STRUCTURAL, DIELECTRIC AND MAGNETIC PROPERTIES OF Fe-DOPED SrZrO$_3$ CERAMICS

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SrZrO$_3$-based perovskite oxides have been extensively studied for their outstanding physical characteristics, chemical stability, and mechanical properties. With the recent development of multiferroics, room temperature ferromagnetism is expected to be introduced to ferroelectric or dielectric materials by magnetic ion doping in order to obtain single-phase magnetoelectric or magnetodielectric materials. In this work, SrZrO$_3$ and SrZr$_{0.9375}$Fe$_{0.0625}$O$_3$ ceramics were fabricated by a conventional solid-state reaction method. Their structural, dielectric and magnetic properties were carefully investigated. It was found that Fe-doping could effectively improve the dielectric constant of SrZrO$_3$. Moreover, ferromagnetism with a Curie temperature of about 685 K was successfully introduced by a small amount of Fe dopant. The saturation magnetization and coercive field of SrZr$_{0.9375}$Fe$_{0.0625}$O$_3$ ceramics were 3.0 emu/g and 1.3 kOe, respectively, at room temperature. The origin and mechanism of ferromagnetism introduced by Fe dopant is discussed based on the valence fluctuation of Fe ions.

INTRODUCTION

Perovskite materials have been the subject of a great deal of researches for their impressive physical characteristics, good chemical stability, and remarkable mechanical properties. Strontium zirconate (SrZrO$_3$), one of the typical perovskite materials, has a high melting point (above 2600°C), and could be employed as a high-temperature material [1, 2]. SrZrO$_3$, which possesses high dielectric constant, low dielectric loss, high breakdown strength, and low leakage current density, is a potential candidate for high voltage and high-reliability capacitor applications [3-5]. When Zr^{4+} in SrZrO$_3$ is partially substituted by aliovalent metal ions, excellent ionic conductivity can also be observed under high temperature [6].

During the recent decade, multiferroics that simultaneously present ferroelectric and magnetic ordering have attracted much attention for their potential applications in information storage, spintronics, sensors etc. However, most single-phase materials exhibit multiferroic properties at low temperature. Therefore, the synthesis of room temperature multiferroics is a hot research topic of materials science. Doping magnetic ions into room temperature ferroelectric or dielectric matrices is one of the most effective ways to obtain room temperature multiferroics as evidenced by many publications over the past few years. Lee *et al.* observed

magnetic ordering at low or room temperature for Co and Mn doped BaTiO$_3$, SrTiO$_3$, and KTaO$_3$ single crystals [7]. Nakayama *et al.* investigated the doping effect of Sc, V, Cr, Mn, Fe, Co, Ni, and Cu on BaTiO$_3$, and based on first-principles total-energy calculations [8], they predicted that ferromagnetism can be introduced in BaTiO$_3$ by Cr, Mn, Co and Fe doping. This prediction has been experimentally confirmed by Xu *et al.* with the coexistence of ferroelectricity and ferromagnetism for BaTi$_{1-x}$Fe$_x$O$_3$ ceramics at room temperature [9]. Previously, the ferroelectricity of Pr-doped SrTiO$_3$ thin films [10] as well as the surface states and electronic band structure of Fe-doped SrTiO$_3$ material [11-13] have been studied. In a former work, we mainly focused on the theoretical and experimental research on SrZrO$_3$ materials, as the structure and performance of SrZrO$_3$ and SrTiO$_3$ are similar [14]. We also theoretically concluded that Fe-doped BaTiO$_3$ material can simultaneously exhibit ferroelectric and ferromagnetic orders [15] while there is no experimental evidence for Fe-doped SrZrO$_3$ ceramics. In the present work, SrZrO$_3$ (SZO) and SrZr$_{0.9375}$Fe$_{0.0625}$O$_3$ (SZFO) ceramics were prepared by the solid-state reaction method and their structural, dielectric, and magnetic properties were systemically investigated. It is found that ferromagnetism with a Curie temperature of about 685 K can be successfully introduced in SZO by a small amount dopant of Fe.

EXPERIMENTAL

Both SZO and SZFO ceramics were prepared by a standard solid-state reaction method using high purity starting materials (Sinopharm Chemical Reagant Co., Ltd.), including Fe_2O_3 (99.99 %), $SrCO_3$ (98.50 %), and ZrO_2 (99.00 %). Detailed preparation steps are as follows: (a) $SrCO_3$, ZrO_2, and Fe_2O_3 were accurately weighed according to stoichiometric ratio. The reactants were ground into uniform powders in a ball mill, and then the mixed powders were preheated at 1100°C for 10 h and naturally cooled to room temperature. (b) The preheated powders were ground again, pressed into pellets under 20 MPa pressure, and sintered at 1300°C for 1.5 h in air. (c) Platinum electrodes were sputtered on top and bottom of the cleaned ceramics by sputtering.

