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# Enhanced thermoelectric properties of the SrTiO<sub>3</sub> by Zr-doping with different doping level

# Tamal Tahsin Khan, Il-Ho Kim and Soon-Chul Ur\*

Department of Materials Science and Engineering and Research Center for Sustainable Eco-Devices and Materials (ReSEM), Korea National University of Transportation, Chungju, Chungbuk, Republic of Korea, 27469

The enhancement of the thermoelctric properties of the SrTiO<sub>3</sub> by doping with Zr were investigated in our study. The Zrdoped SrTiO<sub>3</sub> with different doping level were synthesized by the conventional solid-state reaction method. The formation of single phase cubic perovskite structure and the changing behavior of the average grain size confirmed that the Zr-doped SrTiO<sub>3</sub> were prepared to control doping level. The thermoelctric properties including Seebeck coefficient, electrical conductivity, and thermal conductivity has been investigated in a moderate temperature regime from 300 K to 1000 K. The absolute value of Seebeck coefficient decreased and the electrical conductivity increased monotonically with increasing doping level. The thermal conductivity decreased with increasing doping level. The power factor increased with increasing doping level-up to x = 0.03 mole and the dimensionless figure of merit ZT, increased up to x = 0.03 mole of Zr. The maximum ZT value was observed for SrTi<sub>0.97</sub>Zr<sub>0.03</sub>O<sub>3</sub> at 873 K.

Key words: Ceramic oxide, Doping, Thermoelectric properties, Ball mill, Vacuum hot-pressing.

# Introduction

The demand for energy conversion technologies is significantly important because of the increase in energy demand and limited availability of fossil fuels. However, approximately two-thirds of energy is lost as waste heat during its conversion, storage, transfer, and usage [1]. The conversion of this waste heat into electricity by using thermoelectric materials has attracted worldwide interest, particularly in the high-temperature range. Thermoelectric materials can convert waste heat into electricity by taking advantage of the Seebeck effect from different sources such as industrial processes, furnaces, and engine exhaust streams. The energy conversion efficiency of thermoelectric materials is governed by the magnitude of the dimensionless figure of merit, which is defined as  $ZT = \sigma S^2 T / \kappa$ , where S,  $\sigma$ ,  $\kappa$  and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. So far, the thermoelectric materials with the best performances have been PbTe [2, 3], Bi<sub>2</sub>Se<sub>3</sub> [4], Bi<sub>2</sub>Te<sub>3</sub> [5], and so on. However, these materials contain hazardous constituents which have detrimental effects on the environment and are only promising for low-temperature applications. Thus, the current focus of research is on developing potential materials that are stable for high-temperature applications and environmentally friendly.

Metal oxides have greater chemical and thermal stability over heavy metal alloys [6-8] and recently attracted significant attention for thermoelectric (TE) power generation at high temperatures. Furthermore, metal oxides are naturally more abundant and less toxic than heavy metal alloys whose use is limited to specific applications such as in space exploration. Several research studies have been reported that perovskite-type oxides such as LaCoO<sub>3</sub> [9], SrTiO<sub>3</sub> [10, 11], and CaMnO<sub>3</sub> [12, 13] are found to exhibit moderate performance of thermoelectric properties. Among them, crystalline SrTiO<sub>3</sub> (STO) is nowadays a promising TE material, which has the cubic perovskite structure (lattice parameter a = 3.905 Å, space group pm3m). The electrical conductivity of STO can be easily changed from insulating to metallic by substitutional doping on different sites [14] (A-site and B-site) in the lattice or by creating oxygen vacancies [15]. In our study, we investigated the electrical and thermal transport properties of SrTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> systems prepared by conventional solid-state reaction method in order to clarify the influence of Zr doping on the electronic and phonon transport of SrTiO<sub>3</sub>, which provides few important fundamental information for the design of future high-performance thermoelectric materials based on SrTiO<sub>3</sub> at high temperature regime.

