Thermoelectric Properties of Dy-Doped SrTiO₃ Ceramics

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Sr_{1-x}Dy_xTiO₃ ($x = 0.02, 0.05, 0.10$) ceramics were prepared by the reduced solid-state reaction method, and their thermoelectric properties were investigated from room temperature to 973 K. The resistivity increases with temperature, showing metallic behavior. The Seebeck coefficients tend to saturate at high temperatures, presenting narrow-band behavior, as proved by *ab initio* calculations of the electronic structure. The magnitudes of the Seebeck coefficient and the electrical resistivity decrease with increasing Dy content. At the same time, the thermal conductivity decreases because the lattice thermal conductivity is reduced by Dy substitution. The maximum value of the figure of merit reaches 0.25 at 973 K for the Sr_{0.9}Dy_{0.1}TiO₃ sample.

Key words: Strontium titanates, thermoelectric properties, narrow band

INTRODUCTION

Thermoelectric oxides, a group of materials capable of converting thermal energy into electrical energy, have attracted growing attention because of their intrinsic advantages, including low manufacturing cost, nontoxic character, and high service temperatures. The conversion performance is evaluated by the thermoelectric figure of merit $ZT = S^2T/\rho\kappa$, where T , S , ρ , and κ represent the absolute temperature, Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively. SrTiO₃ is one of the most important candidate n -type thermoelectric oxides,^{1,2} and many researchers have studied the thermoelectric properties of SrTiO₃-based materials.^{3–7} There have been many investigations into fabrication methods for SrTiO₃ ceramics, for example, the hydrothermal method,⁸ the sol-gel method,⁹ combustion synthesis combined with spark plasma sintering (SPS),¹⁰ and the solid-state reaction method (SSR).¹¹ In our previous studies, it was found that performing the solid-state reaction method in an oxygen-reduced atmosphere (reduced SSR method) could significantly improve the thermoelectric performance of

SrTiO₃-based materials.^{12–14} This method has many benefits: it only requires simple equipment, it has a lower operating temperature than the traditional SSR method, and it produces samples of high density, comparable to that of samples prepared by SPS.^{12,13} It could be widely used in the preparation of n -type thermoelectric oxides.

Lanthanide elements are frequently used to modify the physical properties of thermoelectric oxides. Muta et al.¹⁵ reported the thermoelectric properties of SrTiO₃ doped by several lanthanide elements, and found that Dy-doped samples present the highest thermoelectric performance ($ZT \approx 0.22$). However, those samples were prepared by conventional SSR method, and the densities were relatively low. It is necessary to investigate the thermoelectric properties of Dy-doped SrTiO₃ ceramics prepared by the reduced SSR method, which might present higher thermoelectric performance.

EXPERIMENTAL PROCEDURES

Sr_{1-x}Dy_xTiO₃ ($x = 0.02, 0.05, 0.10$) ceramics were prepared by the reduced solid-state reaction technique using high-purity SrCO₃ (99.8%), TiO₂ (99.8%), and Dy₂O₃ (99.99%) powders. Appropriate amounts of the starting materials were ground and pressed into pellet discs. These discs were calcined

Fig. 1. XRD patterns for $\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ ($x = 0.02, 0.05, 0.10$) ceramics.

at 1300°C for 6 h in an air atmosphere. Then, after intermediate grinding and pressing, the discs were sintered at 1450°C for 4 h in a reduced atmosphere (5 mol.% hydrogen in argon). The phase structures were investigated by powder x-ray diffraction (XRD) with a Rigaku D/MAX-2550P diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 0.154056$ nm). The sintered discs were cut into rectangular columns ($16\text{ mm} \times 2\text{ mm} \times 2\text{ mm}$) for measurement of the Seebeck coefficient and the electrical resistivity using an ULVAC ZEM-2 instrument in a helium atmosphere. The thermal conductivity was calculated from the thermal diffusivity, the specific heat capacity, and the sample density measured on a laser flash apparatus (Netzsch LFA 427), on a thermal analyzer (Netzsch STA 449C), and by Archimedes' method, respectively.

RESULTS AND DISCUSSION

XRD patterns from the $\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ powders are shown in Fig. 1. All samples are of single phase and have cubic structure. The lattice parameters and theoretical densities of samples were calculated from the XRD data and are listed in Table I. The sample densities were measured by Archimedes' method, and then the relative densities were obtained. The measured densities and relative densities are also listed in Table I. The relative densities of all samples are higher than 95%, comparable to those of samples prepared by SPS.¹⁰

The temperature dependence of the electrical resistivity (ρ) of the $\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ ceramics is shown in Fig. 2. To show all of the data clearly, the resistivity of the $\text{Sr}_{0.98}\text{Dy}_{0.02}\text{TiO}_3$ sample is shown as $\rho/2$. As the Dy content increases, the electrical resistivity decreases, indicating that more carriers are introduced. ρ of each of the samples shows metallic behavior at high temperatures, increasing with temperature as T^α , as shown in Fig. 2 by the solid

lines. The deviation near room temperature may be due to localization caused by disorder. Such insulating behavior was not observed in single crystals,¹⁶ therefore the disorder might be related to grain boundaries. The power α was fitted to be approximately 2.7, as listed in Table I. This indicates that there are several types of scattering mechanism that influence the carrier transport, such as electron–electron scattering (T^2), electron–acoustic phonon scattering (T^5 , at high temperatures), and electron–optical phonon scattering.¹⁷ The power (~ 2.7) in the resistivity of $\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ ceramics is larger than that (~ 2.0) in $\text{Sr}_{1-x}\text{Nd}_x\text{TiO}_3$ ceramics.¹³ This larger power may come from the stronger electron–acoustic phonon scattering in $\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ ceramics.

