THERMOELECTRIC PROPERTIES OF RARE EARTH-DOPED SRTIO$_3$ PREPARED BY COMBUSTION SYNTHESIS(CS) AND SPARK PLASMA SINTERING(SPS)[1]

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Abstract

Thermoelectric properties of combustion synthesized and spark plasma sintered rare-earth-doped (Y, La, Sm, Gd and Dy) $SrTiO_3$ was investigated from room temperature to 870 K from viewpoint of energy and time saving without deterioration in thermoelectric properties. All single phases of rare-earth-doped $SrTiO_3$ were successfully synthesized and sintered with high densities. With temperature increasing, the absolute value of Seebeck coefficient of all the samples increased and the electric conductivity decreased; the power factor of all the samples decreased except Y-doped sample in the considering temperature range. In all the samples, the La-doped sample and the Y-doped sample had the highest and lowest power factor, respectively. The figure of merit of La-doped samples with different doping amounts was evaluated and the maximum figure of merit 0.22 was obtained at 800 K from $Sr_{0.92}La_{0.08}TiO_3$ sample. Comparing Y and La-doped samples prepared by our synthesis method with that of conventional solid-state reaction method, the thermoelectric properties of our samples were relatively higher. Thus the combination of combustion synthesis and spark plasma sintering has a potential to prepare perovskite-oxide materials with relatively higher thermoelectric properties for high-temperature application.

Key words: Thermoelectric properties; Combustion synthesis; Spark plasma sintering; Rare earth; Power factor

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[1] *Technical contribution to the 7th Japan-Brazil Symposium on Dust Processin-Energy-Environment in Metallurgical Industries and 1st International Seminar on Self-reducing and Cold Bold Agglomeration, September 8-10 2008, São Paulo City – São Paulo State – Brazil*

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1 INTRODUCTION

In the process of ironmaking and steelmaking, a large amount of heat is exhausted. For example, in a typical steelworks in Japan, the outflow heat is 11.14 GJ/t-s, however, the recovery ratio of outflow heat is only 17.5% in enthalpy basis and 25.3% in exergy basis. There are still large rooms for exhaust heat recovery in steelworks.

Thermoelectric material is recently concerned very much because it can be used to convert thermal energy into electric energy directly and vice versa.[1-3] The energy conversion properties of the material is usually evaluated by dimensionless figure of merit ZT, which is defined as

$$ZT = T\alpha^2\sigma/\kappa \qquad (1)$$

where T, α, σ, and κ are the absolute temperature (K), Seebeck coefficient ($\mu V \cdot K^{-1}$), electric conductivity ($S \cdot m^{-1}$), and thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$), respectively; $\alpha^2\sigma$ is called power factor ($W \cdot m^{-1} \cdot K^{-2}$). [4,5]

Recently, a typical transition metal perovskite-oxide $SrTiO_3$ has attracted considerable research interest in thermoelectric application [6-8] because the electron-doped $SrTiO_3$ has relatively high mobility and large effective mass, which results in high electric conductivity as well as large negative Seebeck coefficient. Okuda *et al.* [9] studied the thermoelectric properties of single crystals $Sr_{1-x}La_xTiO_3$ ($0 \le x \le 0.1$) and found a large power factor of 3.6×10^{-3} $Wm^{-1}K^{-2}$ at room temperature, which is comparable to that of practical bismuth telluride alloy. In order to improve the thermoelectric performance, other elements were also partially substituted for Sr or Ti site in the reported study. Muta *et al.*[10] showed an increasing ZT value of rare-earth-doped $SrTiO_3$ by decreasing the thermal conductivity without deterioration of the electrical properties. Obara *et al.*[11] measured the thermoelectric properties of Y-doped $SrTiO_3$, and found an increasing in power factor. Ohta *et al.*[12-13] prepared the La- and Nb-doped $SrTiO_3$ single crystals and obtained the maximum ZT value of 0.37 (20% Nb doped), which is the largest value among *n*-type perovskite oxide semiconductors ever reported. Although the thermoelectric properties of these electron-doped $SrTiO_3$ were still low compared with the up-to-date intermetallic materials, perovskite oxide has its special advantages, such as good heat, oxidation resistance and low toxicity; therefore, it has potential for high-temperature *n*-type thermoelectric application.