### **Experimental Procedure**

The Zr-doped SrTiO<sub>3</sub> samples with different doping level were prepared by a conventional solid-state reaction method. According to the stoichiometric ratio the analytical grade reagents SrCO<sub>3</sub> (Sigma-Aldrich, -

<sup>\*</sup>Corresponding author:

Tel : +82-43-841-5385

Fax: +83-43-841-5380

E-mail: scur@ut.ac.kr

325 mesh, 99.9%),  $TiO_2$  (Sigma-Aldrich, -325 mesh, 99.9%), and  $ZrO_3$  (Sigma-Aldrich, -325 mesh, 99.9%) as starting materials were accurately weighed and then ballmilled in ethanol for 24 h. Before sintering, the dried powders were calcined at 1273 K for 6 h in the air. The calcined powders were then ball-milled for 72 h to get the desired fine particle size. The disk sample was prepared by vacuum hot-pressing under a pressure of 70 MPa and sintered at 1573 K for 2 h.

The crystal structure of all the studied samples was measured by using the powder X-ray diffraction (Bruker D8 Advance system) in the range of  $2\theta = 20$ -80 °C with Cu-Ka radiation at room temperature. The lattice parameters were calculated by using multiple peak-separation methods. The densities of the sintered samples were calculated based on Archimedes principle. The microstructure of all the specimens was observed by using a scanning electron microscope (SEM; FEI Quanta 400 system). The van der Pauw method (Keithley 7065) was used to measure the Hall coefficient, Hall mobility and Carrier concentration at room temperature in a 1 T magnetic field at a 50 mA electric current. The electrical conductivity and Seebeck coefficient were measured from room temperature to 873 K in Ar atmosphere by using the temperature differential and the 4-probe methods (Ulvac-Rico ZEM-3 system). Thermal conductivity was determined from the thermal diffusivity, and the specific heat capacity was obtained by laser flash measurement (Ulvac-Rico TC-9000 system), from room temperature to 973 K. The lattice thermal conductivity was estimated by subtracting the electrical thermal conductivity from the total thermal conductivity. The electrical thermal conductivity was measured from the electrical conductivity, obtained by laser flash measurement (Ulvac-Rico TC-9000 system), from room temperature to 973 K.

#### **Results and Discussion**

The XRD patterns for calcined SrTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> (x = 0.02, 0.03, 0.04, and 0.05) samples with standard SrTiO<sub>3</sub> (ICDD # 01-079-0174) are shown in Fig. 1(a). The samples obtained in the present study show single phase of cubic perovskite structure although a few of samples contain a small amount of secondary phase (SrZrO<sub>3</sub>). Fig. 1(b) shows the XRD patterns of sintered sample of Zr-doped SrTiO3 with different doping levels. From Fig. 1(b) it is seen that there is no second phase of (SrZrO<sub>3</sub>) after sintering. The average grain size was increased with increasing doping level up to x= 0.03 and then decreased (as shown in Fig. 3). The single-phase of cubic perovskite structure and the doping dependence of the average grain size clearly suggested that the Zr-doped SrTiO<sub>3</sub> powders with different doping level were prepared with controlled doping levels.

The lattice parameters with a different doping level of Zr were calculated by using multiple peak-



**Fig. 1.** XRD patterns of  $SrTi_{1-x}Zr_xO_3$  samples, (a) calcined samples, (b) sintered samples.



**Fig. 2.** (a) Lattice parameter as a function of the Zr content, and (b) density of  $SrTi_{1-x}Zr_xO_3$  samples sintered at 1573 K.

separation methods and are plotted in Fig. 2(a). From the Fig. 2(a), it is found that the lattice parameter increased with increasing Zr contents. Such an increase in the lattice parameter is related to the replacement of small-sized Ti<sup>4+</sup> ions (60.5 pm) with the large-sized Zr<sup>4+</sup> ions (72.0 pm) [16]. Fig. 2(b) illustrates the relative density of all the sintered samples with different Zr substitution. The relative density varied from 99.49% to 99.73%. The density increase with increasing doping level up to x = 0.03 mole and then decreases with increasing further doping level. In this research, the SrTi<sub>0.97</sub>Zr<sub>0.03</sub>O<sub>3</sub> sample showed the highest density of 5.096 g/cm<sup>3</sup> as well the highest ZT value because of the higher electrical conductivity.

