Materials Transactions, Vol. 48, No. 5 (2007) pp. 1079 to 1083

Thermoelectric Properties of Combustion-Synthesized Lanthanum-Doped Strontium Titanate

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The possibility of combustion synthesis of perovskite-oxide thermoelectric materials with the attendant saving of energy and time and without deterioration in the thermoelectric properties was investigated by evaluating the thermoelectric properties of lanthanum-doped strontium titanate ($Sr_{1-x}La_xTiO_3$, $0 \leq x \leq 0.1$). The materials were successfully combustion synthesized and spark plasma sintered with 98.0–99.6% of true density, and their thermoelectric properties were evaluated from room temperature to 850 K. The optimal lanthanum doping amount ratio x in the considered temperature range was from 0.06 to 0.08, in which $Sr_{0.92}La_{0.08}TiO_3$ sample showed the maximum ZT of 0.22 at 800 K. This value was close to the highest recorded ZT at the same temperature up to now, and the ZT of most samples are higher than those synthesized by the conventional solid state reaction method. Thus, combustion synthesis is promising for producing perovskite-oxide thermoelectric materials for high-temperature application. [doi:10.2320/matertrans.48.1079]

(Received January 9, 2007; Accepted February 20, 2007; Published April 25, 2007)

Keywords: *thermoelectric materials, perovskite oxide, combustion synthesis*

1. Introduction

Thermoelectric materials that can convert thermal energy into electric energy (Seebeck effect[1)]) and vice versa directly (Peltier effect[2)]) have been expected as a new method to achieve energy savings and recover waste heat efficiently such as the exhaust heat from power plant and steelworks.[3)] The performance of thermoelectric conversion is usually evaluated by the dimensionless figure of merit ZT, which is defined as

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

where T, α, σ, and κ are the absolute temperature, Seebeck coefficient, electric conductivity, and thermal conductivity, respectively; $\alpha^2\sigma$ is called power factor.[4,5)] The conventional intermetallic thermoelectric materials such as alloys of bismuth telluride and antimony telluride should be protected from oxidation at high temperature because of their low heat resistance and low chemical stability in air.[6)] In this regard, oxide materials that have good heat and oxidation resistance as well as low toxicity have become the focus of attention for developing chemically stable thermoelectric materials, especially since 1997, when Terasaki *et al.*[7)] found that the single crystal of the layered sodium cobalt oxide ($NaCo_2O_4$) exhibits a high thermoelectric performance. Heavily electron-doped perovskite oxide is considered as an appropriate *n*-type oxide semiconductor for high-temperature thermoelectric application.[8–12)] Okuda *et al.*[8)] found a high power factor of single crystals $Sr_{1-x}La_xTiO_3$ ($0 \leq x \leq 0.1$) at room temperature; the power factor was comparable to that of the bismuth telluride alloy. Although the ZT decreased due to the high thermal conductivity, electron-doped strontium titanate ($SrTiO_3$) had the potential to be used as a thermoelectric material. Subsequently, many studies[13–15)] were carried out on the thermoelectric properties of the doped $SrTiO_3$ of single crystals and polycrystals synthesized by solid state reaction (SSR). Evidently, the cost of single crystals is very high because the synthesis procedure involves many steps and the yield is very small. In contrast, SSR method is widely used in production of many electronic ceramics such as PZT and $BaTiO_3$. However, this method is time and energy consuming, for instance the materials are usually calcined several times for a long time to obtain a homogeneous production; there still has room for improvement. These problems of the conventional synthesis methods limit the application of the material even if the material has high thermoelectric properties; therefore, it is necessary to find an economical synthesis method. Reportedly, combustion synthesis (CS),[16,17)] which uses the energy of an exothermic reaction from the raw materials without any additional energy, can produce polycrystalline $SrTiO_3$ successfully;[18,19)] however, thus far, no research has been reported on the thermoelectric properties of these CSed materials despite their attractiveness from an engineering viewpoint. 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 La-doped $SrTiO_3$ and the thermoelectric properties of the product were compared with those of the single crystal samples and polycrystalline samples synthesized by the conventional methods.

