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**Bifunctional europium doped SrTiO₃ ceramics with energy storage and
photoluminescence**

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Abstract: Rare-earth ion Eu^{3+} was doped into SrTiO_3 ceramic to improve its dielectric energy storage properties and act as luminescence centres. Typically, SrTiO_3 ceramics doped with 0.2% Eu^{3+} exhibit high breakdown strength up to 354 kV/cm and a relatively high recoverable energy density of 2.13 J/cm³. Compared to those of the undoped sample, the doped ceramic breakdown strength and recoverable energy density are enhanced by about 22% and 58%, respectively. The doping effect can be explained by the inhibition of the long-range movement of carriers. Moreover, the europium doped SrTiO_3 ceramic capacitor exhibits an excellent power density of 37 MW/cm³ in an ultrafast discharge time of 25 nanoseconds at 200 kV/cm. Meanwhile, the Eu^{3+} doped sample exhibits obvious red photoluminescence. The bifunctional ceramics offer an excellent prospect for energy storage and optical applications.

Keywords: energy storage, photoluminescence, SrTiO_3 ceramics, europium doping, bifunctional.

1. Introduction

Multifunctional materials are becoming a demand with the rapid development of electronic, optoelectronic, and energy devices [1-3]. SrTiO₃, as an incipient ferroelectric, has always been an essential electronic ceramic material due to its versatile properties, e.g., magnetic, luminescent, and dielectric characteristics via ion doping [4-6]. Recently, it has received increasing attention in the field of energy storage because it possesses a relatively high dielectric constant (ϵ_r), low dielectric loss, and moderate dielectric breakdown strength (E_b) [7-9]. Increasing the energy density (W) of dielectric capacitors is a major challenge as it is significantly inferior to other energy storage devices such as supercapacitors and batteries. Theoretically there are two methods to increase the W of SrTiO₃ ceramic capacitors: by increasing its ϵ_r or E_b , according to $W = \frac{1}{2} \epsilon_0 \epsilon_r E_b^2$, where ϵ_0 is the dielectric constant of vacuum. Although colossal permittivity up to thousands was obtained in some doped SrTiO₃ systems, their breakdown strengths are unclear [10-13]. Therefore, increasing E_b is a more effective strategy. Zhu et al. It is found that adding an appropriate amount of Bi³⁺ can enhance the polarity, reduce the sintering temperature and reduce the grain size, thereby obtaining a higher E_b [14]. Pu et al. introduced Zr⁴⁺ into Ca_{0.5}Sr_{0.5}TiO₃ ceramics to suppress grain growth, and the barrier effect at grain boundaries is enhanced by annealing in oxygen. Finally, a high E_b of 440 kV/cm was obtained [15]. Pan prepared SrTi_{0.985}(Zn_{1/3}Nb_{2/3})_{0.015}O_{3-xwt%ZnNb₂O₆} ceramics through synergy manipulation and obtained a high E_b of 422 kV/cm and an energy storage density of 2.35 J/cm³ [16]. In particular, Dy-doped SrTiO₃ obtains a high recoverable energy

density of 4.00 J/cm^3 and an extremely high breakdown strength of 510 kV/cm through oxygen treatment and increasing the resistance of crystal grains and grain boundaries [17]. Such doping effect could also be valid in other rare-earth elements doped SrTiO_3 , which needs further investigation.

SrTiO_3 has been regarded as a potential host of phosphor due to its good chemical stability. Therefore, rare-earth elements have been doped into SrTiO_3 to investigate the luminescent properties, including Pr, Eu, Yb and Er [4, 18-20]. In this regard, the doping of rare-earth ions could improve energy storage properties and meanwhile endow luminescent properties to SrTiO_3 . In addition, it has been reported that proper doping of Eu^{3+} can suppress grain growth due to its relatively low diffusion coefficient, which may help improve the dielectric strength of the matrix [4, 21]. Nevertheless, so far Eu^{3+} doping effect of dielectric storage performance of SrTiO_3 has not been reported. Therefore, we chose Eu^{3+} to study its influence on the energy storage and luminescence properties of SrTiO_3 in this work.

2. Experimental procedure

According to the chemical formula $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ($x = 0\%, 0.1\%, 0.2\%, 0.3\%, 0.4\%$), weigh the powders of SrCO_3 (99.95%), TiO_2 (99.99%) and Eu_2O_3 (99.99%) and then put them in ethanol Middle ball milling for 8 hours. The dried slurry is pre-sintered at 1200°C for 4 hours. The coarse powders obtained in the pre-sintering process were ground again and then pressed into a circle 10 mm in diameter and 0.5 mm thick by adding 5 wt% PVA binder. These disc samples were kept at 650°C for 3

hours to remove the PVA binder and calcined in an air atmosphere at 1400 °C for 3 hours to obtain sintered samples. Finally, the pellets were polished to about 0.2 mm in thickness, then an Ag electrode with a diameter of 2 mm was coated by screen printing method for electrical measurement.

