Effect of SiO$_2$ additives on the microstructure and energy storage density of SrTiO$_3$ ceramics

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The compositions of (1-x) SrTiO$_3$-x SiO$_2$ were prepared by a solid-state reaction. The crystalline structure, microstructure and energy storage performance were studied for the purpose of a potential application in high energy density capacitors. Fine grains with an average size of about 400 nm were obtained by adding SiO$_2$ to SrTiO$_3$ ceramics, which leads to a great enhancement in the breakdown performance of the samples. For SiO$_2$-added samples, the notable increase in breakdown strength makes an obvious increase in energy storage density. With 15 vol.% addition, the sample exhibited an average breakdown strength of 36.1 kV/mm, and an energy storage density of 1.155 J/cm^3.

Key words: Dielectric ceramics, Microstructure modification, Energy storage density

Introduction

Ferroelectric ceramics are being developed for a wide range of applications in electrical engineering, especially as dielectrics for high energy density capacitors [1-2]. In general, energy storage density of ferroelectric ceramics, is given by the following equation after Fletcher et al. [3]:

$$W = \int_0^{E_{max}} E dP \qquad (1)$$

where P and E are the polarization and the electric field, and E_{max} is the breakdown electric field. Thus, the energy storage density can be evaluated by integrating the area between the polarization axis and the discharge curve in the $P-E$ hysteresis loops. Although ferroelectric ceramics generally have a large polarization, the energy loss from the hysteresis and a relatively lower dielectric breakdown limits their energy density values [4]. Thus, reducing the energy loss from the hysteresis and improving the breakdown strength of ferroelectric ceramics have become very important issues for their high energy density applications.

In this study, SrTiO$_3$ was selected as the material for investigation because of its relatively high breakdown strength, and linear dielectricity which results in an extremely low energy loss from the hysteresis. As can be seen in Eq. (1), a high breakdown strength makes more contribution toward the energy storage density. Our work is focused on increasing the breakdown strength of SrTiO$_3$ ceramics for the purpose of

enhancing the energy storage density.

It is well known that the breakdown strength is mainly affected by density and grain size of dielectric ceramics [5]. Thus, microstructural modification of ceramics has a long tradition because it is a smart way to improve the breakdown strength. In many previous studies, several low-melting point glasses [6-7] and fine oxide additives [8-9] have been added into ceramics for this purpose. According to the literature, it has been shown that SiO$_2$ is an effective additive for microstructural modification of both particles [10] and ceramics [11]. But so far as we know, SiO$_2$-added ceramics for use in energy storage applications have been rarely reported. Therefore, SiO$_2$ was selected as our additive, the crystalline structure, microstructure and energy storage performance of ceramics were studied.

Experimental

The ceramics studied were prepared by conventional solid-state reactions. As starting materials, high purity SrTiO$_3$ and SiO$_2$ with densities of 5.12 g/cm^3 and 2.20 g/cm^3, respectively, were mixed according to the composition: (1-x) SrTiO$_3$-x SiO$_2$, with x=00 vol.%, 05 vol.%, 10 vol.%, 15 vol.% and 20 vol.%. After ball milling with ZrO$_2$ balls for 24 hours, the mixed powders were granulated with polyvinyl alcohol (PVA) as an organic binder, and then pressed into pellets of 12 mm diameter and about 0.5 mm thickness by uniaxial pressing at 200 MPa. Preheated at 650 °C for 2 hours to remove the PVA, the pellets were sintered at 1200-1300 °C for 2 hours in air.

The density measurements were performed using Archimedes method. The crystalline structure of sintered samples was analyzed by an X-ray diffractometer (XRD,

