O U R N A L O F

Ceramic Processing Research

Structure and energy storage properties of $Re_{0.02}$ Sr_{0.98}TiO₃ (Re = La, Pr, Sm) ceramics

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The $Re_{0.02}Sr_{0.98}TiO_3$ (*ReST*, Re = La, Pr, Sm) ceramics with single cubic perovskite structures were prepared by a solid state reaction method. The structure and dielectric properties of the *ReST* ceramics were investigated for energy storage capacitor applications. Strongly improved dielectric constant ($\varepsilon_r > 2000$ @1 kHz) with a good bias electric field stability was achieved for the *ReST* ceramics. Together with relatively low dielectric loss ($\tan \delta \le 3\%$ @1 kHz) and normally high breakdown strength ($E_b > 15 \text{ kV/mm}$), the *ReST* ceramics should be very promising for energy storage capacitors in pulsed power electronics.

Key words: Dielectric ceramics, Strontium titanate, Rare earth doping, Energy storage.

Introduction

New development of ceramic capacitors for high power electronics, such as electric armors and guns, particle beam accelerators, and ballistic missile systems, has advanced the active investigation and innovation of energy storage dielectric materials with both high dielectric constant and high breakdown strength [1-5]. Normally, strong nonlinear ferroelectric ceramic materials have extremely high dielectric constant. It is found, however, such high dielectric constant decreases markedly as the applied electric field increased, so that the energy storage density which can be achieved is disappointingly low [6]. Consequently, linear dielectric ceramics, which generally possess moderate dielectric constant $\varepsilon_{\rm p}$ high breakdown strength $E_{\rm b}$ and low dielectric loss tan δ , are more suitable for high power electronic applications. Among linear ceramic candidates, strontium titanate (SrTiO₃, ST) is a typical one for energy storage capacitors owing to its medium high $\varepsilon_{\rm r}$ and relatively strong $E_{\rm b}$. During the past several decades, impurity modified ST ceramics have been extensively studied to increase the $\varepsilon_{\rm r}$ and/or $E_{\rm b}$ and then obtain improved possible storing energy per unit volume. For example, Nishigaki *et al.* reported a high ε_r (> 3000) in Pb, Ca, and Bi co-modified ST ceramics, which can be used for high-voltage capacitors [7]. Triani et al. discussed the suitability of Pb modified ST ceramics for application as the dielectric layer in high energy density capacitors [8]. Zhao et al. obtained great enhancement in the breakdown performance of the SiO₂ modified ST ceramics for energy storage applications [9]. Chao and

Dogan designed BaTiO₃-SrTiO₃ layered dielectrics for energy storage [10].

On the other hand, rare earth doped ST ceramics have been attracted increasing interests owing to some reported distinctive characteristics such as enhancement of tetragonality and visible-light photocatalytics [11, 12]. More recently, we reported the enhancement of energy storage properties in trivalent rare earth doped ST ceramics with A-site Sr vacancies or B-site Ti vacancies charge compensated composition [13, 14]. In this work, however, rare earth doped ST ceramics with self-charge compensated composition, i.e. $Re_{0.02}Sr_{0.98}TiO_3$ (*ReST*, Re = La, Pr, Sm), are selected to investigate their potential for energy storage capacitor applications.

Experimental

The $Re_{0.02}$ Sr_{0.98}TiO₃ (*Re*ST, Re = La, Pr, Sm) ceramics were prepared by a solid state reaction method using SrCO₃ (99%), TiO₂ (98%), La₂O₃ (99.9%), Pr₂O₃ (99.9%) and Sm₂O₃ (99.9%) as raw materials. The raw materials were weighed according to the stoichiometric composition of ReST, and then mixed by planet ball milling for 6 hrs in a nylon bottle with deionized water and zirconia balls. The mixed slurry were dried and calcined at 1000 °C for 2 hrs in an alumina crucible. The calcined powders were planet ball milled again for 10 h, dried and granulated with polyvinyl alcohol (PVA) as a binder, then pressed into disks of 12 mm diameter and about 1.1 mm thick under 120 ± 10 MPa. The disks were first preheated in air at 650 °C for 1 hr to remove organic binders, and then sintered at $1380 \sim 1440$ °C for 3 hrs in air with a heating rate of 3 °C/min and finally furnace-cooled to ambient temperature.

X-ray diffraction (XRD: X' Pert Pro PANalytical, CuK_{α} radiation) was carried out to determine the phase

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structure of the sintered samples and the lattice parameter was precisely calculated using an X'Pert HighScore software. The microstructure features of the polished and thermally etched surfaces of the sintered samples were examined by a field emission scanning electron microscopy (FE-SEM, JSM-5610LV, JEOL). The ceramic samples were carefully polished to about 0.6 mm thick for dielectric measurements. Silver pastes were painted on both sides of the polished ceramic samples, and then fired to electrodes at 650 °C for 30 min. Room temperature relative dielectric constant $\varepsilon_{\rm r}$ and dielectric loss tan δ were measured by a precision impedance analyzer (HP4294A, Agilent) at 1 kHz. Breakdown strength measurements were performed using a breakdown strength testing instrument (JJC9906-A) in silicone oil medium to avoid arcing. An AC voltage ramp of about 1 kV/s was applied to the sample until the dielectric breakdown occurred. For each composition, an average electrical breakdown strength $E_{\rm b}$ was obtained from at least 6 specimens testing. The relationship between $\varepsilon_{\rm r}$ and bias electric field was conducted using a bias electric field testing system (FMRL) at the measuring frequency of 1 kHz.