The microstructures of the sintered samples with different doping contents are shown in Figs.  $3(a) \sim (d)$ . The microstructures were observed by SEM and the surface micrographs showed the significant change in surface morphology. The average grain size are 2.80 µm, 4.80  $\mu$ m, 4.10  $\mu$ m, and 3.10  $\mu$ m for x = 0.02 mole, x = 0.03 mole, x = 0.04 mole, and x = 0.05 mole, respectively. It is clearly seen that the grain size seems to be increased by the introduction of ZrO<sub>2</sub> into SrTiO<sub>3</sub> up to the doping level of x = 0.03 mole. Such an increase is related to the replacement of small-sized Ti<sup>4+</sup> ions (60.5 pm) in the B sites of the perovskite structure with the larger  $Zr^{4+}$  ions (72.0 pm) [16]. The average grain size then decreased to a doping level of x > 0.03 mole. This decreasing behavior could be explained based on a pinning effect due to the secondary phases as indicated in the XRD patterns, Fig. 1(a). The similar observation was also reported by Yoon and Mahmud [17, 20]. Probably, the amount of the second phases  $(SrZrO_3)$ increases with increasing Zr contents, which may be hindered the grain growth. The change of grain size with increasing doping contents suggests that the microstructure of SrTiO<sub>3</sub> materials could be influenced



Fig. 3. SEM images of  $SrTi_{1-x}Zr_xO_3$  samples (a) x = 0.02 mole, (b) x = 0.03 mole, (c) x = 0.04 mole, and (d) x = 0.05 mole, respectively.

**Table 1.** Electronic transport properties in terms of Hall coefficient, Hall mobility and carrier concentration of Zr-doped  $SrTiO_3$  samples at room temperature.

Composition	Hall coefficient (cm <sup>3</sup> C <sup>-1</sup> )	Hall mobility (µ, cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Carrier concentration (n, cm <sup>-3</sup> )
x = 0.02 mole	-1.210	423.0	$5.62 \times 10^{19}$
x = 0.03 mole	-0.934	658.1	$6.98 \times 10^{19}$
x = 0.04 mole	-0.767	587.7	$7.78 \times 10^{19}$
x = 0.05 mole	-0.330	316.0	$8.67 \times 10^{19}$

by incorporation of Zr.

The changing behavior of the electronic and thermal transport properties of  $SrTi_{1-x}Zr_xO_3$  samples, such as the Seebeck coefficient, the electrical conductivity, the thermal conductivity and the lattice thermal conductivity with temperature is shown in Figs. 4(a)~(d). The changing behavior of the Seebeck coefficient of  $SrTi_{1-x}Zr_xO_3$  samples with temperature is shown in Fig. 4(a). In this research, the negative values of Seebeck coefficient as well as the Hall coefficient of all the samples in the experimental temperature range confirming that they are an n-type conducting and the major carriers are electrons. Generally, the absolute value of the Seebeck

coefficient depends on both carrier concentration and temperature and it should increase in magnitude with increasing measurement temperature and decreasing charge carrier concentration, [18]. In this study, the Seebeck coefficient increased with increasing temperature due to decreasing the chemical potential of the materials [19]. The absolute value of the Seebeck coefficient decreased with increasing Zr contents due to the fact that the carrier concentration slightly increased with increasing Zr contents (as shown in Table 1). The maximum absolute value of the Seebeck coefficient was observed for x = 0.02 mole of Zr contents.

The changing of electrical conductivity of  $SrTi_{1.x}Zr_xO_3$  samples with temperature is shown in Fig. 4(b). The electrical conductivity decreased with increasing temperature up to x = 0.05 mole of Zr-doping level due to the degenerating behavior. The electrical conductivity of  $SrTi_{1-x}Zr_xO_3$  samples is higher than that of pure  $SrTiO_3$  because the carrier concentration of  $SrTi_{1-x}Zr_xO_3$  samples slightly increased due to the replacement of  $Ti^{4+}$  by  $Zr^{4+}$ . The similar observation was reported by Mahmud et al [20]. In this study, the electrical conductivity increased with increasing doping level of Zr up to x = 0.03 mole due to the increasing behavior of the carrier mobility is



Fig. 4. Temperature dependence TE properties of  $SrTi_{1-x}Zr_xO_3$  samples: (a) Seebeck coefficient, (b) electrical conductivity, (c) thermal conductivity, and (d) lattice thermal conductivity.