The polycrystalline perovskite oxide is usually synthesized by the conventional solid-state reaction (SSR) method, which has already been widely used in the production of many electronic ceramics such as PZT (lead-zirconate-titanate ceramics) and $BaTiO_3$.[14-16] However, in SSR method, the materials are usually calcined several times to obtain a homogeneous production; thus this method is time and energy consuming. Therefore, it is necessary to find an economical synthesis method.

Combustion synthesis (CS),[17,18] which uses the energy of an exothermic reaction from the raw materials without any additional energy, has been used to manufacture many inorganic materials such as, carbides, nitrides and borides. It offers many potential advantages over conventional synthesis methods, including relatively simple equipment, shorter processing times, lower energy requirements, higher product purities, and the possibility to synthesize metastable phases. Reportedly, this method has been successfully used to synthesize perovskite oxide with high purity;[19-23] the production of

CS is usually porous, which is easy to be ground into fine powder. However, no research has been reported on the thermoelectric properties of CSed perovskite oxides despite their attractiveness from an engineering viewpoint thus far. Therefore, the purpose of this paper is to study the possibility of CS to produce perovskite-oxide thermoelectric materials without deterioration in the thermoelectric properties. Based on this consideration, in present study, the CS method was explored for the synthesis of rare-earth-doped $SrTiO_3$ ($Sr_{1-x}R_xTiO_3$, R = Y, La, Sm, Gd and Dy; $0 \le x \le 1$, simplified as SRTO in this paper) and the synthesized materials were sintered by spark plasma sintering (SPS), which is an efficient method to obtain dense product in a short time. The thermoelectric properties of the product were then compared with those synthesized by the conventional method.

2 MATERIALS AND METHODS

Polycrystalline samples of SRTO were prepared from $SrCO_3$ (99.9% purity, Kanto Chemical, Tokyo, Japan), TiO_2 (99.9% purity, Kojundo Chemical, Sakado, Japan), Ti (99.9% purity, Kojundo Chemical), $NaClO_4$ (98.0% purity, Sigma–Aldrich), and the oxide of doping elements (La_2O_3, Sm_2O_3, Gd_2O_3, Dy_2O_3, 99.9% purity; Y_2O_3, 99.99% purity; Kojundo Chemical). The function and the ratio of TiO_2 to Ti will be discussed later. The desired amounts of the raw materials were mixed by ball milling at 60 revolutions per min for 3 hr in air; the raw materials were then placed in a graphite crucible (112 mm × 32 mm × 22 mm) and contacted with a disposable carbon foil that served as the igniter. The combustion was conducted in argon atmosphere at atmospheric pressure, and the foil was ignited at 50 V and 100 A at room temperature with an internal oxygen supplied from $NaClO_4$. The as synthesized samples were ultrasonic washed to remove solid NaCl and dehydrated in a vacuum drying oven (DP23, Yamato Scientific), following which, the samples were pulverized into powders by a zirconia mortar and pestle and ground by a planetary ball mill (P-6, Fritsch) operated at 350 revolutions per min for 40 min in air. The obtained powders were sintered into pellets with a diameter of 10 mm in a graphite die by the SPS (SPS-511S, Sumitomo Coal Mining). Sintering was carried out for 30 min at a pressure of 34 MPa in vacuum and the sintering temperature was 1573 K.

The phase composition and morphology of the samples were analyzed by X-ray diffraction (XRD) (Minifiex, Rigaku) and scanning electron microscope (SEM) (JSM-7000F, JEOL). The electric conductivity and the Seebeck coefficient were simultaneously measured by the Seebeck coefficient/electric resistance measurement system (ZEM-2, ULVAC-RIKO) from room temperature to 870 K. The thermal conductivity was calculated as

$$\kappa = DC_P\rho \qquad (2)$$

where D, C_P, and ρ are the thermal diffusivity ($m^2 \cdot s^{-1}$), heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$), and experimental density ($kg \cdot m^{-3}$), respectively. The densities of the samples were measured by the density measurement (Ultrapycnometer 1000, Quantachrome Ltd), and the thermal diffusivity and the heat capacity were measured by the laser flash thermal constant analyzer (TC-7000, ULVAC-RIKO).

