

The microstructures and dielectric properties of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ceramics

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Published online: 7 April 2007
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Abstract In this paper, the microstructures and the dielectric properties of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ($x=0.01, 0.03, 0.05,$ and 0.07) ceramics were investigated. The composition can form a single-phase structure solid solution as x increases from 0.01 to 0.07, and the average grain size decreases from 15 to 2 μm with the x increasing. With the variation of SrZrO_3 content, dielectric constant, dielectric loss, and breakdown strength (BDS) of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ samples are changed. When $x=0.05$, the samples exhibit high BDS more than 14 kV/mm and low dielectric loss about 1×10^{-3} with dielectric constant of 330. It can be a candidate material of energy storage for pulsed power application.

Keywords Dielectric constant · Breakdown strength · SrTiO_3 · SrZrO_3

1 Introduction

To develop transmission lines with higher energy storage capabilities for compact pulsed power applications, one of the efforts focused on developing and studying ceramic dielectrics with high dielectric constant (ϵ_r) and high breakdown strength (BDS) [1]. Typical candidate ceramics that are being studied in this regard are TiO_2 and BaTiO_3 [2–4]. Because the tradeoff between high dielectric constant and high BDS has been identified as a major issue in the search for suitable dielectric materials with high energy density, the perovskite SrTiO_3 ceramic was selected as our study material for its relatively high permittivity [5]. However, one

limitation of these dielectric ceramics is its low BDS. So the challenge for us lies in improving its BDS without decreasing its relative permittivity.

Various investigations show a tiny amount of doping will affect the dielectric properties of SrTiO_3 ceramic [6]. In the present work, SrZrO_3 was selected to add to the SrTiO_3 ceramic for its several characteristics: neither SrZrO_3 nor SrTiO_3 is ferroelectric, therefore, these materials are not expected to experience electromechanical failure mechanisms that may result in dielectric breakdown. In addition, orthorhombic perovskite SrZrO_3 and cubic perovskite SrTiO_3 can form a solid solution [7], and no species in the SrTiO_3 – SrZrO_3 system volatilize appreciably under typical sintering conditions. Furthermore, the carefully prepared SrZrO_3 ceramics were reported to exhibit high BDS (~ 40 kV/mm) [5]. For the reasons mentioned above, we expect to synthesize materials with improved BDS and high dielectric constant by the combination of SrTiO_3 with SrZrO_3 . In the present work, samples of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ were prepared in different sintering conditions and their properties were studied.

2 Experimental detail

$x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ powders with compositions of $x=0, 0.01, 0.03, 0.05,$ and 0.07 were prepared using the conventional ceramics processing method. As starting materials, highly pure SrCO_3 (99%), TiO_2 (99%), and ZrO_2 (99%) were used. First, SrZrO_3 and SrTiO_3 powders were synthesized at 1,250 °C for 6 h and 1,150 °C for 4 h, respectively. Second, the synthesized products were mixed for 12 h according to the molar fraction $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ($x=0, 0.01, 0.03, 0.05,$ and 0.07) in a ball mill with 2.5% PVA as a binder. These powders were pressed into

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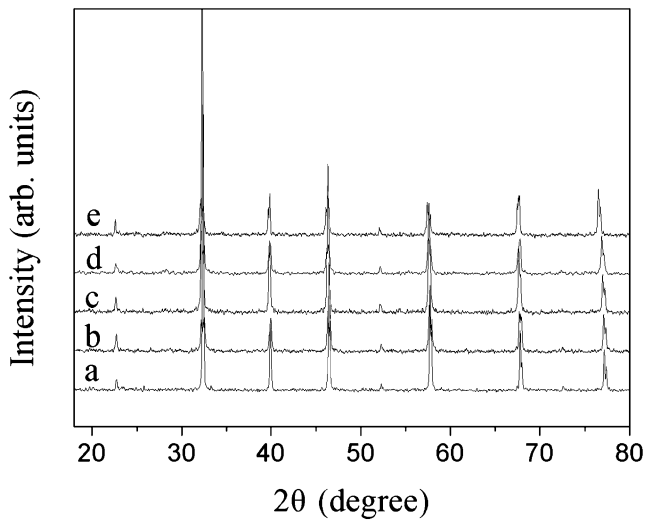