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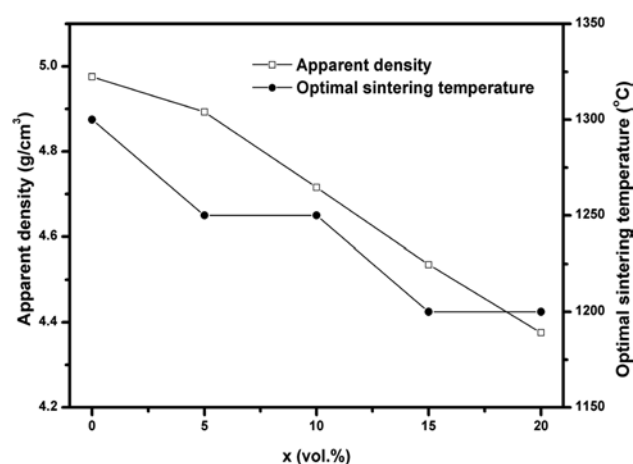Fax: +86 27 87651779
E-mail: lhxhp@whut.edu.cn

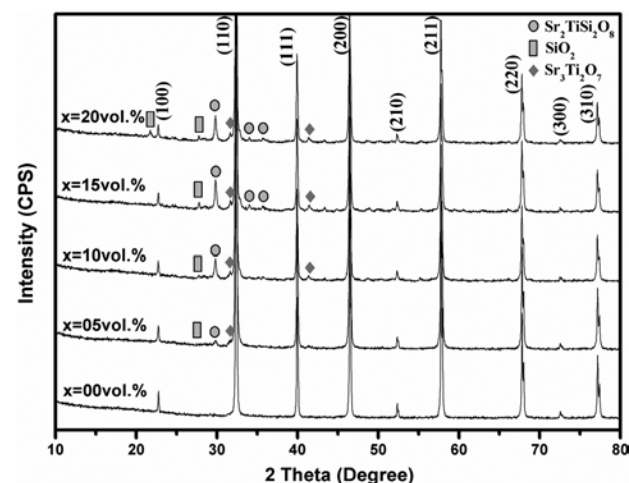**Fig. 1.** The optimal sintering temperature and apparent density of samples with different x values.

Fig. 2. XRD patterns of samples sintered at their respective optimal sintering temperatures for 2 hours.
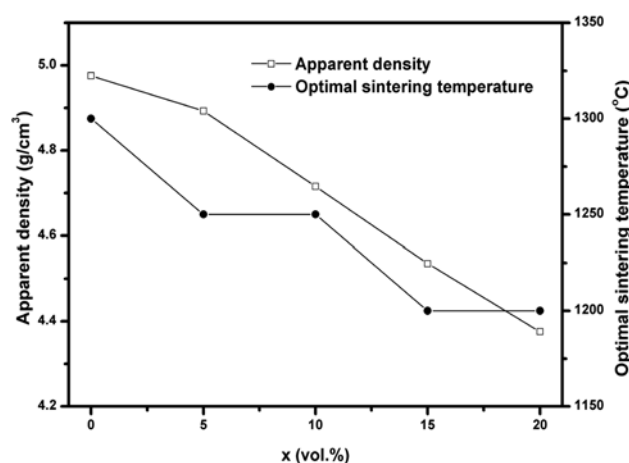

Fig. 3. Dielectric constant and dielectric loss of samples measured at room temperature and in the frequency range of 0.04-2 MHz.

PANalytical X'Pert PRO). The microstructure of ceramics was observed using a scanning electron microscope (SEM, JSM-5610LV).

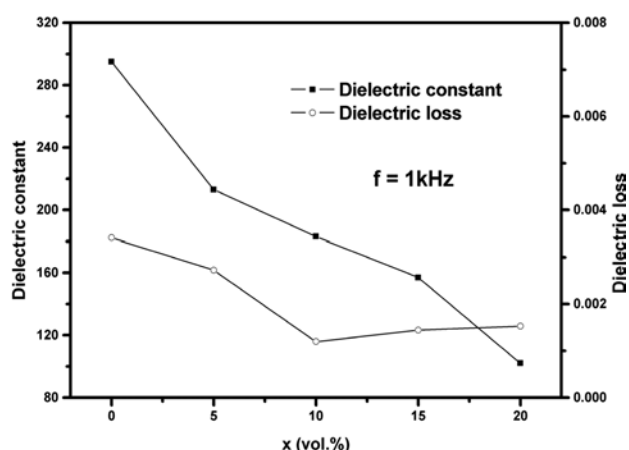For the electrical measurements, the sintered ceramics

