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High temperature-stability of $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})O_3$ ceramic for energy-storage applications at finite electric field strength

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ABSTRACT

Temperature stability is one of the key factors for energy storage application of dielectric capacitors especially under stringent environmental conditions. In this work, we report that the $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})O_3$ ceramic exhibits small variation of energy density (<15%) over a wide temperature range (24 °C ~ 83 °C) at low field strength ($E < 25$ kV/cm). Further TEM observation and phase field simulations suggest that it can be attributed to continuous formation and growth of polar nanoregions with temperature and electric field, resulting in high-temperature stability for dielectric permittivity and energy density. Our finding may have implications for developing dielectric energy-storing devices with high thermal reliability.

Dielectric material, which exhibits polarization when applying external electric field, enables the storage of electric energy and thus plays an important role in the storage and manipulation of electric power. Although the energy storage devices (e.g. supercapacitors, rechargeable batteries, fuel cells etc.) with high energy density have been drawing significant attention [1], dielectric energy-storing device, on the other hand, is capable of fast delivering the electric energy. Owing to high power density, the dielectric materials have the potential to be utilized on power pulse devices, hybrid electric vehicles, portable electronic devices and so on [2,3], and have also triggered wide research interests [4–19].

Most of the dielectric energy-storing devices are designed for high electric field strength applications, aiming to achieve high level of energy density [20–27], and the associated materials (e.g. polymers, ferroelectrics and antiferroelectrics etc.) should be able to withstand large electric field, resulting in an elevated voltage level [2–27]. For example, the lowest voltage is as high as sub-kilo volt even for a thin film specimen with the thickness down to several micron-meters [25]. Nevertheless, high voltage level restricts the application of energy-storing material as wearable or portable electronic devices with miniaturized dimension and high integration. Hence, it is necessary to develop the dielectric energy storage materials within a finite electric field strength. Our earlier work proposed an approach to enhance the energy density in $Ba(Ti,Sn)O_3$ (BTS) system through elevating its permittivity using a so-called tricritical transition [28,29]. However, although the energy density for such a material is higher than most of ferroelectric systems with the same field strength ($E = 10$ kV/cm), it is poor in temperature stability for energy storage performance due to large thermal variation of dielectric permittivity [29]. This deteriorates its thermal reliability, which reduces the endurance with ambient temperature change as well as device temperature rise. It is of great importance to broaden the usage temperature for the application of dielectric materials in energy storage devices, which enables the designing of reliable devices.

It is well-known that energy storage performance highly relies on dielectric permittivity. Thus, the relaxor ferroelectric material, which has high thermal stability of dielectric permittivity [30], could be a potential candidate. In this manuscript, we study the temperature-dependence of energy density for a relaxor $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})O_3$ (PLZT) ceramic. The result indicates that it exhibits a high degree of temperature-stability for energy density at low electric field ($E < 25$ kV/cm). Further transmission electron microscopic observation uncovers its microstructure origin, and a phase field simulation has also been employed to understand the underneath mechanism. Our results may provide guideline for developing energy storage dielectric materials with excellent thermal stability.

The $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})O_3$ relaxor ferroelectric ceramics were fabricated by using the conventional solid-state sintering method from the raw chemical powders of PbO, La_2O_3, ZrO_2, TiO_2. Calcination and

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final sintering were performed at the temperature of 1000 °C (3 h) and 1250 °C (3 h) in oxygen atmosphere. We used thin column specimens with different dimensions for energy density test (Φ = 7.31 mm, d = 2 mm) and dielectric coefficients measurement (Φ = 20.6 mm, d = 2.6 mm). In order to measure the energy density of the samples, a Premier II ferroelectric test system (Radiant Technologies Inc.) was employed to detect the polarization-electric field (*P-E*) loops at 10 Hz. Further temperature-dependence of energy storage properties were measured by using the same test system equipped with a heating chamber. Dielectric permittivity and loss tangent at 10 Hz were measured with a broad frequency dielectric spectrometer (Concept 80, Novocontrol Technologies Inc.), and the applied AC voltage is 1 V in amplitude. Moreover, the evolution of microstructure with temperature was observed by using a JEM 2100F transmission electron microscope (TEM) in combination with a heating specimen stage (Gatan 652). Furthermore, the underlying mechanism was studied by phase field simulation. Domain structure is described by spatial distribution of spontaneous polarization $\mathbf{P} = (P_1, P_2, P_3)$. The total free energy of the system includes the following physically distinctive terms (local chemical free energy f_{bulk}, coupling term f_{couple} caused by doping, long range elastic interaction f_{elas}, static electric interaction f_{elec}, external electric field f_{elappl} and domain wall energy of gradient term f_{grad}):

$$F = F(\mathbf{P}, \bar{c}) + F(\mathbf{P}, \varphi) + F(\mathbf{P}) = \int_V f_{bulk} dV + \int_V f_{couple} dV + \int_V \left(f_{elas} + f_{elec} + f_{elappl} + f_{grad} \right) dV \quad (1)$$

