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Original article

Effect of oxygen treatment on structure and electrical properties of Mn-doped $Ca_{0.6}Sr_{0.4}TiO_3$ ceramics

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ABSTRACT

Different oxygen treatment methods, including O_2 and N_2 annealing, were conducted on $Ca_{0.6}Sr_{0.4}TiO_3$ (CST) ceramics with varying Mn content (0 mol%, 0.5 mol% and 2.0 mol%). Structure characterization, including XRD and SEM, indicated the minimal effect of annealing on the microstructure. Grain boundaries were found to be sensitive to oxygen treatments, and annealing in O_2 resulted in increased grain boundary resistance, while in N_2 led to the opposite result. The insulating properties of bulk ceramics were found to be dominated by grain boundaries. Both the concentration and mobility of oxygen vacancies were confirmed to affect the energy storage properties to some extent in this work.

1. Introduction

Due to the fast charge-discharge time and high power density, conventional dielectric capacitors play an important role in energy-storage field [1–3]. However, the energy density of capacitors is several orders of magnitude lower than that of batteries and electrochemical capacitors [4]. Thus, it is a challenge to explore new material systems which can meet the requirement of high energy density and high power density simultaneously. The up-to-date commercialized dielectric capacitors are mainly based on polymers, ceramics and polymer-ceramic composites [5], in which ceramics are favorable due to their higher operating ceiling compared to polymer, making them suitable for extreme environment application, such as hybrid electric vehicles, aerospace power systems, and deep oil/gas extraction [6–8].

In dielectric ceramics, oxygen vacancies can be easily formed by acceptor doping, reduced sintering atmosphere, high sintering temperature ($> 1350\,^{\circ}C$) or fast cooling conditions [9–13], which have significant effect on electrical properties of dielectrics. Thus, the concentration, distribution and diffusion kinetic of oxygen vacancies are widely studied [14], both from microscopic scale (i.e., transmission electron microscope, analytical electron microscopy, electron energy-loss spectroscopy, electron paramagnetic resonance, infrared spectra) and macroscopic scale (i.e., spectra of dielectric constant/loss as a function of temperature/frequency, thermally stimulated depolarization current, impedance spectra) characterization [15–22].

In our previous research, $Ca_{0.6}Sr_{0.4}TiO_3$ (CST) was selected as the research object, due to the high breakdown strength, high charge-discharge efficiency and low dielectric variation over a wide temperature and frequency range [23], being potential for energy storage application. Additionally, Mn doping was employed to improve the energy storage performance, especially at high temperature. Previous work verified that the improved energy storage performance was due to the existence of defect dipoles, which retards the motion of oxygen vacancies, i.e., the mobility of oxygen vacancies was regulated [24]. However, in addition to the mobility, the concentration of oxygen vacancies contributes to ionic conductivity as a positive factor, which should be given full consideration. Thus, in this work, the concentration of oxygen vacancies was regulated through controlled oxygen treatment, including O_2 and N_2 annealing, to further improve the electrical properties of CST ceramics. Three compositions, i.e., 0 mol%, 0.5 mol% (at solid solution limit, as was confirmed in previous research [24]) and 2.0 mol% (above solid solution limit) Mn-doped CST, were selected. Structure, electrical properties, and energy storage performance were investigated to establish the relationship between oxygen vacancies and

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energy storage performance.

2. Experimental procedure

2.1. Samples preparation

Dense $Ca_{0.6}Sr_{0.4}TiO_3$ (CST) ceramics with varying Mn dopant (0 mol %, 0.5 mol% and 2.0 mol%) were prepared via solid state reaction method with high purity commercial powders of $CaCO_3$, $SrCO_3$, TiO_2, and MnO_2. The stoichiometric mixtures were ball milled with zirconium media for 24 h, dried and then calcined at 1200 °C for 2 h. The calcined powders were then remilled, granulated and pressed to form disk-shaped samples with 12 mm in diameter and 1.5 mm in thickness. The green pellets were sintered at 1400 °C for 2 h. For oxygen treatment, as-sintered samples were annealed in pure O_2 and N_2, respectively, at 1000 °C for 10 h.

2.2. Structure and properties characterization

The phase structure was examined by X-ray diffraction (XRD) (X'Pert PRO, PANalytical, Holland). Microstructure was observed on the surface of the sample by field-emission scanning electron microscope (HR-SEM) (Quanta FEG 450, FEI, USA).

Impedance spectroscopy measurements were taken by a frequency response analyzer (Solartron 1255B, Westborough, USA) over a frequency range of 0.1 Hz–1 MHz with an ac voltage of 1 V. The obtained data was fitted using Z-view software (Scribner Associates Inc., North Carolina, USA). To evaluate the energy storage performance, polarization versus electric field (P-E) hysteresis loops were measured by ferroelectric material test system (HVI0403-239, Radiant Technology, USA) in a silicone oil bath over temperature range of 25–150° C, using triangular voltage waveforms at a frequency of 10 Hz.

