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Enhanced energy storage density and its variation tendency in $CaZr_xTi_{1-x}O_3$ ceramics

Hai Yang Zhou, Xiao Na Zhu, Guang Rong Ren, Xiang Ming Chen*

Laboratory of Dielectric Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China

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ABSTRACT

The improved energy storage density and its variation tendency have been investigated for $CaZr_xTi_{1-x}O_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) solid solution ceramics. The dense ceramics with high bulk density above 97% could be obtained, and X-ray diffraction analysis confirms the orthorhombic single phase structure in all compositions. Substitution of Zr^{4+} obviously increases the sintering temperature, and the homogeneous fine grain structure is obtained. With increasing x, the dielectric constant ε_r decreases from 175 to 103, while the dielectric strength E_b increases from 435 kV/cm to 756 kV/cm. The highest energy storage density of 2.7 J/cm^3 is achieved at $x = 0.4$, which is much higher than that of $CaTiO_3$ end-member. The energy storage density significantly increases with decreasing the thickness due to the increased dielectric strength (For the samples with $x = 0.5$, the dielectric strength increases from 584 kV/cm to 756 kV/cm while the energy storage density increases from 1.6 J/cm^3 to 2.6 J/cm^3 when the thickness changes from 0.50 mm to 0.15 mm).

1. Introduction

Dielectric capacitors with high power density and fast charge and discharge rates are widely used in the power electronics, hybrid electric vehicles and pulsed power systems [1–7]. However, the lower energy storage density has been remained as an essential issue [4,5]. In order to minimize the size, weight and cost of the energy storage devices, dielectric capacitors with high energy storage density and low loss are strongly required [2,6,8]. As it is well known, the energy storage density (U) of the dielectric materials can be calculated according to the equation of $U = \int \boldsymbol{E}d\boldsymbol{D}$, indicating that the large polarization ($\boldsymbol{P}$) and large dielectric strength (E_b) are both required for high energy storage density. Therefore, a lot of studies have been focused on the energy storage performance about ferroelectrics and antiferroelectrics due to their large polarization $\boldsymbol{P}$, but their dielectric strength E_b are usually low (<300 kV/cm) [8–11].

Differing from the ferroelectric materials, the linear dielectrics generally indicates a dielectric constant ε_r independent of external applied field, and therefore the electrical energy storage density is directly proportional to the dielectric constant ε_r and the square of the dielectric strength E_b [5,6]. It should be noted that although linear dielectrics have a low dielectric constant ε_r, a high energy storage density can be achieved because of the higher dielectric strength E_b compared to ferroelectrics and antiferroelectrics [12,13]. Moreover, linear dielectrics generally have low dielectric loss and favorable bias stability [5,14]. Thus, linear dielectrics are more deserved to investigate for energy storage applications. Apparently, the most important issue to enhance the energy storage density in linear dielectric ceramics is to further improve the dielectric strength E_b. In fact, the intrinsic dielectric strength in solid insulators is much higher than 1 MV/cm [15], while the breakdown properties of ceramics are significantly influenced by the extrinsic factors, such as pores, impurities and grain boundaries [16–20]. Therefore, single phase and dense ceramics with fine grain microstructure are generally desired for achieving high energy storage density.

$CaTiO_3$ is a typically linear dielectric material with a high dielectric constant of about 170, which is a promising candidate for high energy storage device. Considering that Ti^{4+} is easily changed to Ti^{3+} during sintering process, leading to a higher ionic conductivity, Ti^{4+} is partial substituted by more chemically stable Zr^{4+} to suppress the valence change [21]. In addition, the substitution of Ti^{4+} with Zr^{4+} has been reported to reduce the grain size in $Ba(Zr,Ti)O_3$ [22]. It is known that grain boundary may act as a barrier layer for charge migration [20], and the smaller grain size

* Corresponding author.
E-mail address: xmchen59@zju.edu.cn (X.M. Chen).

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benefits the dielectric strength because of denser grain boundary. In the previous work by Randall et al. [12], a high dielectric strength (1.5 MV/cm) and a high energy density (4 J/cm^3) at 250 °C are obtained for $CaTi_{0.2}Zr_{0.8}O_3$ single dielectric layer at 10 μm thickness. It is worth noting that the energy storage density has a significant correlation with thickness, as a result of the strong dependence of that on dielectric strength [23,24]. Hence, it remains as an important issue to deepen the understanding on the energy storage density in $CaZr_xTi_{1-x}O_3$ ceramics. Also, it is necessary to explore the relation between the energy storage density and thickness in detail. Moreover, it is important to obtain single phase $CaZr_xTi_{1-x}O_3$ ceramics without secondary phase such as ZrO_2, because the impurity may affect the space charge distribution, leading to a local field enhancement and consequently a reduced dielectric strength [25].

In the present work, the improved dielectric strength and energy storage density are systematically investigated in $CaZr_xTi_{1-x}O_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) solid solution ceramics, and the effects of composition and microstructure are revealed together with the thickness. The improved dielectric strength and energy storage density are interpreted by the increased band gap, suppressed defect structure, increased bulk density and finer microstructures.

2. Experimental procedure

$CaZr_xTi_{1-x}O_3$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) ceramics were prepared by a standard solid-state reaction process, using high-purity $CaTiO_3$ (99.99%), TiO_2 (99.99%) and ZrO_2 (99.99%) powders as raw materials. Stoichiometric quantities of the raw powders were weighted and mixed by ball milling with zirconia media in alcohol for 24 h, and then calcined at 1100 °C–1150 °C in air for 3 h. The calcined powders were re-milled, mixed with 6 wt% PVA solution, and then pressed into cylindrical disks of about 12 mm in diameter and 2 mm in thickness under a pressure of about 98 MPa. Finally, all samples were sintered at 1325 °C–1600 °C in air for 3 h.