3 RESULTS AND DISCUSSION

The equation of the reaction is as following:

$$\begin{aligned}&(1-x)\mathrm{SrCO_3}+\mathrm{Ti}+\frac{x}{2}\mathrm{R_2O_3}+\frac{4-x}{8}\mathrm{NaClO_4}\rightarrow\\&\mathrm{Sr}_{1-x}\mathrm{R}_x\mathrm{TiO_3}+\frac{4-x}{8}\mathrm{NaCl}+(1-x)\mathrm{CO_2}\end{aligned}\qquad(3)$$

In Equation (3), x is the doping amount; R_2O_3 indicates the rare-earth metal oxide. The adiabatic temperature T_{ad} of Equation (3) was calculated, which is an important parameter in CS. It refers to the temperature that would be achieved during the reaction, assuming adiabatic conditions and complete conversion of reactants into final products. For formation of compounds, it has been demonstrated empirically that the reaction will not be self-sustaining unless $T_{ad} \geq 1800$ K.[24] In our experiment, T_i was 298 K. As the result of the calculation, the T_{ad} of Equation (3) was higher than 4000 K, and the reaction was successfully ignited and propagated. However, there still had a little unreacted reagent in the production. It was believed that high propagation velocity caused by the high T_{ad} affected the process of the reaction. Therefore, TiO_2 was added in the raw materials to partly replace Ti. The TiO_2 had a two-fold effect: one was to control the reaction velocity to realize homogeneous production and the other was to reduce the cost of the raw materials. Equation (4) shows the reaction equation.

$$\begin{aligned}&(1-x)\mathrm{SrCO_3}+(1-y)\mathrm{Ti}+y\mathrm{TiO_2}+\frac{x}{2}\mathrm{R_2O_3}+\frac{4-x-4y}{8}\mathrm{NaClO_4}\rightarrow\\&\mathrm{Sr}_{1-x}\mathrm{R}_x\mathrm{TiO_3}+\frac{4-x-4y}{8}\mathrm{NaCl}+(1-x)\mathrm{CO_2}\end{aligned}\qquad(4)$$

In Equation (4), x is the ratio of doping elements, and y is the ratio of TiO_2 amount. According to the research result of Ishikawa *et al.*,[25] when the a value is higher than 0.4, the reaction cannot be ignited. Therefore, in our study, the TiO_2 ratio a was performed as 0.25 after some exploratory experiments, and the T_{ad} of Equation (4) with 0.25 TiO_2 added was a little higher than 3000 K, which was 1000 K lower than that of the Equation (3). As a result, all the reactions were ignited and propagated fully. After synthesis, the color of the samples changed from gray to dim gray, and there was a layer of white powder on the inside wall of the graphite crucible. From the X-ray diffraction analyses, the white powder was NaCl, which was evaporated during the synthesis.

Figure 1 shows the XRD patterns of the CSed SRTO powder and the analytic reagent $SrTiO_3$ (99.9% purity, Kojundo Chemical) without sintering. The samples were cubic crystals and all the peaks were corresponded to that of $SrTiO_3$ very well. No impurity peaks was detected in Figure 1, which indicated that the raw materials were fully reacted during the synthesis by adding appropriated amount of TiO_2. Table 1 shows the lattice parameters of CSed powder calculated by XRD data. In all the samples, Sm, Gd, Dy, and Y-doped samples had a decreased lattice parameter compared with that of $SrTiO_3$, which was similar to the previous report.[10] The decrease of lattice parameter was regarded to be caused by the smaller ionic radius of these rare-earth elements compared with that of Sr^{2+}. The La-doped sample had the same lattice parameter as that of the $SrTiO_3$; it was probably caused by the formation of Ti^{3+}, the ionic radius of which was larger than that of Ti^{4+}.[10] After sintering the color of the samples changed from dim gray to black, however, no impurity peaks were detected in the XRD patterns. It was considered that there was a diffusion of oxygen vacancies to the cathode during the sintering and the buildup of oxygen vacancies reduced the material and caused a color change. [26]