3. Results and discussions

3.1. Structure characterization: the role of oxygen treatment

Fig. 1 shows the XRD patterns of 0 mol%, 0.5 mol% and 2.0 mol% Mn-doped CST ceramics subjected to oxygen treatment. Typical perovskite structure was revealed, neither the appearance of secondary phase nor peak shifting was observed after post-annealing. Thus, the variations in bulk electrical properties, which will be discussed in next section, are not due to variations in phase structure.

SEM images of Mn-doped CST ceramics with oxygen treatment were given in Fig. 2. Oxygen treatment did not lead to any variation in the average grain size or the uniformity of grain size distribution. A uniform grain size distribution for 0 mol% and 0.5 mol% Mn was revealed, while abnormal grain size growth/non-uniform grain size distribution was observed at 2.0 mol% Mn doping.

Consequently, structure characterization, including XRD and SEM, indicated the minimum effect of annealing on phase structure and microstructure.

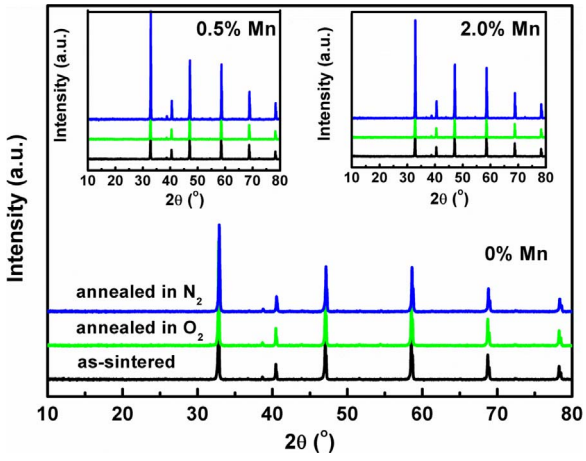

Fig. 1. XRD patterns of Mn-doped CST with oxygen treatment.

3.2. Impedance spectra analysis: sensitive grain boundary

To investigate the effect of oxygen treatment on grain and grain boundary region of Mn-doped CST, both impedance and modulus spectra were investigated, since useful information can be revealed by this mothod for many heterogeneous dielectric ceramics, as shown in Figs. 3 and 4. The maximum value of Z" and M" can be calculated when $\omega = (RC)^{-1}$ with [25]

$$Z''_{max} = \frac{R}{2} \tag{1}$$

$$M''_{max} = \frac{C_0}{2C} = \frac{1}{2\varepsilon_r} \tag{2}$$

Where R, C are the resistance and capacitance of the resistor and capacitor representing an electroactive region, thus, the imaginary part of impedance as a function of frequency gives the information of region with higher resistance, i.e., grain boundary in this case, while imaginary part of electric modulus gives the information of region with lower capacitance, i.e., grain in this case.

In case of an equivalent circuit with resistor and capacitor connected in parallel, the relaxation frequency f_r can be correlated with the conductivity σ using the following equations [21]

$$R = \frac{d}{\sigma A} \tag{3}$$

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \tag{4}$$

$$f_r = \frac{1}{2\pi RC} = \frac{\sigma}{2\pi\varepsilon_0\varepsilon_r} \tag{5}$$

The most important implication of Eq. (5) is that the relaxation frequency f_r is proportional to the conductivity σ within the considered RC element, since the variation of ε_r can be neglected before and after oxygen treatment. Thus the shift of peak to lower frequency can be correlated to a decrease in conductivity.

In Fig. 3, *M"-f* remained unchanged while *-Z"-f* changed obviously with annealing treatment, meaning the effect of oxygen treatment was mainly on grain boundaries. The peak of *-Z"* moves to lower frequency with O_2 annealing, accompanied with higher magnitude, demonstrating the increased grain boundary resistance. On the contrary, N_2 annealing resulted in decreased grain boundary resistance. The oxyge treatment results are in agreement with those reported in literature [15,20,26], attributing to faster oxygen diffusion rate in grain boundaries.

To summarize, upon oxygen treatment, grain resistance was unaffected, while grain boundary resistance increased after O_2 annealing and decreased after N_2 annealing, which was due to the concentration variation of oxygen vacancies.

3.3. Electrical properties: grain boundary dominated bulk resistivity and activation energy

To investigate the effect of oxygen treatment on the bulk insulating properties of Mn-doped CST ceramics, the ac conductivities were measured from 0.1 Hz–1 MHz over the temperature range of 25–400° C. The ac conductivities can be expressed as [7]:

$$\sigma = \varepsilon_r \varepsilon_0 \tan\delta\ \omega \tag{6}$$

Where ε_0 is the permittivity of vacumm ($\varepsilon_0 = 8.85 \times 10^{-14}$ F/m), ε_r the dielectric constant, and ω the angular frequency, $\omega = 2\pi f$, f is the

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