Determine the phase composition and crystal structure by X-ray diffraction (XRD, X Pert pro) at room temperature. The microstructure of each sample surface was characterised by a scanning electron microscope (SEM, Ultra55). In addition, a precision impedance analyser (Agilent 4294A) was used to measure dielectric properties and impedance spectra. Use the LCR meter (TH2816A) to measure the temperature-dependent dielectric characteristics at a frequency of 1 kHz. Finally, for energy storage property evaluation, the polarisation-electric field (P - E) curves were measured by a ferroelectric analyser (TF Analyzer 3000), and the breakdown strength was measured by RK2671AM. Use the charge and discharge device (CFD-003) to measure the under-damped and over-damped waveforms to calculate the energy release characteristics of the sample. Use Jasco F-4500 spectrometer to test photoluminescence (PL) and photoluminescence excitation (PLE) spectra at room temperature.

3. Results and discussion

SrTiO₃ (PDF#35-0734) with perovskite structure is confirmed as the only phase in all the Sr_{1-3x/2}Eu_xTiO₃ ceramics, and no impurity phase is detected from the XRD results (not shown here). Fig. 1(a) displays the SEM images of the Sr_{1-3x/2}Eu_xTiO₃ ceramics with various doping contents. Fewer pores were observed on the surface micrograph of Sr_{1-3x/2}Eu_xTiO₃ ceramics, indicating the dense microstructure. From the

distributions of grain sizes in the insets of Fig. 1(a), the average grain sizes of $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramics are respectively about 0.85 μm , 1.05 μm , 0.82 μm , 1.08 μm and 0.83 μm for $x = 0, 0.1\%, 0.2\%, 0.3\%$, and 0.4% . All samples have a small grain size that beneficial to increase the grain boundary layer width, reduce the mean electric field for the grain boundary layer, and ultimately improve dielectric strength [16]. Furthermore, it is confirmed that all the $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramic elements were uniformly distributed by the element mapping analysis of Fig. 1 (b). This shows the high chemical uniformity of this system. Small grain size and high chemical uniformity favour high dielectric strength [22, 23].

Fig. 2 shows the frequency dependence and temperature dependence of the dielectric properties of $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramics. Both the permittivity and dielectric loss decrease with increasing frequency, which could be related to the existence of the defect charges. At low frequency, they would contribute to the dielectric polarisation but cannot respond at high frequency. The dielectric loss of the ceramics except the 0.1% doped samples is very low, particularly below 0.01 at a high frequency above 10 kHz. This is beneficial to practical applications for dielectric energy storage. The dielectric permittivity decreases with increasing temperature from -100 to $200\text{ }^\circ\text{C}$, as shown in Fig. 2(b). Interestingly, the dielectric loss is kept stable at the range of $0\text{ }^\circ\text{C} \sim 100\text{ }^\circ\text{C}$. Relaxation peaks are observed at about $-14\text{ }^\circ\text{C}$ in the inset of Fig. 2(b) ascribed to the first ionisation of oxygen vacancies ($\text{V}_\text{O} \rightleftharpoons \text{V}_\text{O}^\bullet + \text{e}'$) [24]. The loss increases noticeably as the measuring temperature exceeds $150\text{ }^\circ\text{C}$, which can be explained by ionic conduction at high temperatures.

With the purpose of assessing the energy storage characteristics of $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramic samples, the P - E loops of all samples under critical electric field and 10 Hz frequency measurement are described in Fig. 3 (a). All samples show good dielectric breakdown characteristics since their average sizes are small, as shown in Fig. 1(a). The ceramic of $x = 0.2\%$ possesses the highest critical breakdown field strength of 354 kV/cm. Compared with pure SrTiO_3 (290 kV/cm), the breakdown field is enhanced by 22%. The W can be computed to be respectively 1.65 J/cm³, 1.81 J/cm³, 3.28 J/cm³, 2.55 J/cm³, and 2.61 J/cm³ for the ceramics with $x = 0$, 0.1%, 0.2%, 0.3%, and 0.4%, according to $W = \int_0^{P_{\max}} E dp$. The recoverable energy density (W_{rec}) should be corrected by $W_{\text{rec}} = \int_{P_r}^{P_{\max}} E dp$, and the energy efficiency (η) is equal to the proportion of W_{rec} and W [25, 26]. Due to its highest breakdown strength, the highest W and W_{rec} are also achieved in the ceramic of $x = 0.2$. Compared with that of the undoped sample, the W_{rec} increases by 58% to 2.13 J/cm³ after 0.2% Eu doping. The η of the ceramics for $x = 0$, 0.1%, 0.2%, 0.3%, 0.4% is respectively 81.82%, 73.48%, 64.94%, 72.16% and 71.26%. Fig. 3 (b) shows the Weibull distribution of the breakdown electric field for all samples. Compared with that of pure SrTiO_3 , the breakdown strength of Eu modified SrTiO_3 ceramics is improved significantly and shows a more stability distribution, which can be judged from the sloped and intercept of Weibull plots. Moreover, the P - E curves show relatively stability in the frequency range of 1 Hz ~ 600 Hz and the measuring temperature range of 30°C to 150 °C, as shown in Fig. 3(c) and Fig. 3(d). For example, the W_{rec} of $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ with a doping concentration of 0.2% lies between 0.191 J/cm³ to 0.197

