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Research Article

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Posted Date: July 15th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-703463/v1

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Version of Record: A version of this preprint was published at Journal of Alloys and Compounds on January 1st, 2022. See the published version at https://doi.org/10.1016/j.jallcom.2021.163556.
Bifunctional europium doped SrTiO$_3$ 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/cm$^3$. 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/cm$^3$ 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]. SrTiO$_3$, 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 ($\varepsilon_r$), 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 SrTiO$_3$ ceramic capacitors: by increasing its $\varepsilon_r$ or $E_b$, according to $W = \frac{1}{2} \varepsilon_0 \varepsilon_r E_b^2$, where $\varepsilon_0$ is the dielectric constant of vacuum. Although colossal permittivity up to thousands was obtained in some doped SrTiO$_3$ 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 Bi$^{3+}$ can enhance the polarity, reduce the sintering temperature and reduce the grain size, thereby obtaining a higher $E_b$ [14]. Pu et al. introduced Zr$^{4+}$ into Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ 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$_{0.985}$($\text{Zn}_{1/3}\text{Nb}_{2/3}$)$_{0.015}$O$_3$-xwt%ZnNb$_2$O$_6$ ceramics through synergy manipulation and obtained a high $E_b$ of 422 kV/cm and an energy storage density of 2.35 J/cm$^3$ [16]. In particular, Dy-doped SrTiO$_3$ obtains a high recoverable energy
density of 4.00 J/cm³ 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 SrTiO₃, which needs further investigation.

SrTiO₃ has been regarded as a potential host of phosphor due to its good chemical stability. Therefore, rare-earth elements have been doped into SrTiO₃ 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 SrTiO₃. In addition, it has been reported that proper doping of Eu³⁺ 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 Eu³⁺ doping effect of dielectric storage performance of SrTiO₃ has not been reported. Therefore, we chose Eu³⁺ to study its influence on the energy storage and luminescence properties of SrTiO₃ in this work.

2. Experimental procedure

According to the chemical formula Sr₁-3x/2EuₓTiO₃ (x = 0%, 0.1%, 0.2%, 0.3%, 0.4%), weigh the powders of SrCO₃ (99.95%), TiO₂ (99.99%) and Eu₂O₃ (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

SrTiO$_3$ (PDF#35-0734) with perovskite structure is confirmed as the only phase in all the $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramics, and no impurity phase is detected from the XRD results (not shown here). Fig. 1(a) displays the SEM images of the $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramics with various doping contents. Fewer pores were observed on the surface micrograph of $\text{Sr}_{1-3x/2}\text{Eu}_x\text{TiO}_3$ ceramics, indicating the dense microstructure. From the
distributions of grain sizes in the insets of Fig. 1(a), the average grain sizes of Sr$_{1-3x/2}$Eu$_x$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 Sr$_{1-3x/2}$Eu$_x$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 Sr$_{1-3x/2}$Eu$_x$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 $200$ °C, as shown in Fig. 2(b). Interestingly, the dielectric loss is kept stable at the range of 0 °C ~ $100$ °C. Relaxation peaks are observed at about $-14$ °C in the inset of Fig. 2(b) ascribed to the first ionisation of oxygen vacancies ($V_0 \Leftrightarrow V_0 + e'$) [24]. The loss increases noticeably as the measuring temperature exceeds 150 °C, which can be explained by ionic conduction at high temperatures.
With the purpose of assessing the energy storage characteristics of 
\( \text{Sr}_{1-3x} \text{Eu}_x \text{TiO}_3 \) 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 \( \text{SrTiO}_3 \) (290 kV/cm), the 
breakdown field is enhanced by 22%. The \( W \) can be computed to be respectively 1.65 
\( \text{J/cm}^3 \), 1.81 \( \text{J/cm}^3 \), 3.28 \( \text{J/cm}^3 \), 2.55 \( \text{J/cm}^3 \), and 2.61 \( \text{J/cm}^3 \) for the ceramics with \( x = 0, 
0.1\%, 0.2\%, 0.3\%, \) and \( 0.4\% \), according to \( W = \int_0^{P_{\text{max}}} Edp \). The recoverable energy 
density \( (W_{\text{rec}}) \) should be corrected by \( W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} Edp \), and the energy efficiency \( (\eta) \) 
is equal to the proportion of \( W_{\text{rec}} \) and \( W \) [25, 26]. Due to its highest breakdown 
strength, the highest \( W \) and \( W_{\text{rec}} \) are also achieved in the ceramic of \( x = 0.2 \). Compared 
with that of the undoped sample, the \( W_{\text{rec}} \) increases by 58% to 2.13 \( \text{J/cm}^3 \) after 0.2% 
Eu doping. The \( \eta \) 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 
\( \text{pure SrTiO}_3 \), the breakdown strength of Eu modified \( \text{SrTiO}_3 \) 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 \( W_{\text{rec}} \) of 
\( \text{Sr}_{1-3x} \text{Eu}_x \text{TiO}_3 \) with a doping concentration of 0.2% lies between 0.191 \( \text{J/cm}^3 \) 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 Sr₃₋ₓₓ/2EuₓTiO₃ 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 $Z''_{\text{max}}$ peak ($R = 2Z''_{\text{max}}$), 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 Sr₃₋ₓₓ/2EuₓTiO₃ 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]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_BT}\right)$$

(3)
Where $\sigma$ is the conductivity value, $\sigma_0$ 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].

$$\begin{align*}
P_D &= E \cdot I_{max} / 2S \\
C_D &= I_{max} / S
\end{align*}$$

where $S$ is the electrode area, $I_{max}$, $C_D$ and $P_D$ reach 72.7 A, 370.3 A/cm$^2$ and 37.0 MW/cm$^3$ 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 discharging 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/cm$^2$,
13.5 MW/cm$^3$ to 36.5 A, 186.0 A/cm$^2$, 11.2 MW/cm$^3$, 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 205.5$\Omega$. 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]:

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

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/cm$^3$. $\tau_{0.9}$ 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/cm$^3$ to 0.14 J/cm$^3$.

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$_x$TiO$_3$ 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 Eu$^{3+}$ [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 Eu$^{3+}$ ion transitions of $^5D_0\rightarrow^7F_1$ and
$^{5}D_{0} \rightarrow ^{7}F_{2}$, 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/cm$^{3}$. At 200 kV/cm, the peak current, current density, power density, and discharge energy density reached 72.7 A, 370.3 A/cm$^{2}$, 37.0 MW/cm$^{3}$ and 0.56 J/cm$^{3}$, 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.
Acknowledgment

This work was supported by the National Natural Science Foundation of China (51772252), the Sichuan Science and Technology Program (2020JDRC0062), and the Project of State Key Laboratory of Environment-Friendly Energy Materials, Southwest University of Science and Technology (19FKSY09, 20FKSY14).
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Figure captions

Fig.1: (a) SEM images of Sr$_{1-3x/2}$Eu$_x$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 Sr$_{1-3x/2}$Eu$_x$TiO$_3$ ceramics.

Fig.3: (a) The P-E loops of Sr$_{1-3x/2}$Eu$_x$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 Sr$_{1-3x/2}$Eu$_x$TiO$_3$ ($x = 0, 0.2\%$) ceramics at 380 ° C. (C) Frequency dependence of the electrical conductivity of the Sr$_{1-3x/2}$Eu$_x$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) $I_{\text{max}}$, $C_D$, and $P_D$, at different electric fields and room temperature, for $x = 0.2\%$ ceramic. (c) Underdamped discharge waveforms and (d) $I_{\text{max}}$, $C_D$, 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. 2
Fig. 5
Fig. 7