above T_F. This behavior could be directly associated to the intrinsic characteristics of the relaxor ferroelectric materials. It is known that materials showing small P_R, high P_{MAX} and high breakdown strength are better for energy storage applications. It was suggested that the higher recoverable energy density can be obtained under the higher breakdown electric field.

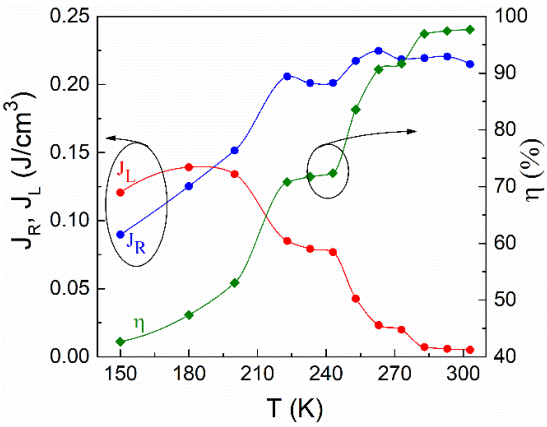

Fig. 3. Temperature dependence of the recoverable energy density (J_R), the loss energy density (J_L) and the energy efficiency (η), in PZN–PT–BT ceramic.

The sudden decrease of the P_R values for $T > T_F$ suggests an important change around this temperature region where the relaxor material goes from the nonergodic to the ergodic phase. The PNRs reach their maximum orientation around T_F, under the influence of the external applied electric field which is also reflected in the energy storage performance mechanism. Moreover, the thermal energy allows the maximum reorientation of the PNRs dipole moments with the applied electric field (highly ordered state). While the system remains in its lower remnant polarization, once the electric field is removed (disordered state), the thermal energy is enough to allow the spontaneous switching of the dipolar moments between equivalent states. Thus, for relaxor ferroelectrics, the freezing temperature reveals to be an important critical temperature for the energy storage behavior.

It can be concluded that the studied PZNT–PT–BT relaxor material is interesting for energy storage capacitors because of its lower freezing temperature value under room temperature, showing slim P-E loops with relatively high maximum polarization and small remnant polarization values.[20,21]

4. Conclusions

$(Pb_{0.8}Ba_{0.2})[(Zn_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}]O_3$ ceramics exhibit relaxor behavior. Slimmer hysteresis loops were observed reflecting the transition from nonergodic to ergodic relaxor behavior around $T_F = 223$ K. This value for the freezing temperature corresponds to the anomalies which were observed on the P-E hysteresis, P_{MAX}, P_R, energy storage, energy loss and energy efficiency curves plotted as a function of temperature. Above this temperature, larger and unsaturated like ferroelectric hysteresis loops were observed. Recovered energy, energy loss and energy efficiency values were determined and plotted versus temperature. While the recoverable energy density shows relatively low values (0.23 J/cm^3), it shows interesting increasing versus temperature, as for the energy efficiency which even reaches the value of 97%.

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