

ENERGY STORAGE POWER OF ANTIFERROELECTRIC AND RELAXOR FERROELECTRIC CERAMICS

PODER DE ALMACENAMIENTO DE ENERGÍA DE CERÁMICAS ANTIFERROELECTRICAS Y FERROELECTRICAS RELAJADORAS

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The development of dielectric materials with high recoverable energy-storage density and high efficiency has attracted increasing attention. To design a proper material, three requirements have to be satisfied simultaneously at least: high electric breakdown field, large saturated polarization, and small remanent polarization [1]. Although, linear dielectrics usually possess higher breakdown field and lower energy loss, their smaller polarization value makes them not suitable for high energy-storage application. Ferroelectrics often have larger saturated polarization and moderate electric-field endurance, but their larger remanent polarization lead to a smaller energy-storage density and lower efficiency. Relaxor ferroelectrics (RFE) and antiferroelectrics (AFE) are more likely to be used for high energy storage because of their larger saturated polarization, smaller remanent polarization and moderate breakdown field.

Antiferroelectrics are nonlinear materials that exhibit high polarization and store large energy density in an electric-field-induced phase transition [2-3]. In these systems, the adjacent dipoles are aligned in opposite orientation, and under sufficient high dc electric-field the orientation of dipoles could be re-arrayed along direction of dc field and be changed into ferroelectric state, because of the smaller free energy between antiferroelectric and ferroelectric phase. Lead-containing ceramics, such as lead zirconate and modified lead zirconate titanate (PZT), are the most important reported antiferroelectrics [4-7]. On the other hand, relaxor ferroelectrics have attracted continued attention because of their peculiar properties, such as high dielectric permittivity and high piezoelectric coefficients, which make them potential candidates for applications in microelectronic devices. These materials are characterized by a high frequency dependence of their dielectric parameters [8-10], which is believed to be

originated from polar nano-regions (PNR). These PNR appear below certain temperature, so-called the Burns' temperature, which is typically hundreds degrees above the temperature of the maximum real dielectric permittivity (T_m). On cooling, the number, size (some of them) and the interaction of the PNR increase. The increasing of such interactions promotes the freezing of some regions around certain temperature below T_m , known as the freezing temperature. Several relaxor ferroelectric materials have been reported until today, but the nature of their dielectric response still remains open [10-13].

The present work shows the study, which has been carried on lanthanum modified PZT antiferroelectric ceramics and lead-free relaxor ferroelectric ceramics under high electric fields. The analysis is focused on the energy-storage characteristics of AFE and RFE compositions whose results have not been previously reported even when interesting achievements have been obtained in high energy-storage materials. The energy-storage characteristics will be presented and discussed, which will show promising ceramics for high energy-storage applications.

$(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{0.90}\text{Ti}_{0.10})_{1-x/4}\text{O}_3$ antiferroelectric ceramic samples were prepared by the traditional solid state reaction method [14] considering $x=4, 5, 6$ at% (PLZT $x/90/10$). The stoichiometric mixture of powders was prepared at 800°C in air for 1 hour. The calcined powders were milled and formed into disks by cold-pressing and sintering in air at 1250°C for 1 hour in a well-covered platinum crucible in order to minimize the evaporation of reagents. Lead-free relaxor ferroelectric ceramics were prepared by the same method [15] considering a nominal composition $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$, where $x=50, 70, 85$ at% (SBBN- x). The oxide mixtures were calcined in air at 950°C for 2 hours. The sintering was carried out at 1100°C for 1 hour

in a well-covered alumina crucible. Conductive electrodes were applied to the ceramic specimens using Ag-loaded paste fired on at 590°C. The hysteresis loops were obtained by using a precision ferroelectric analyzer (Premier II, Radiant Technologies Inc.) combined with a high voltage power supply (TReK Model 663A). The measurements were made at room temperature and 10Hz.

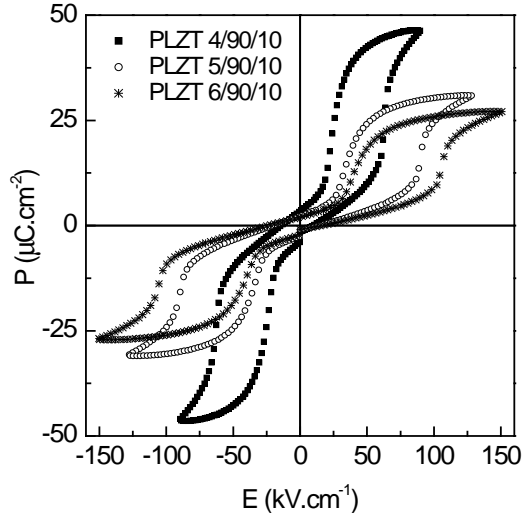


Figure 1. Hysteresis loops for PLZT $x/90/10$ antiferroelectric ceramic samples at room temperature.