Fig. 4. Dielectric properties of samples measured at 1 kHz and at room temperature.
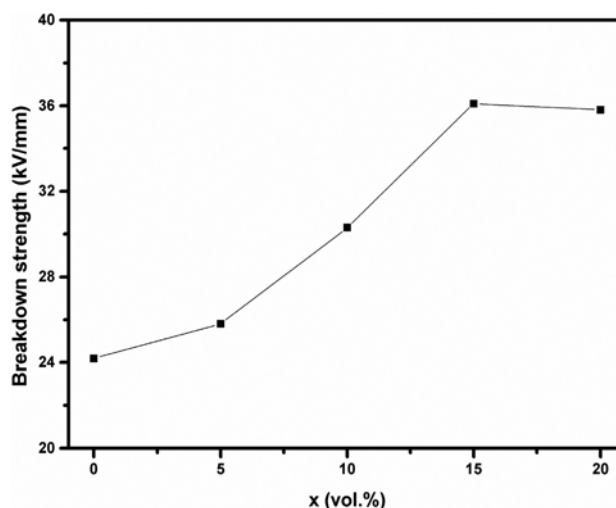

Fig. 5. Average breakdown strength of samples with different x values.

were polished to 0.2 mm in thickness and coated with silver electrodes on both faces. The dielectric constant and loss were measured by a precision impedance analyzer (Agilent 4980A) at room temperature. The breakdown strength and *P-E* hysteresis loop were determined by a DC bias source on a ferroelectric test system (Radiant RT66A), and the energy storage density was calculated from the *P-E* hysteresis loop obtained by Eq. (1). For each composition, at least 8 samples were measured to obtain an average breakdown strength.

Results and Discussion

Fig. 1 shows the optimal sintering temperature and apparent density of samples with different x values. As x increases from 0 to 20 vol.%, the apparent density of samples decreases gradually from 4.98 g/cm³ to 4.38 g/cm³, and the optimal sintering temperature of samples decreases from 1300 ℃ to 1200 ℃, implying that addition of SiO₂ can lower the densification temperature of ceramics. The XRD patterns of sintered samples are
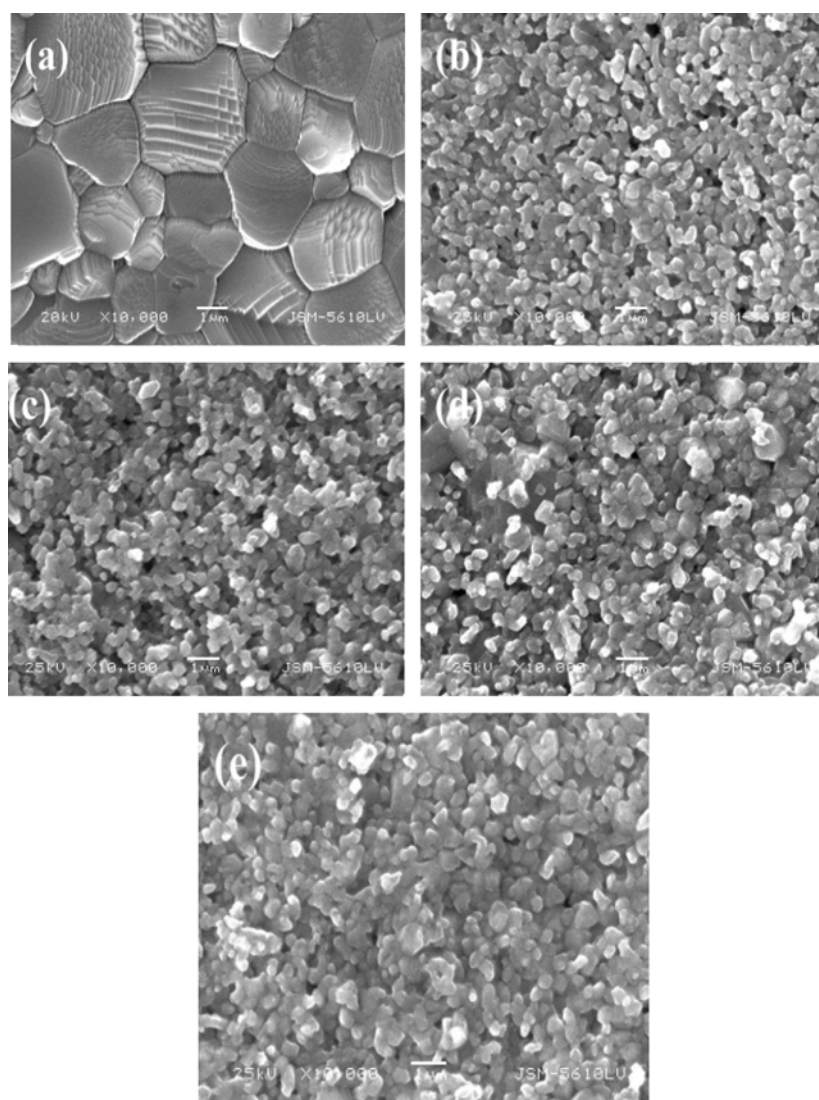
Fig. 6. SEM images of various vol.% SiO$_2$-added SrTiO$_3$ samples sintered at their optimal sintering temperatures for 2 hours: (a) 00 vol.%, (b) 05 vol.%, (c) 10 vol.%, (d) 15 vol.%, (e) 20 vol.%.