J/cm³ under a 115 kV/cm electric field and different frequencies.

Impedance spectra are generally employed to explain the origin of circuit components. Fig. 4 (a) is a complex impedance plot of the Sr_{1-3x/2}Eu_xTiO₃ ceramics measured at 380 °C. Two semicircles are observed in complex impedance plot of $x = 0$, 0.1%, 0.2% ceramics while these in $x = 0.3\%$, 0.4% ceramics are hardly to be distinguished, as shown in the inset of Fig. 4(a). It was apparent to all that low-frequency arcs represent the dielectric response of grain boundaries, and high-frequency arcs represent the dielectric response of grain. Since the resistance can be estimated by the position of the Z''_{max} peak ($R = 2Z''_{max}$), in Fig. 4(b), it can be concluded that grain boundary resistance (R_{gb}) is much greater than grain resistance (R_g) in both doped and undoped samples. The greater the difference between the grain resistance and the grain boundary resistance, the easier it is to form charge accumulation and the lower the E_b . Therefore, $x = 0.2\%$ shows good insulation properties. Fig. 4(c) shows the frequency dependence of conductivity for Sr_{1-3x/2}Eu_xTiO₃ ceramics. Low-frequency conductivity is related to the free diffusion of carriers [15]. It can be seen from the figure that the conductivity of all Eu³⁺ doped samples at low frequencies is lower than that of pure SrTiO₃, indicating that an appropriate amount of Eu³⁺ plays an important role in preventing long-range movement of carriers and reducing carrier jumping. Fig. 4(d) shows the activation energies of grain and grain boundaries at $x = 0.2\%$. According to the equation of the Arrhenius equation [17]:

$$\sigma = \sigma_0 \exp(-Ea/k_B T) \quad (3)$$

Where σ is the conductivity value, σ_0 the constant, k_B the Boltzmann constant and E_a the activation energy of the charge carrier transport. As shown in Fig. 4(d), the E_g of $x = 0$ and 0.2% are 0.856 eV and 0.998 eV respectively, and the E_{gb} are 0.141 eV and 0.326 eV respectively. It can be seen that the ceramic with $x = 0.2\%$ have higher grain activation energy and grain boundary activation energy. It reveals that Eu doping effectively suppresses the long-range movement of carriers, and as a result, the breakdown strength increases.

Energy storage materials need to have high power density, energy density, and fast charge and discharge rates. Therefore, the actual charging and discharging performance can be evaluated by over-damping and under-damping RC circuits. Fig. 5(a) shows under-damped discharge waveforms in various electric fields (40 kV / cm ~ 200 kV / cm) at room temperature. $x = 0.2\%$ ceramic in a short 25 ns reaches the maximum current value of 73 A, demonstrating the pulse characteristics of the dielectric ceramic. Fig. 5(b) depicts the increase in peak current (I_{max}), power density (P_D), and current density (C_D) as the electric field increases [15].

$$P_D = E \cdot I_{max} / 2S \quad (4)$$

$$C_D = I_{max} / S \quad (5)$$

where S is the electrode area, I_{max} , C_D and P_D reach 72.7 A, 370.3 A/cm² and 37.0 MW/cm³ at 200 kV/cm, respectively. The data shows that $x = 0.2\%$ ceramic is of great significance to the research of pulsed systems. Fig. 5(c) shows the under-damped discharge curves measured at different temperatures for $x = 0.2\%$ ceramic. With the temperature from 20 °C to 120 °C, I_{max} , C_D and P_D decrease from 44.0 A, 224.2 A/cm²,