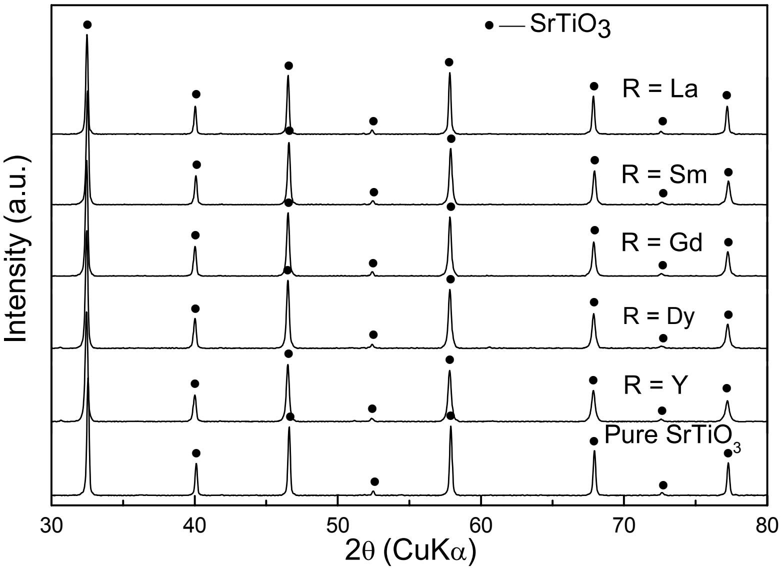

Figure 1. X-ray diffraction of the CSed SRTO powders and the analytic reagent $SrTiO_3$ before sintering.

Table 1 Characteristics of rare-earth-doped $SrTiO_3$

Sample	Lattice constant, a/nm	Bulk density, ρ/kg•m^{-3}
$SrTiO_3$	0.3905	-
$Sr_{0.95}La_{0.05}TiO_3$	0.3905	4.95×10^3
$Sr_{0.95}Sm_{0.05}TiO_3$	0.3903	5.11×10^3
$Sr_{0.95}Gd_{0.05}TiO_3$	0.3903	4.97×10^3
$Sr_{0.95}Dy_{0.05}TiO_3$	0.3903	5.23×10^3
$Sr_{0.95}Y_{0.05}TiO_3$	0.3904	5.02×10^3

Figure 2 shows the SEM cross-section images of the as synthesized SRTO bulk. The samples had homogeneous microstructures with few voids and small grains. The grain size varies in the range 2-10 μm. As shown in Table 1, the bulk densities of these samples were higher than 95% of the true density of $SrTiO_3$, which were 10% higher than the reported data of rare-earth doped $SrTiO_3$ prepared by SSR. The high density of our samples was considered to be caused by the smaller particle size and higher surface areas of our CSed powder compared with those prepared by SSR. And the CSed powders also have small crystallite size, which helps the acceleration of sintering at relatively lower temperature. Thus, the single-phase rare-earth-doped $SrTiO_3$ with high density and small crystal size was successfully obtained by CS and SPS.

