Thermoelectric Properties of Rare Earth-doped SrTiO$_3$ Using Combination of Combustion Synthesis (CS) and Spark Plasma Sintering (SPS)

Noriyuki OKINAKA, Lihua ZHANG and Tomohiro AKIYAMA

1) Center for Advanced Research of Energy Conversion Materials, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060-8628 Japan. 2) University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, China.

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Thermoelectric properties of combustion synthesized and spark plasma sintered rare-earth-doped (La, Sm, Gd, Dy and Y) 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 (CS); spark plasma sintering (SPS); rare earth; power factor; waste heat.

1. Introduction

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

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

where $T$, $\alpha$, $\sigma$, and $\kappa$ are the absolute temperature (K), Seebeck coefficient ($\mu\text{V} \cdot \text{K}^{-1}$), electric conductivity (S·m$^{-1}$), and thermal conductivity (W·m$^{-1}$·K$^{-1}$), respectively; $\alpha^2 \sigma$ is called power factor (W·m$^{-1}$·K$^{-2}$). Recently, a typical transition metal perovskite-oxide SrTiO$_3$ has attracted considerable research interest in thermoelectric application$^{4-8}$ 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$_x$TiO$_3$ ($0 \leq x \leq 0.1$); SLTO and found a large power factor of $3.6 \times 10^{-3}$ W·m$^{-1}$·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$_3$. 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.
2. Experimental Procedure

Polycrystalline samples of Sr_{0.95}R_{0.05}TiO_3 (R = La, Sm, Gd, Dy and Y) were synthesized using the combustion synthesis (CS). The adiabatic temperature (T_{ad}) was calculated as:

\[ T_{ad} = \frac{k \cdot DC_p \cdot \rho}{1 \cdot 1000} \] .................................(2)

where \( D \), \( C_p \), and \( \rho \) are the thermal diffusivity (m²·s⁻¹), heat capacity (J·kg⁻¹·K⁻¹), and experimental density (kg·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:

\[ (1-x)\text{SrCO}_3 + \text{Ti} + \frac{x}{2} \text{R}_2\text{O}_3 + \frac{4-x}{8} \text{NaClO}_4 \rightarrow \text{Sr}_{1-x}\text{R}_x\text{TiO}_3 + \frac{4-x}{8} \text{NaCl} + (1-x)\text{CO}_2 \] ...........................................(3)

In Eq. (3), \( x \) is the doping amount; \( \text{R}_2\text{O}_3 \) indicates the rare-earth metal oxide. The adiabatic temperature \( T_{ad} \) of Eq. (3) was calculated, which is an important parameter in combustion synthesis (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 \( T_{ad} \geq 1800 \text{ K} \). As the result of the calculation, the \( T_{ad} \) of Eq. (3) was higher than 4000 K, and the reaction was successfully ignited. 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.

\[ (1 - x)\text{SrCO}_3 + (1 - a)\text{Ti} + a\text{TiO}_2 + \frac{x}{2} \text{R}_2\text{O}_3 + \frac{4 - 4a - x}{8} \text{NaClO}_4 \rightarrow \text{Sr}_{1-x}\text{R}_x\text{TiO}_3 + \frac{4 - 4a - x}{8} \text{NaCl} + (1 - x)\text{CO}_2 \] ...........................................(4)

In Eq. (4), \( x \) is the ratio of doping elements, and \( a \) is the ratio of TiO_2 amount. According to the research result of Ishikawa et al., 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 Eq. (4) with 0.25 TiO_2 added was a little higher than 3000 K, which was 1000 K lower than that of the Eq. (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(a) shows the XRD patterns of the combustion synthesized (CSed) SrTiO_3 powder and the analytic reagent SrTiO_3 (99.9% purity, Koyo Chemical Co., Ltd.) before sintering. The samples were cubic crystals and all peaks were corresponded to those of SrTiO_3, very well. No impurity peaks were detected except for Dy and Y-doped samples in Fig. 1(a), which indicated that the raw materials were fully reacted during the synthesis by adding appropriate amount of TiO_2 in La, Sm, and Gd-doped samples. 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 to that of SrTiO_3, which was similar to the previous report. The decrease of lattice parameter was regarded to be caused by the smaller ionic radius of these rare-earth elements compared to that of Sr²⁺. The La-doped sample had the same lattice parameter as that of the SrTiO_3; it was probably caused by the formation of Ti³⁺, the ionic radius of which was larger than that of Ti⁴⁺. Figure 1(b) shows the XRD patterns of the spark plasma sintered (SPsed) SrTiO_3. After sintering the color of the samples changed from dim gray to black, however, no impurity peaks were detected except Y-doped sample in Fig. 1(b). It was considered that the desired single-phase products of La, Sm, Gd and Dy-doped samples were successfully CSed and sintered using SPS. Especially, only CS it was difficult to prepare single-phase product of Dy-doped sample, however, we can obtain that using com-
A combination of CS and SPS.

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 SrTiO₃, which were 10% higher than the reported data of rare-earth doped SrTiO₃ 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 SrTiO₃ with high density and small crystal size was successfully obtained by CS and SPS.

Figures 3 and 4 show the temperature and the doping element dependences 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 increasing temperature, 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. The difference in Seebeck coefficient and electric conductivity of Y-doped sample was causally-related to the relatively small carrier density caused by unexpected small doping amount.

In Fig. 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.\textsuperscript{12)}

**Figure 5** shows the temperature and the doping element dependence of the power factor, which was calculated by Seebeck coefficient and electric conductivity. With increasing temperature, 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 \(\times\) 10\(^{-3}\) W m\(^{-1}\) K\(^{-1}\) obtained at 456 K. Comparing our as synthesized Y-doped sample with the reported data on synthesized by SSR and that by hot pressing technique at 1 673 K, and 100 MPa for 1 h,\textsuperscript{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. In all these rare-earth-doped SrTiO\(_3\), La-doped sample had the highest power factor and Y-doped sample had the lowest power factor because of the low electric conductivity. Dy, Gd and Sm doped sample has a similar power factor in the temperature range from 440 to 870 K, which was caused by the similar Seebeck coefficient and electric conductivity as shown in Figs. 3 and 4.

The thermal conductivity of the La-doped SrTiO\(_3\) (SLTO) was evaluated and the \(Z\) value was calculated. **Figure 6** shows the temperature dependence of \(Z\) value of SLTO with various La doping amount measured at 0.02, 0.04, 0.05, 0.06, 0.08, and 0.1. In Fig. 6, we compared our samples with the reference data\textsuperscript{10,12)} of single crystal samples and polycrystals prepared by SSR; the single crystal samples of the reference was the highest \(Z\) record of SLTO. In the temperature range considered, overall, \(Z\) 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 SLTO, \(\text{Sr}_{0.96}\text{La}_{0.08}\text{TiO}_3\) sample showed the largest \(Z\) 0.22 at 800 K; this value was close to the highest record of SLTO\textsuperscript{12)} at the same temperature. Most of our samples had higher \(Z\) value than the reported data\textsuperscript{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,\textsuperscript{10)} the \(Z\) 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 \(Z\) 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. Conclusion

Combustion synthesis, combined with spark plasma sintering, was used to produce rare-earth-doped SrTiO$_3$ (SRTO) 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 SRTO 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$_3$ (SLTO) 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 La-doped samples with the reference data, thermoelectric properties of our samples were relatively higher than the conventional SSR method.

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