given in Fig. 2. As shown in this figure, all patterns show the main phase with a cubic perovskite structure the same as pure SrTiO$_3$ (according to JCPDS file 089-4934). For samples with SiO$_2$ additions, extra weak peaks related to the Sr$_2$TiSi$_2$O$_8$ phase (according to JCPDS file 035-0212), the Sr$_3$Ti$_2$O$_7$ phase (according to JCPDS file 078-2479) and quartz (according to JCPDS file 081-0069) were clearly detected. Thus, the decomposition of SrTiO$_3$, a reaction between SiO$_2$ addition and the main phase SrTiO$_3$ or its decomposition products should occur during the sintering process. For SiO$_2$-added samples, the appearance of secondary phases leads to the decrease of the apparent density observed in Fig. 1, because quartz, the Sr$_2$TiSi$_2$O$_8$ phase and the Sr$_3$Ti$_2$O$_7$ phase have lower theoretical densities compared with pure SrTiO$_3$. Based on the basic theory of liquid phase sintering, these secondary phases created in the reaction should be located at the grain boundaries and influence the dielectric properties and

breakdown strength of sintered ceramics.

The dielectric constant and dielectric loss of samples measured at room temperature and in the frequency range of 40-2000000 Hz are plotted in Fig. 3. The dielectric constant decreases gradually with an increase of the x value, and it shows good frequency stability in the measured frequency range. The dielectric loss of all samples is less than 1×10^{-2} in the frequency range, and decreases with increasing frequency. The dielectric constant and dielectric loss of all samples at 1 kHz AC are given in Fig. 4. The dielectric constant decreases from 295-102 with an increase of the x value. The slight decrease of the dielectric constant is mainly due to the low dielectric constant of the SiO$_2$ addition (~4). A low-loss tangent of less than 3×10^{-3} was observed in all samples, which is also an important parameter for an energy storage application [8].

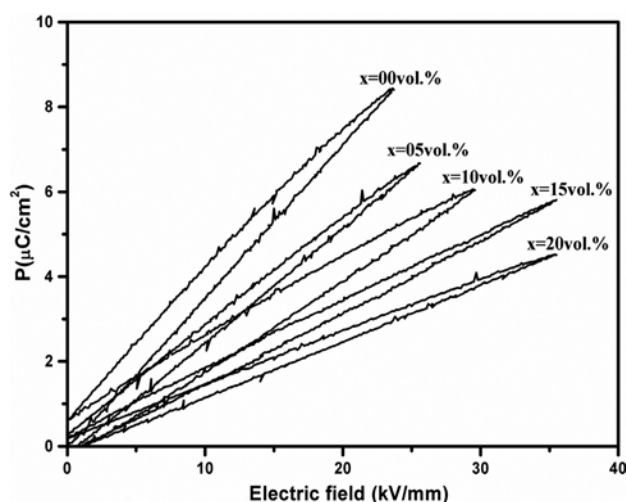The breakdown performance of ceramics as a function of the x value is shown in Fig. 5. Pure SrTiO$_3$