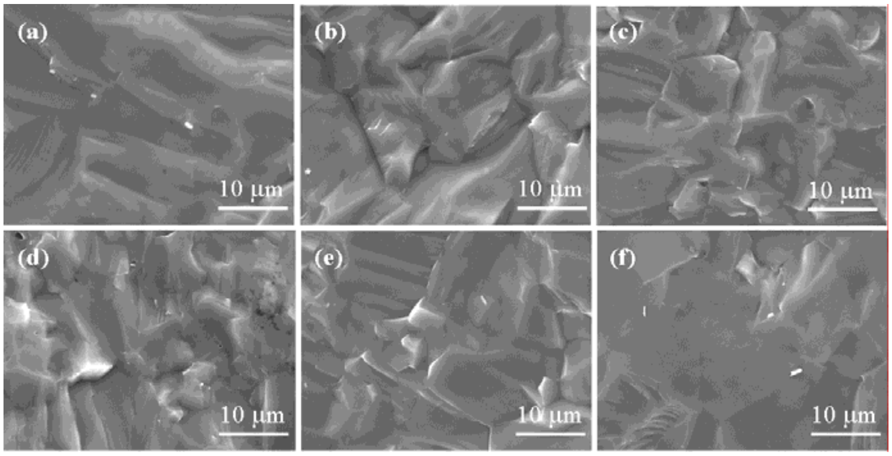

Figure 2. Scanning electron microscopy cross section images of sintered $SrTiO_3$ and $Sr_{0.95}R_{0.05}TiO_3$, (a) $SrTiO_3$, (b) R = Y, (c) R = La, (d) R = Sm, (e) R = Gd, and (f) R= Dy

Figure 3 and Figure 4 show the temperature and the doping element dependence on the Seebeck coefficient and electric conductivity, respectively. The Seebeck coefficient of all the samples in the temperature range considered was negative, which indicated that the samples were *n*-type. With the temperature increasing, the absolute value of Seebeck coefficient increased and electric conductivity decreased, showing the metallic behavior. Furthermore, with different doping element, the absolute value of the Seebeck coefficient and electric conductivity had a reverse sequence. In all the electric-doped samples, the Y-doped sample had the highest absolute value of Seebeck coefficient and lowest value of electric conductivity, and the decreasing slope of electric conductivity with the temperature was relatively lower than the other samples; on the other hand, the other elements doped samples had a similar Seebeck coefficient and electric conductivity at the same temperature.

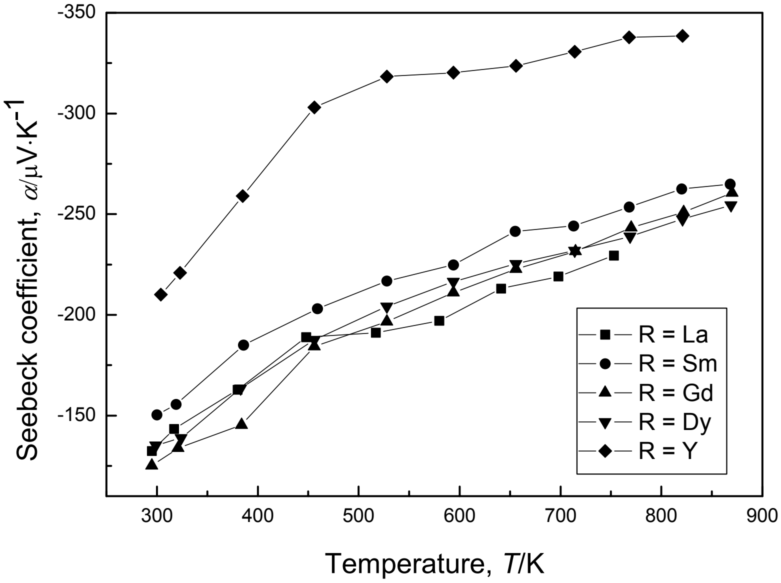

Figure 3. Temperature dependence on the Seebeck coefficient of SRTO.