Temporal evolution of the spontaneous polarization field can be obtained by solving the time-dependent Ginzburg-Landau (TDGL) equation:

$$\frac{dP_i(\mathbf{x}, t)}{dt} = -M \frac{\delta F}{\delta P_i(\mathbf{x}, t)}, \quad i = 1, 2, 3 \quad (2)$$

where M is the kinetic coefficient and t is time. In the expression of free energy (Eq. (1)), the chemical free energy f_{bulk} is the temperature-dependence term, which can be described as follows:

$$f_{bulk} = A_1^0 \left(T - T^0 \right) \sum_{i=1,2,3} P_i^2 + A_{11} \sum_{i=1,2,3} P_i^4 + \frac{A_{12}}{2} \sum_{i,j=1,2,3; i \neq j} \left(P_i P_j \right)^2 + A_{111} \sum_{i=1,2,3} P_i^6 + A_{112} \sum_{i,j=1,2,3; i \neq j} \left(P_i^2 P_j^4 \right) + A_{123} \left(P_1^2 P_2^2 P_3^2 \right) \quad (3)$$

where A_1^0, A_{11}, A_{12}, A_{111}, A_{112} and A_{123} are Landau expansion coefficients and T is the temperature for the materials system. The detailed method and coefficient values can be found in Ref. [31]. Therefore, the microstructures at different temperature can be calculated by solving evolution equation Eq. (2).

In order to detect the energy density, we measured the *P-E* hysteresis loops for the relaxor ferroelectric material PLZT10/65/35 ceramics. As a comparison, we also performed the same measurement for other ferroelectric systems including modified $PbZrTiO_3$ (PZT) ceramics and poly (vinylidene fluoride) (PVDF). In particular, the PVDF is one of the most investigated ferroelectric polymer materials for energy storage application [2,3,9]. Fig. 1(a) shows *P-E* loops for these specimens, and it can be seen that the PLZT10/65/35 ceramic exhibits higher polarization value compared with other selected materials. High polarization value for PLZT10/65/35 ceramic is an indication for larger electric energy density.

We then calculated the energy density for each selected specimen from its *P-E* curve. It is well-known that the energy density u_e can be described as $u_e = \int EdD$, where E and D are field strength and electric displacement respectively. Such an integration can be carried out for *P-E* curve of either charging (with the increase of E) or discharging (with the decrease of E). We then use the one from the discharging *P-E* curve, which is an indication of energy density that can be released from dielectric material. We measure the *P-E* loops for each specimen at a series of field strength, and the corresponding energy densities are shown in Fig. 1(b). These specimens show the similar trend that energy densities are enhanced with the increasing of electric field strength. However, PLZT10/65/35 ceramic exhibits higher value of energy density compared with other selected materials at electric field of $E < 25$ kV/cm. Although u_e for PLZT is far below the one for other dielectrics at high field region ($E \approx 6000$ kV/cm) [2], it may still be found potential applications on the energy storage devices on low electric field occasion.

The inset of Fig. 1(b) further shows the electric field-strength-dependence of dielectric permittivity for the PLZT10/65/35 ceramic. Although the electric field strength is believed to be the dominant factor for energy density, dielectric permittivity ε_r also plays an important role on the energy-storing properties of the material, since the energy density can be expressed as $u_e = \varepsilon_0 \int Ed(\varepsilon_r E)$. The permittivity has been evaluated from the derivative of polarization with respect to electric field from the discharging *P-E* curve. It should be noticed that such a differential permittivity involves the ferroelectric domain switching (or polarization reversal) under relatively large electric field, and it usually shows discrepancy in value with permittivity measured by impedance analyzer (Fig. 2(a)) which only caused by domain wall motion under weak electric field [32]. It can be seen from the inset of Fig. 1(b) that dielectric permittivity decreases with the increasing of electric field. Such a phenomenon has also been observed for other ferroelectric energy-storing materials at higher electric field strength [2,25], and can thus be considered as a general trend. Being different from the conventional dielectric material with linear dielectric response, ferroelectric materials, including relaxor PLZT ceramics, exhibit dielectric nonlinearity with respect to external field [33]. Several models have been proposed

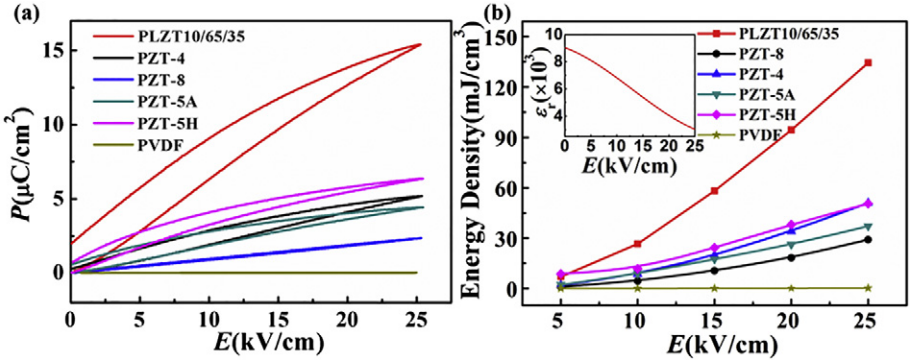

Fig. 1. (a) The polarization-electric field (*P-E*) loops at the field strength of $E = 25$ kV/cm for PLZT10/65/35 ceramic, PZT-based ceramics and PVDF polymer. (b) The field-strength-dependence of energy density for the tested materials. PLZT 10/65/35 shows large value in u_e. The inset shows the differential dielectric permittivity decreases with increase of field strength, suggesting the permittivity has ·higher impact in low field region.