13.5 MW/cm³ to 36.5 A, 186.0 A/cm², 11.2 MW/cm³., as shown in Fig. 5(d).

In order to test the actual pulsed discharge energy density, an over-damped circuit is established with a load resistance of 205.5Ω. Fig. 6 (a) is the over-damped discharge curves of $x = 0.2\%$ ceramic under different electric fields. In practical applications, high energy density capacitors require fast discharge times [27]. The ceramic with $x=0.2\%$ reaches a peak current of 19 A in a short time of about 15 ns. The discharge energy density can be calculated as [28]:

$$W = R \int i^2(t)dt/V \quad (6)$$

Among them, R , I , t and V are load resistance, current, time and sample volume, respectively. Fig. 6(b) and the inset of Fig. 6(a) show that the maximum W_d value reached at 200 kV/cm is 0.56 J/cm³. $\tau_{0.9}$ is defined as the time to release 90% of the stored energy. All $\tau_{0.9}$ are about 56 ns in various electric fields, which means the ceramic has a fast discharge capacity. Fig. 6(c)-(d) illustrates the relationship between the overdamped discharge characteristics of ceramics $x = 0.2\%$ and temperature. As the temperature increases, I_{max} decreases from 11.7 A to 11.1 A, and W_d decreases from 0.2 J/cm³ to 0.14 J/cm³.

The existence of abundant energy levels in rare-earth ions arising from their outer electronic configurations can be utilized in the luminescence field. Fig. 7 shows the luminescent properties for the Sr_{1-3x/2}Eu_xTiO₃ ceramics. As shown in the excitation spectral in Fig. 7(a), the peak between 350-450 may be related to the f-f transition of Eu³⁺ [4, 29]. In the emission spectrum of Fig. 7(b), two emission peaks at the positions of 590 nm and 615 nm are attributed to Eu³⁺ ion transitions of ⁵D₀→⁷F₁ and

$^5D_0 \rightarrow ^7F_2$, respectively [4]. As the Eu^{3+} doping concentration increases, the PL intensity increases and then decreases after reaching the maximum value at $x = 0.3\%$. Therefore, Eu^{3+} doped SrTiO_3 ceramics exhibit excellent dielectric energy properties and possess obvious red photoluminescence. Such multifunctional ceramics would enhance the flexibility in integrated electronic, optoelectronic, and energy devices.

4. Conclusion

In this work, europium ions were doped into SrTiO_3 ceramics to study the effects of doping on crystal structure, morphology, dielectric properties, dielectric breakdown, energy storage and luminescence properties. It is found that 0.2% doped SrTiO_3 ceramics show the maximum breakdown strength of 354 kV/cm and the maximum recoverable energy density of 2.13 J/cm³. At 200 kV/cm, the peak current, current density, power density, and discharge energy density reached 72.7 A, 370.3 A/cm², 37.0 MW/cm³ and 0.56 J/cm³, respectively. The discharge energy reached 90% of the final value of the discharge curve is approximately 56 ns. Through impedance spectroscopy analysis, the incorporation of europium ions can inhibit the long-range movement of carriers. Moreover, a strong luminous intensity was observed in the 590 nm and 615 nm bands. Therefore, dual-functional ceramic materials with dielectric energy storage and light-emitting properties are expected to be used in multifunctional devices.

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Figure captions

Fig.1: (a) SEM images of $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ samples with different doping concentrations. (b) Elemental mappings of the sample with 0.2% doping concentration.

Fig.2: Frequency (a) and temperature (b) dependence of the permittivity and dielectric loss for $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramics.

Fig.3: (a) The P - E loops of $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramics. (b) Weibull distribution of the breakdown electric field. The P - E loops of $x = 0.2\%$ ceramic samples under 10Hz (c) at different frequencies and (d) at different temperatures.

Fig.4: (a) Image of the complex impedance and (b) the resistance value of the $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ($x = 0, 0.2\%$) ceramics at 380°C . (C) Frequency dependence of the electrical conductivity of the $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramics. (d) Activation energy of grains and activation energy of grain boundaries when $x = 0, 0.2\%$.

Fig.5: (a) Underdamped discharge waveforms and (b) I_{max} , C_D , and P_D , at different electric fields and room temperature, for $x = 0.2\%$ ceramic. (c) Underdamped discharge waveforms and (d) I_{max} , C_D , and P_D , at different temperatures and 120 kV/cm, for $x = 0.2\%$ ceramic.

Fig.6: (a) Overdamped discharge current curves and (b) time dependence of W_d , for $x = 0.2\%$ ceramics at different electric fields and room temperature. (c) Overdamped discharge current curves and (d) time dependence of W_d , at different temperatures and 120 kV/cm, for $x = 0.2\%$ ceramic.

Fig.7: PLE (a) and PL (b) spectra of Eu-doped SrTiO_3 sample. Monitor at 590 nm to measure the excitation spectrum, and monitor at 395 nm to measure the emission spectrum.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7