X-ray diffraction (XRD, Bruker D8, Germany) with Cu Kα radiation and scanning electron microscopy (SEM, 1530YP, Leo Co., Germany) were used for analyzing the structure of SZO and SZFO ceramics. Dielectric properties were evaluated using impedance analyzer (HP4194A, USA). Magnetic hysteresis loop and temperature-dependent magnetization were measured by vibrating sample magnetometer (VSM, Microsense EV7, Quantum Design, USA) and the combination states of Fe2*p* electrons were examined by X-ray photoelectron spectroscopy (XPS, PHI-5000, Japan).

RESULTS AND DISCUSSION

Microstructure characterization

Successful doping with Fe is essential for our research. The ionic radius of Fe^{3+}, which is about 0.064 nm, is much smaller than that of Sr^{2+} (around 0.144 nm) but comparable with that of Zr^{4+} (around 0.072 nm) [16,17]. Therefore, Fe^{3+} can enter into the lattice and substitute Zr^{4+}. Figure 1 shows the X-ray diffraction patterns of
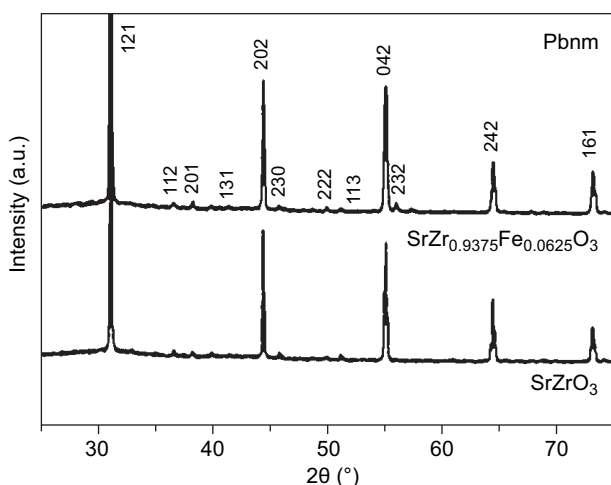
SZO and SZFO ceramics. The peaks, which are indexed on the basis of the *Pbnm* space group for orthorhombic cells, imply that both SZO and SZFO ceramics possess a single-phase perovskite structure and no second phase is observed within the apparatus resolution. These observations indicate that Fe ions enter into the lattice of SZO successfully.

Figure 2 presents the SEM micrographs of SZO and SZFO ceramics. Both SZO and SZFO ceramics have distinct grain structures. The average grain size is about 0.9 μm for SZO ceramics, while that of SZFO ceramics is of about 0.7 μm, indicating that the introduction of Fe either increases the crystallization temperature of
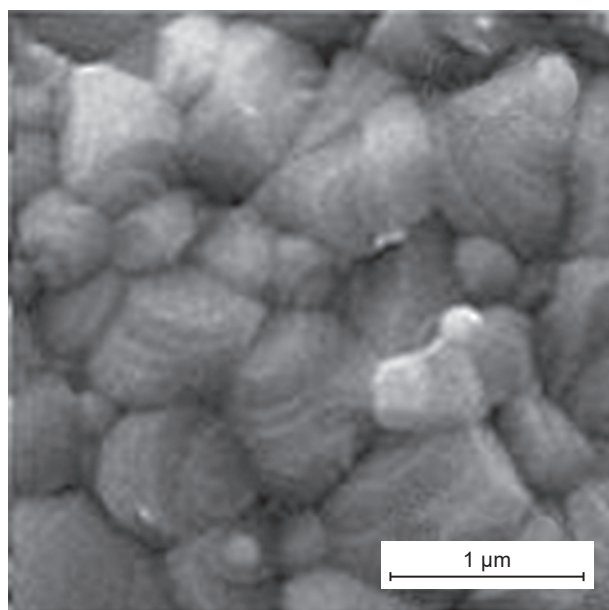
a) SZO
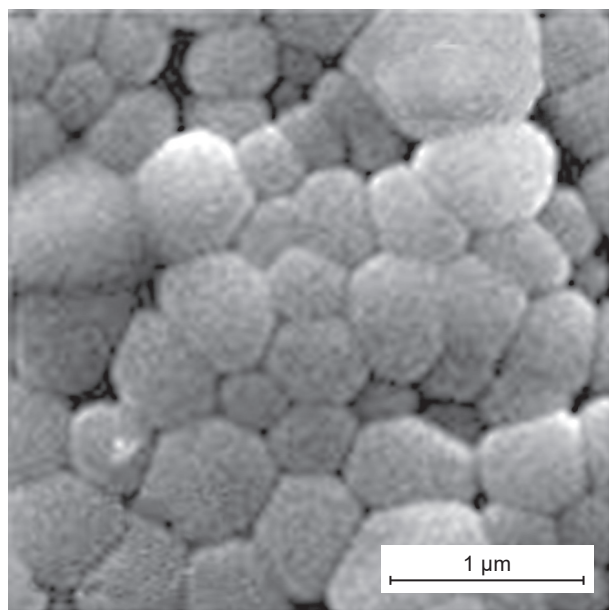
b) SZFO