explained by the grain size effect. The grain size increased with increasing Zr contents up to x = 0.03mole (as shown in Fig. 3) which may be increased the conduction process as well as increased the electrical conductivity. The increasing behavior of the carrier mobility also could be related to the increases of relative density which also increased the conduction process. A similar result has been reported that the average grain size increased with La doping in the SrTiO<sub>3</sub>, which enhanced the conduction process [21, 22]. The electrical conductivity then decreased with doping level of x > 0.03 mole due to low carrier mobility which is attributed to the decreases of grain size. The decreasing behavior of grain size could be explained based on a pinning effect due to the secondary phases as indicated in the XRD patterns, Fig. 1(a).

The changing behavior of the thermal conductivity and lattice thermal conductivity of SrTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> samples with temperature is shown in Fig. 4(c) and Fig. 4(d). The thermal conductivity,  $\kappa$ , is the contribution of both of the lattice thermal conductivity,  $\kappa_{L}$  by phonons and the electronic thermal conductivity,  $\kappa_{E}$  by carriers. From the Wiedemann-Franz law, the thermal conductivity is given by Eq. (1):

$$\kappa = \kappa_{\rm L} + \kappa_{\rm E} = \kappa_{\rm L} + L_0 \sigma T \tag{1}$$

where L<sub>0</sub> is a constant called Lorentz's number, and its value is  $2.44 \times 10^8 \text{ J}^2 \text{ K}^{-2} \text{ C}^{-2}$ . In this study, lattice thermal conductivity is 6.54 Wm<sup>-1</sup>K<sup>-1</sup> (approximately 98.94%) for x = 0.02 mole Zr-doped sample at room temperature plays a major role to the total thermal conductivity (6.61  $\text{Wm}^{-1}\text{K}^{-1}$ ). The lattice thermal conductivity decreased with increasing doping level up to x = 0.05 mole; hence, the total thermal conductivity decreased. The decreasing behavior is caused by the decreased thermal diffusivity [21]. A similar result was reported by Shang et al. and Otha et al. [22, 23]. Another important factor for reducing the thermal conductivity is the reduced phonon scattering due to the presence of a second phase. The second phase located inside the grain

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Fig. 5. Temperature dependence ZT values of  $SrTi_{1-x}Zr_xO_3$ samples.

The ZT values calculated from the measured Seebeck coefficient, electrical conductivity and thermal conductivity for the SrTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> samples are shown in Fig. 5. From the figure, it is clearly seen that, for all doping levels, ZT increased with increasing temperature up to 873 K. It is also shows that the ZT value increased with increasing doping level up to x = 0.03 mole of Zr. This increased behavior of ZT value is related to the increased power factor with decreased thermal conductivity. This result suggests that the thermoelectric figure of merit of SrTiO<sub>3</sub> can be increased by careful incorporation of Zr dopant. In this study, the SrTi<sub>0.97</sub>Zr<sub>0.03</sub>O<sub>3</sub> sample shows relatively high power factor with relatively low thermal conductivity thus the highest value of the dimensionless figure of merit.

# Conclusions

The Zr-doped SrTiO<sub>3</sub> with different doping level was successfully synthesized by using a conventional solidstate reaction method and vacuum hot-pressing process. The substitution of Zr was confirmed by the phase characterization such as X-ray diffraction patterns and scanning electron micrographs of the Zr-doped SrTiO<sub>3</sub> samples. The changing behavior of electronic and thermal transport properties of Zr-doped SrTiO<sub>3</sub> with temperature has been investigated in this study. The Seebeck coefficient decreased with increasing doping level but the electrical conductivity increased with increasing doping level of Zr. The power factor thus increased due to increase electrical conductivity up to x = 0.03 mole of Zr contents. The thermal conductivity decreased with increasing doping level of Zr up to x = 0.03 mole. Therefore the dimensionless figure of merit obviously enhanced by the high value of power factor with a relatively low value of thermal conductivity. In this research, the SrTi<sub>0.97</sub>Zr<sub>0.03</sub>O<sub>3</sub> sample shows the highest value of the figure of merit, ZT = 0.15 at 873 K.



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