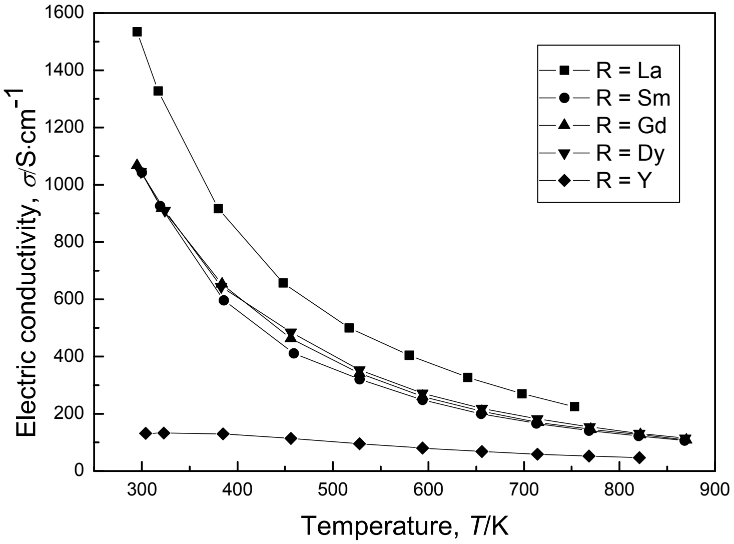

Figure 4. Temperature dependence onthe electric conductivity of SRTO.

The difference in Seebeck coefficient and electric conductivity of Y-doped sample was considered probably caused by the relatively small ionic radius of Y^{3+} with nearly equal atomic mass to Sr, which caused a stronger carrier scattering than the other elements. In Figure 3, the increasing slope of Seebeck coefficient for Y-doped sample had an obviously change at 528 K. This phenomenon was considered to be caused by the change of dominant mechanism of carrier scattering with increasing temperature from coupled scattering by polar optical phonons together with acoustic phonons to mere acoustic phonon scattering.[12]

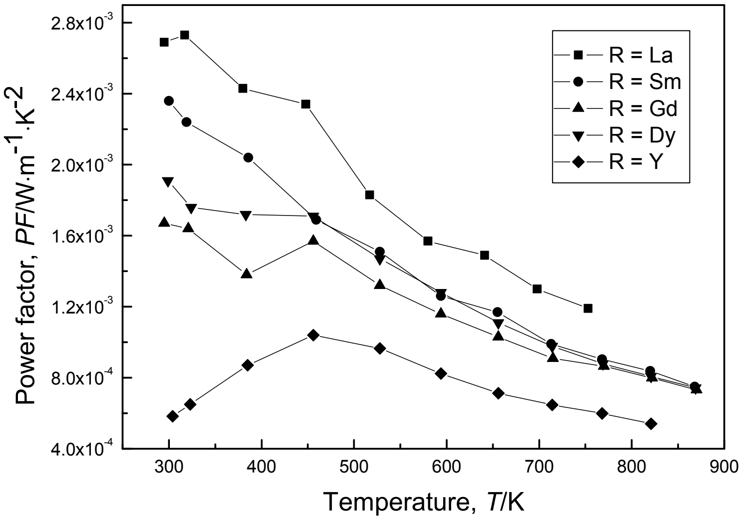

Figure 5. Temperature dependence on the power factor of SRTO.

Figure 5 shows the temperature and the doping element dependence on the power factor, which was calculated by Seebeck coefficient and electric conductivity. With temperature increasing, the power factor of La, Dy, Gd, and Sm-doped samples decreased; the power factor of Y-doped sample increased firstly then decreased and the highest power factor was 1.04×10^{-3} W·m^{-1}·K^{-1} obtained at 456 K. Compare our as synthesized Y-doped sample with the reported data synthesized by SSR and sintered by hot pressing technique at 1673 K for 1 h under a pressure of 100 MPa,[11] the temperature dependencies on the power factor were similar to the reported data, and our sample had a relatively higher power factor and the maximum power factor of our Y-doped sample was more than one time higher than the reference data of the same doping amount. It was considered that the small particle size of the CSed powder and the small crystal size caused the little higher Seebeck coefficient and electric conductivity, which resulted in the high power factor of our sample. In all these rare-earth-doped $SrTiO_3$, the La-doped sample had the highest power factor and Y-doped sample had the lowest power factor because of the low electric conductivity. The Dy, Gd and Sm doped sample has a similar power factor in the temperature range from 440 K to 870 K, which was caused by the similar Seebeck coefficient and electric conductivity as shown in Figure 3 and 4.