Figure 2. SEM micrographs of SZO and SZFO ceramics.

Figure 1. X-ray diffraction patterns of SZO and SZFO ceramics measured at room temperature.

SZO or inhibits grain growth. Therefore, the change of sintering temperature is worth to be paid attention to for $SrZr_{1-x}Fe_xO_3$ ceramics with larger Fe content.

Dielectric behavior

The dielectric properties of SZO and SZFO ceramics are crucial for their electrical applications. Frequency dependent dielectric constant and loss of SZO and SZFO ceramics were measured at room temperature by the HP4294A impedance analyzer with an applied electric field of 50 mV. As shown in Figure 3, no obvious change is observed with the increase of frequency for both dielectric constant and loss of SZO ceramics, meaning that pure SZO ceramics possess good dielectric stability within the measuring frequency range. At 10 kHz, the dielectric constant and loss of SZO ceramics are 54 and 0.003, respectively, indicating that SZO is a good dielectric material. Compared with SZO, larger dielectric constant (88) and loss (0.1) are observed for SZFO at 10 kHz, as shown in Figure 3. However, SZFO still possess lower dielectric loss, compared to other magnetodielectric materials [18, 19]. Both dielectric constant and loss of SZFO decrease with increasing frequency, see Figure 3. Such frequency-dependent dielectric properties are probably due to the defects induced by Fe doping. Compared with pure SZO, more oxygen vacancies are introduced in SZFO due to the requirement of charge balance compensation when Zr^{4+} is substituted by Fe^{3+}. The increased oxygen vacancies lead to increased dielectric losses.
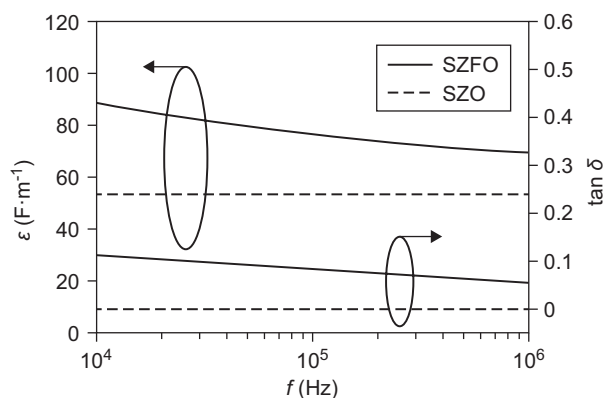

Figure 3. Room temperature dielectric constant and loss of SZO and SZFO ceramics.

Characterization of magnetic properties

Figure 4 shows the hysteresis loop of SZFO ceramics at room temperature. It shows that ferromagnetism is successfully introduced in SZO ceramics by a small amount dopant of Fe, and the saturation magnetization and the coercive field are 3.0 $emu \cdot g^{-1}$ and 1.3 kOe, respectively. In addition, temperature-dependent magnetization of SZFO is carried out to obtain its Curie temperature.

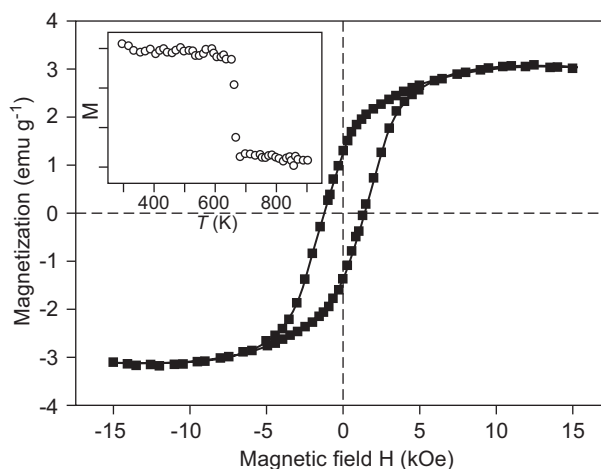As shown in the inset of Figure 4, the ferromagnetic Curie temperature of SZFO ceramics is approximately 685 K.