The bulk density of sintered disks was calculated from weight and dimension. The crystalline phases of sintered samples were determined by powder X-ray diffraction (XRD) using Cu$K\alpha$ radiation (D/MAX 2550/PC, Rigaku, Tokyo, Japan). The microstructures were observed for the thermal-etched surfaces by using scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan). The dielectric constant and dielectric loss were measured under 1 V in the frequency range of 100 Hz–1 MHz with a LCR meter (Agilent 4284A, Agilent Technologies Inc., Santa Clara, CA). The dielectric strength measurement was performed by a withstanding voltage tester (MS2677; Minsheng Electronics Co. Ltd., Nanjing, China) under a DC voltage ramp of 500 V/s at ambient temperature. All samples were polished into about 0.15 mm in thickness, and gold film was sputtered as the electrodes. In order to prevent surface flashover, all samples were immersed in silicone oil. For each composition, at least 9 samples were used to evaluate the dielectric strength.

3. Results and discussion

Fig. 1 shows the XRD patterns of $CaZr_xTi_{1-x}O_3$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) ceramics, indicating an orthorhombic structure in space group *Pbnm*. No second phase is detected for all compositions, and this is different from the previous work [12,26]. The ionic radius of Ti^{4+} and Zr^{4+} is 0.605 Å and 0.720 Å, respectively. Thus, the XRD peak positions slightly shift to the lower angles with increasing Zr^{4+} content due to the increase of lattice constant. For the composition of $x = 0.0$, the lattice parameters a, b, c are 5.388 Å, 5.447 Å and 7.654 Å, respectively, while in the composition of x = 0.5, the lattice parameters a, b, c are 5.490 Å, 5.607 Å and 7.837 Å, respectively. The theoretical X-ray densities are calculated

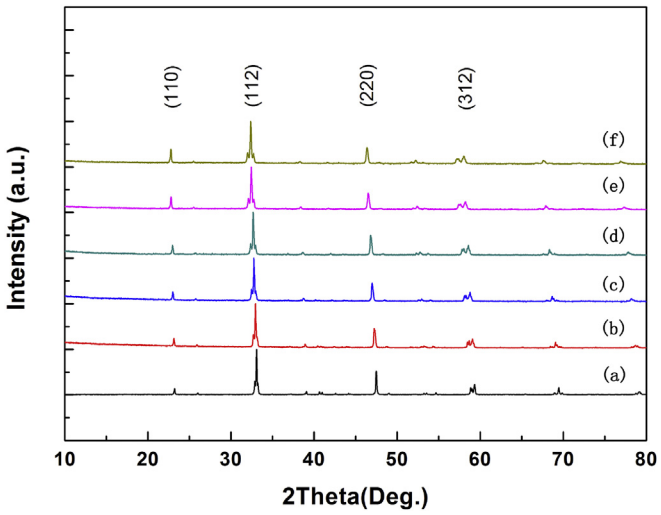

Fig. 1. XRD patterns for $CaZr_xTi_{1-x}O_3$ ceramics with various compositions: (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$, and (f) $x = 0.5$.

to be 4.02 g/cm^3 and 4.34 g/cm^3 for $x = 0.0$ and $x = 0.5$, respectively. Dense $CaZr_xTi_{1-x}O_3$ ceramics are obtained by sintering at different temperatures according to the composition (see Fig. 2). Zr^{4+}-substitution increases the densification temperature greatly compared to that of $CaTiO_3$ end-member. The optimized sintering temperatures are chosen at 1350 °C for $x = 0.0$ and 1575 °C for x = 0.1, 0.2, 0.3, 0.4, 0.5, to ensure the relative densities in all the compositions are above 97%. Fig. 3 (a) shows the SEM image for the thermal-etched surfaces of $CaTiO_3$ ceramics sintered at 1350 °C, showing an average grain size of about 7 μm. As shown in Fig. 3 (b)–(f), finer grain structures are observed with increasing x, revealing that Zr-substitution effectively inhibits the grain growth. The homogeneous grain distribution with the smallest grain size of about 3 μm is obtained for $x = 0.5$ sintered at 1575 °C, and this corroborates to the best dielectric breakdown performance.

In order to reliably evaluate the dielectric strength, two-parameter Weibull distribution [11,27–29] is adopted in the present work. The cumulative distribution function is defined as $P = 1-\exp(-(E/\alpha)^{\beta})$, where P is the cumulative probability of failure, E is the breakdown field for each sample, α is the scale

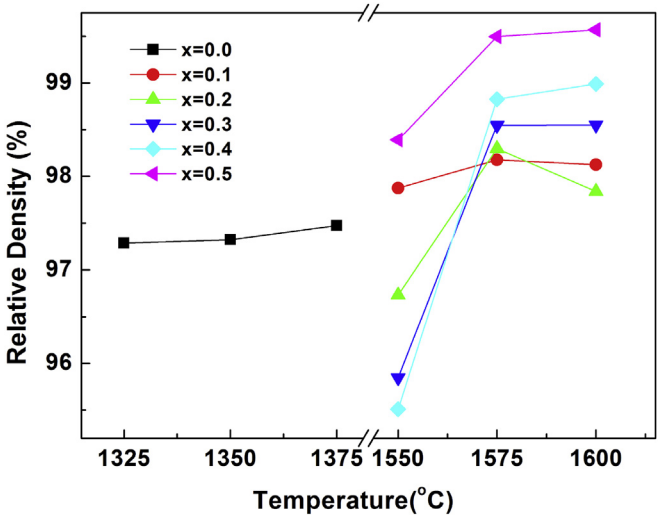

Fig. 2. Relative density of $CaZr_xTi_{1-x}O_3$ ceramics as function of sintering temperature.