Results and Discussion

Fig. 1 shows the XRD patterns of ReST ceramics with different doping rare earth ions, comparing with the one of pure ST from our previous work [15]. All ReST ceramics have a single cubic perovskite structure similar to pure ST without any traced secondary phases. The lattice parameters of the ReST ceramics are calculated and listed in Table 1. It can be seen that the lattice parameter of the ReST ceramics gradually decreases in the order of LaST, PrST, and SmST, but all lower than that of pure ST, in accordance with the (200) diffraction peak shifting to higher angle as shown in Fig. 1(b). This should be owing to the shrinkage of unit cell caused by the ionic radii of the substituent Re^{3+} smaller than that of Sr^{2+} ($r_i = 1.44$ Å, CN = 12), and the ionic radius gradually decreases in the order of La³⁺ $(r_i = 1.36 \text{ Å}, \text{ CN} = 12), \text{ Pr}^{3+} (r_i = 1.307 \text{ Å}, \text{ CN} = 12), \text{ and}$ Sm^{3+} ($r_1 = 1.24$ Å, CN = 12) [16]. Here we should note that the ionic radius of Pr^{3+} in 12 coordinate is based on the relationship between coordination number and effective ionic radii after Shannon's table [16].

The $\varepsilon_{\rm r}$, tan δ , and $E_{\rm b}$ of the *Re*ST ceramics are also listed in Table 1. Strongly improved dielectric constants



Fig. 1. XRD patterns of the ST and ReST ceramics.



Fig. 2. Polished and thermally etched surface SEM images of the ST and *Re*ST ceramics: (a) ST, (b) LaST, (c) PrST, and (d) SmST.

($\varepsilon_r > 2000$) are obtained for the *Re*ST ceramics as compared to the reported $\varepsilon_r 300$ of pure ST [15]. The mechanism of such enhancement of ε_r should be closely related to the defect structures after trivalent ions doping similar to Bi-doped ST reported by Chen *et al.* and La-doped BaTiO₃ by Morrison *et al.* [17, 18], as discussed in our previous work [19, 20]. In particular, as also shown in Table 1, the *Re*ST ceramics possess relatively low dielectric loss (tan $\delta \le 3\%$) and medium high breakdown strength ($E_b > 15$ kV/mm), meeting the requirement of high-voltage capacitors fabrication for the purpose of energy storage.

Fig. 2 shows the polished and thermally etched surface SEM images of the ST and *ReST* ceramics. It

Table 1. Lattice parameters and dielectric properties of the ReST ceramics.

Ceramic samples	Lattice parameters a = b =c (Å)	Unit cell volume (Å ³)	(@ 1 kHz)	tanδ (@ 1 kHz)	E _b (kV/mm)
LaST	3.8990	59.27	3050	0.028	16.3
PrST	3.8983	59.24	2190	0.030	15.9
SmST	3.8976	59.21	2090	0.022	15.3



Fig. 3. The ε_r of the *ReST* ceramics as a function of bias electric field. Filled pattern: increasing bias; Open pattern: decreasing bias.



Fig. 4. The energy storage density of the *Re*ST ceramics under different bias electric fields.

can be seen from Fig. 2(a) that the grain size of pure ST ceramics is normally higher than 10 μ m, in accordance with reported by Tkach *et al.* [21]. However, for *Re*ST ceramics, the grain size is basically suppressed to low than 10 μ m, indicating that rare earth doping can inhibit grain growth. Actually, rare earth often plays a grain growth inhibitor role in the fabrication of many functional ceramics [22, 23].

Fig. 3 shows the ε_r of the *Re*ST ceramics as a function of bias electric field. With the increase of bias electric field, as seen from Fig. 3, the ε_r first decreases and then reaches a stable value. Meanwhile, it also can be seen from Fig. 3 that the ε_r is almost recoverable as the bias electric field decreases, i.e., no apparent hysteresis effect can be detected. In particular, for LaST ceramics, it is calculated that the ε_r changes only within 2% under the applied bias electric field testing ranges in this work, showing superior ε_r versus bias electric field stability and very beneficial to high voltage energy storage capacitor applications.

Using the applied bias electric field E and the corresponding experimental ε_r data in Fig. 3, the energy

storage density γ of the *Re*ST ceramics is calculated and given in Fig. 4 followed by the equation of $\gamma = 0.5 \varepsilon_0 \varepsilon_r E^2$, where ε_0 (= 8.85 × 10⁻¹² F/m) is the vacuum dielectric permittivity. As noted in Fig. 4, the calculated experimental energy storage density data can be well fitted to quadratic parabola function by least squares method, demonstrating the linear characteristics of the *Re*ST ceramics suitable for high power electronic applications.

Conclusions

In this work, the $Re_{0.02}$ Sr_{0.98}TiO₃ (*ReST*, Re = La, Pr, Sm) ceramics were prepared and evaluated for the suitability of energy storage capacitor applications. The relative dielectric constant of the *ReST* ceramics at room temperature was enhanced to higher than 2000, and showed good stability with the applied bias electric field. The dielectric loss of the *ReST* ceramics was lower than 0.03, while the breakdown strength higher than 15 kV/mm. In addition to their linear characteristics, the *ReST* ceramics should be very promising for energy storage capacitors in high power electronics.

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