Figure 1 shows the hysteresis loops for the PLZT $x/90/10$ antiferroelectric ceramic samples. Double-hysteresis loops have been obtained, which is typical of antiferroelectric behavior under a strong electric field. Table I shows the backward switching electric field (E_{FE-AFE}), the forward switching electric field (E_{AFE-FE}) and the hysteresis loop width [$\Delta E = (E_{AFE-FE} - E_{FE-AFE})$], for the studied AFE samples. E_{FE-AFE} is the electric field at which the reverse ferroelectric (FE) to antiferroelectric (AFE) transition occurs while E_{AFE-FE} is the electric field which forces the AFE to FE transition, respectively. For simplicity, E_{AFE-FE} has been taken as the electric field that causes the polarization to increase up to half of its maximum value and E_{FE-AFE} as the electric field that reduces the polarization down to half of its maximum value, respectively. It can be seen that the increasing of lanthanum concentration has an important influence on the hysteresis characteristics, i.e. the antiferroelectricity and switching electric field values are enhanced with the replacement of Pb^{2+} by La^{3+} ions. For lanthanum modified PZT materials [4], the stability of the long-range interactions is suppressed by decoupling effects caused by the incorporation of La^{3+} into the A-site of the perovskite structure providing a stabilized AFE state.

AFE Samples	E_{FE-AFE} (kV.cm ⁻¹)	E_{AFE-FE} (kV.cm ⁻¹)	ΔE (kV.cm ⁻¹)
PLZT 4/90/10	22.28	63.32	41.04
PLZT 5/90/10	32.29	86.99	54.70
PLZT 6/90/10	38.03	102.96	64.93

Samples	J_R (J.cm ⁻³)	J_L (J.cm ⁻³)	η
PLZT 4/90/10	1.23	1.52	0.45
PLZT 5/90/10	1.30	1.43	0.48
PLZT 6/90/10	1.37	1.40	0.49
SBBN-50	1.02	0.89	0.54
SBBN-70	1.13	0.61	0.65
SBBN-85	1.15	0.42	0.73

Table II shows the recoverable electrical energy density (J_R), the loss electrical energy density (J_L) and the energy-storage efficiency (η) for the studied samples. The energy-storage efficiency is calculated by using equation 1.

$$\eta = \frac{J_R}{J_R + J_L} \quad (1)$$

The AFE samples show lower J_R values than that of other similar AFE materials based on PZT but the energy-storage efficiency (η) is higher because the lower J_L values [16]. The J_R values are higher than that of typical $PbZrO_3$ AFE ceramic [17] and also similar to PLZT thick films [18]. The results suggest potential AFE ceramics for energy-storage.

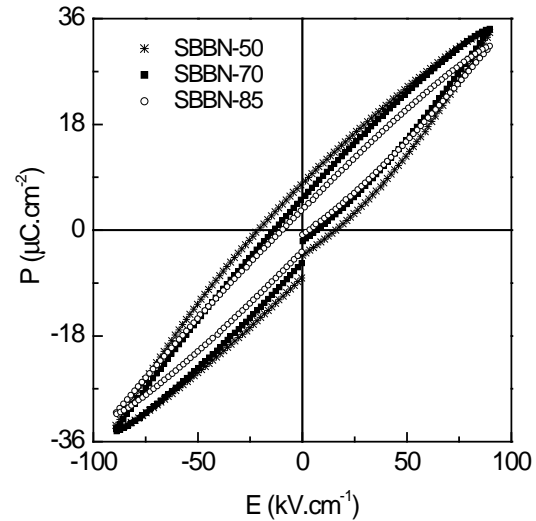


Figure 2. Hysteresis loops for relaxor ferroelectric ceramic samples at room temperature.

Figure 2 shows the hysteresis loops for SBBN- x samples. Slim loops are observed, which are typical of relaxor ferroelectric materials [15]. It can be seen that the increasing of the barium concentration has an important influence on the hysteresis characteristics, i.e. the loop area decreases when the barium concentration increases. It is associated to the relaxor characteristics which are enhanced by the barium concentration [15]. Table II also includes the J_R , J_L and η for the relaxor samples, showing similar values than those for PLZT relaxor ferroelectric thin films for the same applied electric field [19]. The energy-storage efficiency is higher than 50% in all compositions, which show promising relaxor ceramics for high energy-storage applications.

It is known that the bulk ceramic materials show lower breakdown strengths than those in thin films, which prevents the recoverable electrical energy density. Higher values have been achieved in thin film forms but the thickness limitation not always meets the practical requirements. Thus, the development of bulk ceramics continues receiving special attention in order to obtain materials with higher breakdown fields in order to increase the energy-storage density.

As summary, antiferroelectric and relaxor ferroelectric ceramics have been studied under high electric fields. The characteristics of the hysteresis loops have been discussed considering the doping concentration. The energy-storage characteristics have been also analyzed showing high energy-storage efficiency values.

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