Fig. 1 XRD patters of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ system sintered at $1,400\text{ }^\circ\text{C}$ for 3 h: (a) $x=0$, (b) $x=0.01$, (c) $x=0.03$, (d) $x=0.05$, and (e) $x=0.07$

pellets of 24 mm in diameter and 2 mm in thickness under a uniaxial pressure of 200 MPa. After debinding, these pellets were sintered in alumina crucibles at $1,300\text{--}1,450\text{ }^\circ\text{C}$ for 3 h in air.

The crystalline phases of the prepared samples were investigated by powder X-ray diffraction (XRD) (model D/MAX-RB, RIGAKU Corporation, Japan). The samples thermally etched at $50\text{ }^\circ\text{C}$ below the sintering temperature after polishing, and then were observed by a scanning electron microscope (SEM) (model JSM-5610LV, JEOL Ltd., Japan) to get the microstructure of the samples. The bulk densities of the sintered pellets were measured by Archimedes method. The dielectric constant and the dielectric loss were measured at room temperature at the frequency 50 MHz using HP4291 impedance analyzer. The DC breakdown tests were performed at room temperature. All samples were immersed in silicon oil to prevent flashover and corona discharge.

3 Results and discussion

Figure 1 shows the XRD patterns of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ceramics. All patterns of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ceramics

Table 1 Unit cell parameters and X-ray density of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ system.

x	Phase	a (Å)	c (Å)	Primitive volume(Å ³)	X-ray density (g/cm ³)
0	Cubic	3.9082	—	59.6940	5.105
0.01	Cubic	3.9104	—	59.7948	5.110
0.03	Cubic	3.9121	—	59.8728	5.125
0.05	Cubic	3.9163	—	60.0659	5.133
0.07	Tetragonal	5.5483	7.8321	60.2751	5.139

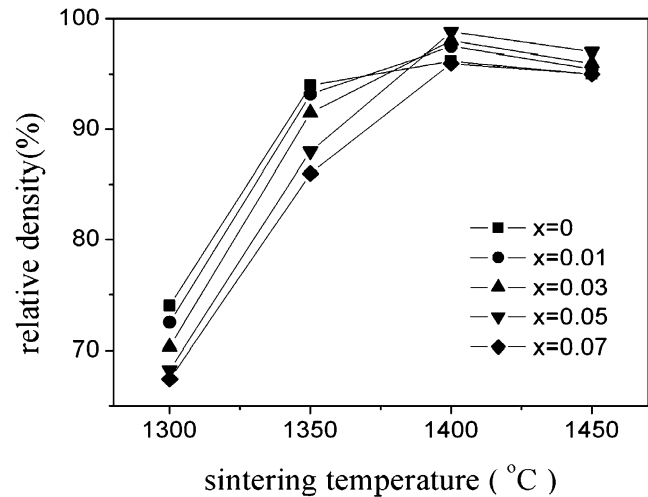


Fig. 2 The relative density as a function of sintering temperature for $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ system

measured by XRD show that each of these compositions is composed of a single phase. It indicates the solid solution structure is formed in the SrZrO_3 and SrTiO_3 mixture. Because of the larger lattice parameter of SrZrO_3 , the unit cell volume of solid solution phase increases and it can be proved by the peaks of the diffraction shifting to lower angle when the x value increases. Using program DIVOL91, we calculated the unit cell parameters of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ (as shown in Table 1). The results indicate this solid solution exists as a phase transition from cubic to tetragonal with the SrZrO_3 content increasing. Similar reports had been given for the $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ system by Wong et al. [7].