Fig. 7. *P-E* hysteresis loops of samples measured up to their breakdown electric fields.
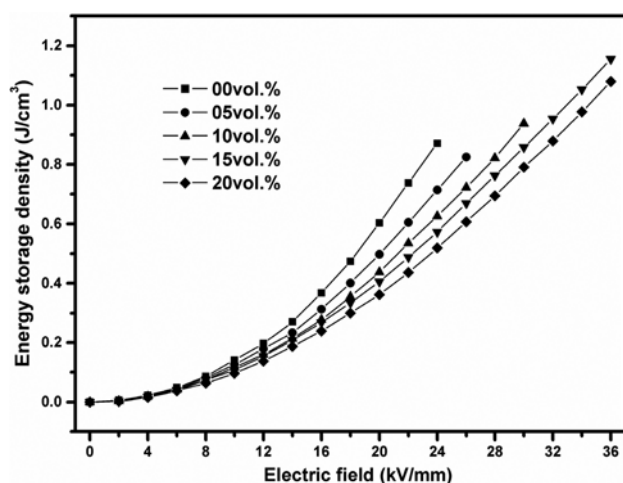

Fig. 8. Energy storage density of various vol.% SiO₂-added SrTiO₃ samples as a function of electric field.

has an average breakdown strength of 24.2 kV/mm. When the x value increases from 0 to 15 vol.%, the average breakdown strength increases gradually from 24.2 kV/mm to 36.1 kV/mm. A further increase in the x value from 15 vol.% to 20 vol.% leads to a small decrease in the average breakdown strength from 36.1 kV/mm to 35.8 kV/mm. Thus, the sample with x=15 vol.% has the highest average breakdown strength of 36.1 kV/mm. For energy storage ceramics, a high relative density, a small and homogeneous grain size usually enhance the breakdown strength of the ceramics. Fig. 6 shows SEM images of the sintered ceramics. Pure SrTiO₃ exhibits an average grain size of about 2ìm. With SiO₂ additions, the samples show average grain sizes of about 400 nm which is obviously smaller than for pure SrTiO₃. The result indicates that SiO₂ additions could inhibit the grain growth of SrTiO₃ ceramics. According to literature by Zhao et al. [12], nanocrystalline TiO₂ was seen to exhibit a higher breakdown strength as compared to micrometre TiO₂.

In this study, a similar phenomenon was observed. Therefore, the enhancement of breakdown performance should be associated with the submicrometre grains in SiO₂-added samples. In addition, the insulating capacity of the SiO₂ additive [11] is also a factor for an improvement of the breakdown strength. *P-E* hysteresis loops of samples measured up to the breakdown electric field are plotted in Fig. 7, and the energy storage density calculated from the *P-E* hysteresis loops by equation (1) is given in Fig. 8. Pure SrTiO₃ exhibits an energy storage density of 0.871 J/cm³. With x=10 vol.%, 15 vol.% and 20 vol.%, samples reveal higher energy storage density ranges between 0.938 J/cm³ and 1.155 J/cm³ because of the enhanced breakdown performance, although they have a lower dielectric constant compared with pure SrTiO₃. With an x value of 15 vol.%, the highest energy storage density of 1.155 J/cm³ was obtained. Such an improvement of energy storage performance makes SrTiO₃ a promising candidate for energy storage applications.

Conclusions

The (1-x) SrTiO₃-x SiO₂ compositions were prepared by conventional solid-state reactions. Under 1 kHz AC, all samples reveal a dielectric loss of less than 3×10^{-3}, and the dielectric constant decreases from 295-102 with an increase of the x value. With SiO₂ additions, the samples show submicrometre grains with an average size of about 400 nm, which leads to an obvious improvement in breakdown performance of the samples. The samples with 15 vol.% addition reveal the highest average breakdown strength of 36.1 kV/mm which results in the highest energy storage density of 1.155 J/cm³. Therefore, it is a promising way to improve the energy storage performance of SrTiO₃ ceramics by adding SiO₂.

Acknowledgments

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