Figure 4. Room temperature magnetization hysteresis loop of SZFO ceramics; the inset shows the temperature dependent magnetization measured at 2 kOe.

To analyze the origin of the ferromagnetism of SZFO ceramics, the combination states of Fe2p electrons were examined by X-ray photoelectron spectroscopy (XPS). Figure 5a shows Fe 2p XPS spectrum. It is found that Fe 2p core level splits into 2$p_{1/2}$ and 2$p_{3/2}$
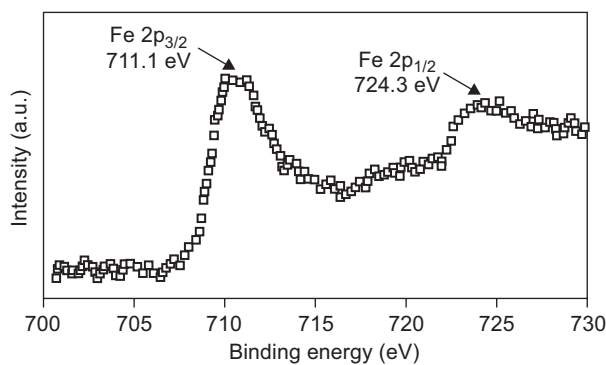
a)
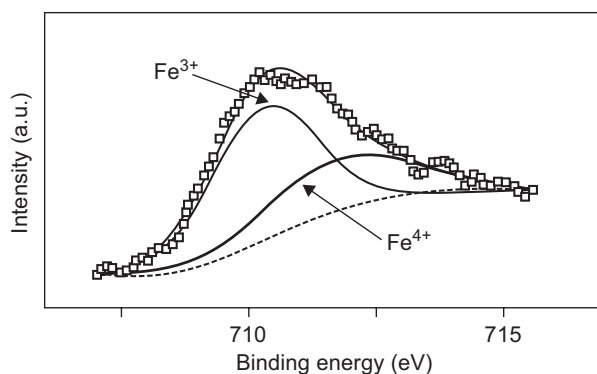
b)

Figure 5. Fe 2p XPS spectrum (a) and its Lorentzian-Gaussian dividing results (b) for SZFO ceramics.

components. The binding energy of Fe $2p_{3/2}$ is expected to be 710.7 eV for Fe^{3+} and 711.8 eV for Fe^{4+} [11, 12]. However, an asymmetric broad band of about 711.1 eV is identified for the SZFO ceramics, demonstrating that the oxidation state of Fe is the coexistence of Fe^{3+} and Fe^{4+}. Therefore, we divide Fe $2p_{3/2}$ band into two subbands centered at 710.7 eV and 711.8 eV, respectively, by Lorentzian-Gaussian curve fitting, see Figure 5b. According to the fitting results, the percentage of Fe^{3+} to the entire Fe component, which is estimated by peak area, is about 64 % for SZFO ceramics. That is, the content of Fe^{4+} ions in SZFO ceramics is about 36 %, although Fe_2O_3 is initially used for fabrication. In general, it is difficult to control the valence fluctuation of Fe^{3+}, especially the change from Fe^{3+} to Fe^{4+}. In our $SrZr_{0.9735}Fe_{0.0625}O_3$ ceramics, as Zr^{4+} ions were partial substituted by Fe^{3+}, a small amount of Fe^{4+} ions can be formed due to the requirement of charge balance. As a result, the ferromagnetism is observed through the double exchange interaction between Fe^{3+} and Fe^{4+}.

CONCLUSIONS

In summary, SZO and SZFO ceramics were prepared by a solid-state reaction method. It was observed that Fe ions enter into the lattice successfully, increasing the dielectric constant of SZO ceramics. Ferromagnetism was also introduced by Fe doping, with a ferromagnetic Curie temperature of approximately 685 K. The origin of the ferromagnetism induced by Fe doping is considered to lie in the appearance of Fe^{4+} ions and the double exchange interaction between Fe^{3+} and Fe^{4+}.

Acknowledgements

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