According to the calculated X-ray density, we obtained the relative density of samples sintered at different temperatures. As shown in the Fig. 2, the relative density of each composition increases as the sintering temperature increases. For each of these five compositions, the highest relative

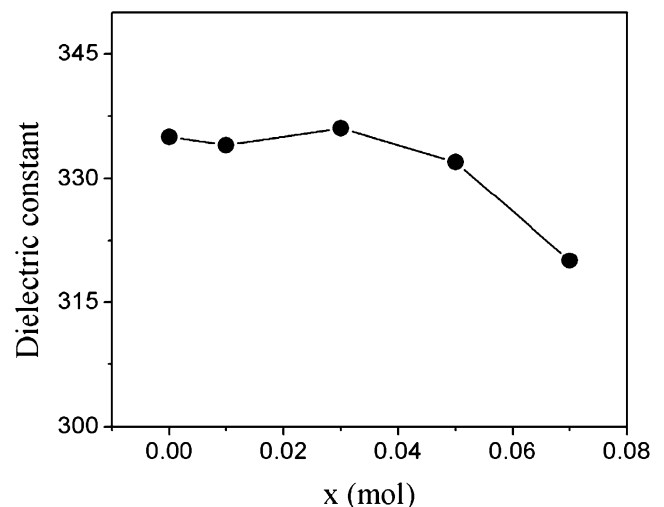


Fig. 3 Dielectric constant as a function of x for $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ system sintered at $1,400\text{ }^\circ\text{C}$ for 3 h

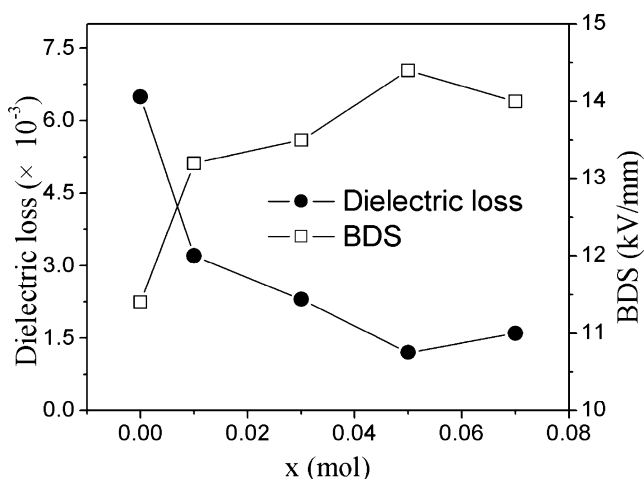


Fig. 4 Dielectric loss and BDS as a function of x for $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ system sintered at $1,400^\circ\text{C}$ for 3 h

density can be obtained at $1,400^\circ\text{C}$ for 3 h, which is larger than 96% of the X-ray density. We will discuss the microstructure and properties of the samples sintered at $1,400^\circ\text{C}$ in this paper.

Figure 3 shows the variation of dielectric constant of the $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ceramics measured at 50 MHz. The results show that a tiny amount of SrZrO_3 additive has a small effect on the dielectric constant initially. When $x \leq 0.03$, the dielectric constant varies around 335 with the SrZrO_3 increasing. However, a further increase of the SrZrO_3 causes a decrease of dielectric constant, which obeys the volume–mixture rule between the high dielectric constant of SrTiO_3 and the low dielectric constant of SrZrO_3 ceramics ($\epsilon_r \sim 22$) [8].

The variation of dielectric loss and BDS of the $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ceramics is shown in Fig. 4. The results show that the dielectric loss reduces as the SrZrO_3 increases. However, the dielectric loss of the specimen increases slightly at 0.07 mol SrZrO_3 . The BDS value of the samples increases initially as the SrZrO_3 is added in. The sample

exhibits the maximum BDS of 14.4 kV/mm at 0.05 mol SrZrO_3 . A further increase of the additive concentration to 0.07 mol causes a slightly decrease of BDS.

The BDS and dielectric loss of ceramics depend strongly on the relative density, porosity, and grain size of the ceramics. The BDS of the ceramics can be improved through increasing density, eliminating large size pore and reducing the grain size [2–4]. Because the relative density of all the $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ($x \geq 0.01$) specimens is higher than 96%, the effect of density on the dielectric properties can be neglected [9]. Therefore, in the present study, the decrease of the grain size may be one of factors to explain the change in the dielectric loss and the BDS values of the specimens. As shown in Fig. 5, SEM of the surfaces for the specimens give an average grain size decrease from 15 to $2\ \mu\text{m}$ as the content of added SrZrO_3 increases. Especially at 0.05 mol SrZrO_3 , the specimen reveals a very dense microstructure with fine grains, whose average dimension of the crystal grain is about $4\ \mu\text{m}$. This is consistent with the resultant dielectric loss and BDS value shown in Fig. 4.