The temperature dependence of the Seebeck coefficient of $\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ ($x = 0.02, 0.05, 0.10$) ceramics is shown in Fig. 3. The Seebeck coefficient of all samples is negative and increases with increasing Dy content, showing that electron carriers are introduced by Dy substitution. In the low temperature region, the Seebeck coefficient decreases with increasing temperature. However, at high temperatures, the Seebeck coefficient tends to saturate, with a slope decreasing towards zero. In the $\text{Sr}_{0.98}\text{Dy}_{0.02}\text{TiO}_3$ sample, the Seebeck coefficient is temperature independent at high temperatures. In the other two samples, such temperature-independent behavior might occur at temperatures higher than we measured, because the saturation temperature increases with increasing doping content.^{12,13} This saturation behavior indicates that there is a narrow conduction band around the Fermi energy E_F , according to the Heikes theory.¹⁸ This narrow-band feature was proved by the *ab initio* calculation of the density of states (DOS) of $\text{Sr}_{0.875}\text{Dy}_{0.125}\text{TiO}_3$. The electronic structure calculations were performed using the full-potential linearized augmented plane wave (FLAPW) method in the framework of density functional theory, as implemented in WIEN2K.¹⁹ The exchange and correlation potential is considered in the generalized gradient approximation (GGA) proposed by Perdew et al.²⁰ The details of the calculation will be published elsewhere. The calculated DOS is plotted in Fig. 4. After Dy doping of SrTiO_3 , the Fermi level shifts in the bottom of the conduction band, and a narrow band associated with the 4f states of Dy occurs near the conduction-band edge. This narrow band dominates the behavior of the Seebeck coefficient.

The temperature dependence of the total thermal conductivity is shown in Fig. 5. It can be seen that Dy substitution for Sr causes a decrease in the thermal conductivity. The thermal conductivity of all of the samples decreases with increasing temperature. The total thermal conductivity can be expressed by the sum of the lattice component (κ_l) and the electronic component (κ_e) as $\kappa = \kappa_l + \kappa_e$. κ_e can be estimated from the Wiedemann–Franz law

Table I. List of lattice parameters, sample density, theoretical density, relative density, and the fitted power α

	a (nm)	Theoretical Density (g/cm ³)	Density (g/cm ³)	Relative Density (%)	α
$x = 0.02$	0.3892	5.213	5.010	96.1	2.60
$x = 0.05$	0.3894	5.268	5.107	96.9	2.78
$x = 0.10$	0.3883	5.419	5.158	95.2	2.67

Fig. 2. Temperature dependence of electrical resistivity of Sr_{1-x}Dy_xTiO₃ ($x = 0.02, 0.05, 0.10$) ceramics. The lines are fitting results changing with temperature as T^{α} . **Fig. 4.** Density of states (DOS) of Sr_{0.875}Dy_{0.125}TiO₃ from *ab initio* calculations. The Fermi level lies at 0 eV. **Fig. 3.** Temperature dependence of Seebeck coefficient of Sr_{1-x}Dy_xTiO₃ ceramics. **Fig. 5.** Temperature dependence of thermal conductivity of Sr_{1-x}Dy_xTiO₃ ceramics.

as $\kappa_e = LT/\rho$ (here $L = 2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ is the Lorenz number). Consequently, κ_l can be obtained from κ and κ_e , as shown in Fig. 6. By comparing Fig. 5 with Fig. 6, it can be seen that the temperature dependences of the lattice thermal conductivity κ_l are similar to those of the total thermal conductivity. This result indicates that the thermal conductivity of Sr_{1-x}Dy_xTiO₃ is primarily determined by the lattice thermal conductivity.

Figure 7 shows the temperature dependence of the dimensionless figure of merit ZT of Sr_{1-x}Dy_xTiO₃ ceramics. The ZT values of all of the samples increase with increasing temperature. The maximum ZT value of each sample increases with increasing Dy concentration and reaches 0.25 at 973 K for the Sr_{0.9}Dy_{0.1}TiO₃ sample, which is larger than that in Ref. 15. It is thereby shown that the

Fig. 6. Temperature dependence of lattice thermal conductivity of $\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ ceramics.

Fig. 7. Temperature dependence of figure of merit ZT of $\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ ceramics.

reduced SSR method is better than the conventional SSR method for preparation of thermoelectric SrTiO_3 ceramics. Moreover, as compared with the samples prepared by the same reduced SSR method, the ZT value of $\text{Sr}_{0.9}\text{Dy}_{0.1}\text{TiO}_3$ ceramic is larger than that of $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ (0.21)¹² but smaller than that of $\text{Sr}_{0.9}\text{Nd}_{0.1}\text{TiO}_3$ (0.29),¹³ while the Dy-doped sample presented the highest ZT value in Ref. 15. This indicates that the effects of doping different lanthanide elements into SrTiO_3 should be further investigated in samples prepared by the reduced SSR method.

CONCLUSIONS

$\text{Sr}_{1-x}\text{Dy}_x\text{TiO}_3$ ($x = 0.02, 0.05, 0.10$) ceramics were prepared by the reduced solid-state reaction method, and their thermoelectric properties were

investigated from room temperature to 973 K. The resistivity increases with temperature, showing metallic behavior. The Seebeck coefficients tend to saturate at high temperatures, presenting narrow-band behavior, as proved by *ab initio* calculations of the electronic structure. The magnitudes of the Seebeck coefficient and the electrical resistivity decrease with increasing Dy content. At the same time, the thermal conductivity decreases because the lattice thermal conductivity is reduced by Dy substitution. The maximum value of the figure of merit reaches 0.25 at 973 K for the $\text{Sr}_{0.9}\text{Dy}_{0.1}\text{TiO}_3$ sample.

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