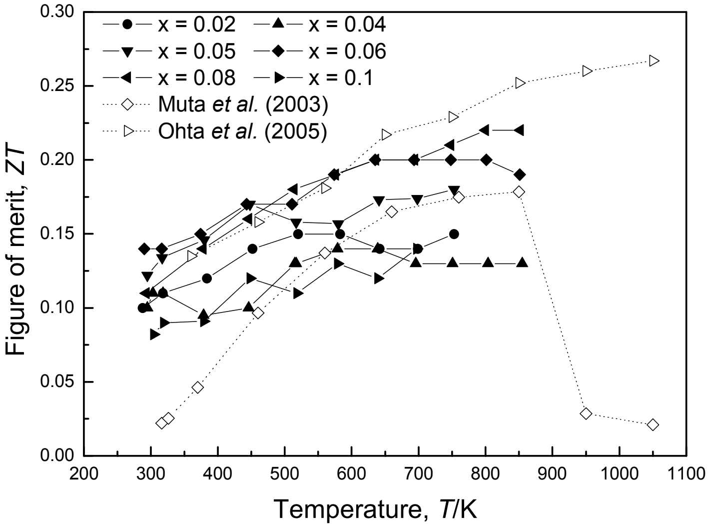

Figure 6. Temperature and La doping amount dependence on *ZT* value, together with recently reported data.[10,12]

The thermal conductivity of the La doped samples was evaluated and the *ZT* value was calculated. Figure 6 shows the temperature and doping amount dependences on *ZT* value of La doped $SrTiO_3$. The La doping amount was 0.02, 0.04, 0.05, 0.06, 0.08, and 0.1. In Figure 6, we compared our samples with the reference data[10,12] of single crystal samples and polycrystals prepared by SSR; the single crystal samples of the reference was the highest *ZT* record of La-doped $SrTiO_3$. In the temperature range considered, overall, *ZT* increased with temperature; it had a tendency to increase at even higher temperatures; this showed that the material was suitable for high-temperature application. Among all the La-doped $SrTiO_3$, the $Sr_{0.92}La_{0.08}TiO_3$ sample showed the largest *ZT* 0.22 at 800K; this value was close to the highest record of the La-doped $SrTiO_3$[12] at the same temperature. Most of our samples had higher *ZT* value than the reported data[10] prepared by SSR method. It indicated that the CS combined with SPS is an appropriate method to prepare the oxide perovskite materials for thermoelectric application because the production has high density and small crystal size which can increase the electric conductivity and decrease the thermal conductivity.

As for the other rare-earth-doped $SrTiO_3$, according to the reported thermal conductivity data,[10] the *ZT* value was estimated between 0.15 and 0.3, which was relatively higher for the thermoelectric properties of electric-doped $SrTiO_3$. Furthermore, our samples had small crystal size and the thermal conductivity was expected to be lower than the reported data, thus, our samples had the potential in relatively higher *ZT* value than the reported data. These results implied that it is possible to get an improvement in thermoelectric properties by using a CS combined with SPS technique and CS is a promising method to synthesize perovskite-oxide thermoelectric materials for high-temperature application.

4 CONCLUSIONS

Combustion synthesis, combined with spark plasma sintering, was used to produce rare-earth-doped $SrTiO_3$ perovskite-oxide materials for high-temperature thermoelectric application. The following results were obtained:

(1) The desired single-phase products with various doping elements were successfully combustion synthesized and sintered with high density by spark plasma sintering.
(2) In the temperature range considered, all the SLTO were *n*-type materials, and the Y-doped sample had highest absolute value of Seebeck coefficient and lowest electric conductivity among all the doping rare-earth elements.
(3) With temperature increasing, the power factor of Y-doped sample increased firstly and then decreased. In contrast, the other elements doped samples had a decreasing power factor with temperature on the whole.
(4) In the all rare-earth-doped $SrTiO_3$ samples, the highest and lowest power factor was obtained in the La-doped sample and Y-doped sample, respectively.
(5) With temperature increasing, the *ZT* of the La-doped $SrTiO_3$ with various doping amount from 0.02 to 0.1 showed an increasing tendency, and the maximum *ZT* of 0.22 was obtained with a doping amount of 0.08 at 800 K.
(6) Compared Y and La-doped samples with the reference data, thermoelectric properties of our samples were relatively higher than the conventional SSR method.

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