An undesirable change of dielectric properties at 0.07 mol SrZrO_3 has been found in our study results. Although the average grain size of specimens reduced to $2\ \mu\text{m}$, as shown in Fig. 3(c), the BDS was not improved. This change could be due to occurrence of the large pores on the specimen surface, which reduced the relative density and damaged the BDS. Though the specimens with $x=0.07$ were sintered at a temperature as high as $1,450^\circ\text{C}$, the large pores still could not be eliminated. It seems that it is not grain size but the large flaw, which is the dominating cause of the damage of the BDS of the samples. We also examined several other compositions with $x > 0.07$. The results indicated that the optimum sintering temperature increased and the dielectric constant decreased as the fraction of SrZrO_3 in the composition increased. But the BDS and the dielectric loss of these compositions were not improved compared to pure SrTiO_3 because of the occurrence of the large pores in the samples.

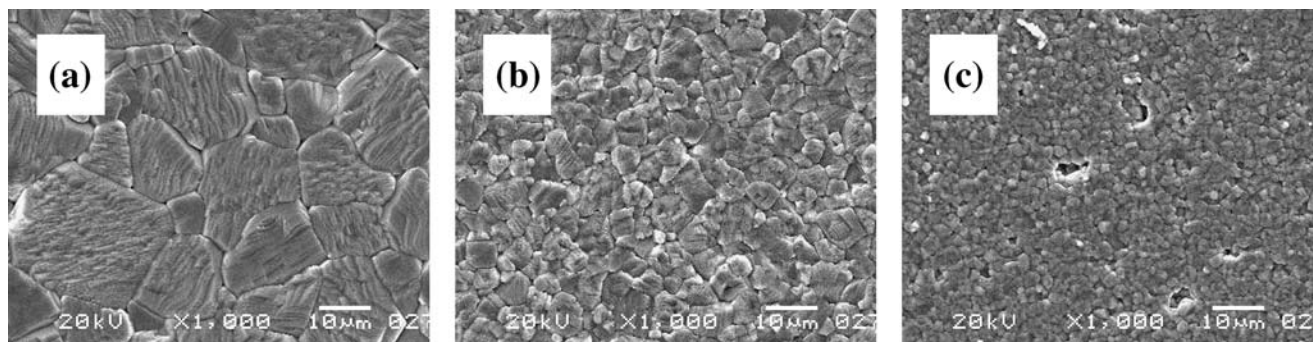


Fig. 5 SEM photographs of $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ system sintered at $1,400^\circ\text{C}$ for 3 h: (a) $x=0$, (b) $x=0.05$, and (c) $x=0.07$

4 Conclusion

The $x\text{SrZrO}_3-(1-x)\text{SrTiO}_3$ ($x=0.01, 0.03, 0.05, \text{ and } 0.07$) solid solution ceramics have been synthesized by a solid-state reaction method and their microstructure and dielectric properties were investigated. Sintered at 1,400 °C for 3 h, high relative density above 96% was obtained for these compositions. Through the modification of microstructure with the addition of SrZrO_3 , the BDS and dielectric loss of the samples have been improved without significant decrease of the dielectric constant. These results could be explained by the effect of grain size and large flaw on the dielectric properties of the specimens. The sample with the addition of 0.05 mol SrZrO_3 reveals a very dense microstructure with fine grains. Then high BDS of 14.4 kV/mm, high dielectric constant of 330 with low dielectric loss of 1.2×10^{-3} were obtained for this composition.

Acknowledgement The authors would like to thank the support of Natural Science Foundation of China (grant no. 50472016), Ministry

of Education of China (main project), and Foundation for Innovative Research Team of Hubei province (grant no. 2005ABC004).

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