2. Experimental Procedure

Polycrystalline samples of $Sr_{1-x}La_xTiO_3$ ($0 \leq x \leq 0.1$) (SLTO) were prepared from strontium carbonate ($SrCO_3$, 99.9% purity, Kanto Chemical, Tokyo, Japan), titania (TiO_2, 99.9% purity, Kojundo Chemical, Sakado, Japan), titanium (Ti, 99.9% purity, Kojundo Chemical, Sakado, Japan), lanthanum oxide (La_2O_3, 99.9% purity, Kojundo Chemical, Sakado, Japan), and sodium perchlorate ($NaClO_4$, 98.0% purity, Sigma–Aldrich, St. Louis, USA) as raw materials. It should be noted that the addition of TiO_2 in the raw materials

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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. In this study, the ratio of Ti to TiO_2 was 0.75 : 0.25. Appropriate amounts of the raw materials were mixed by ball milling at 60 revolutions per min for 3 h 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 ignitor. 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 supply from $NaClO_4$. The CSed samples were ultrasonic washed to remove solid sodium chloride (NaCl) and dehydrated in a vacuum drying oven (DP23, Yamato Scientific, Tokyo, Japan), following which, the samples were pulverized into powders by a zirconia mortar and pestle and ground by a planetary ball mill (Pulverisette 6, Fritsch, Idar-Oberstein, Germany) operated at 350 revolutions per min for 40 min in air. The obtained powders were sintered into a pellet with a diameter of 10 mm in a graphite die by the spark plasma sintering (SPS) method (SPS-511S, Sumitomo Coal Mining, Tokyo, Japan). 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, Tokyo, Japan) and scanning electron microscope (SEM) (JSM-7000F, JEOL, Tokyo, Japan). The electric conductivity and the Seebeck coefficient were simultaneously measured by the Seebeck coefficient/electric resistance measuring system (ZEM-2, ULVAC-RIKO, Yokohama, Japan) from room temperature to 850 K. The thermal conductivity was calculated as

$$\kappa = DC_P d \tag{2}$$

where D, C_P, and d are the thermal diffusivity, heat capacity, and experimental density, respectively. The densities of the samples were measured by the Archimedes method, and the thermal diffusivity and the heat capacity were measured by the laser flash thermal constant analyzer (TC-7000, ULVAC-RIKO, Yokohama, Japan).

3. Results and Discussion

3.1 Reaction analyses and the crystal structure of SLTO

The equation of the reaction is as follows:

$$\begin{aligned}&(1-x)\mathrm{SrCO_3} + 0.75\mathrm{Ti} + 0.25\mathrm{TiO_2}\\&\quad + \frac{x}{2}\mathrm{La_2O_3} + \frac{3-x}{8}\mathrm{NaClO_4} \rightarrow\\&\mathrm{Sr}_{1-x}\mathrm{La}_x\mathrm{TiO_3} + \frac{3-x}{8}\mathrm{NaCl} + (1-x)\mathrm{CO_2}\uparrow\end{aligned} \tag{3}$$

In eq. (3), x is the ratio of the La doping amount. In all the experiments, the mixtures of raw materials were successfully ignited and propagated. During CS procedure, a large amount of white smoke was emitted because of the evaporation of the NaCl produced. The propagation time was very short, 3–10 s. Figure 1 shows the XRD patterns of the CSed powder before sintering. XRD pattern of the analytic reagent $SrTiO_3$ (99.9% purity, Kojundo Chemical, Sakado, Japan) was also shown in Fig. 1. The samples were cubic crystals and all the peaks were corresponded to that of $SrTiO_3$ very well; this indicated that SLTO with high purity was prepared by CS. After sintering, there was no difference in the XRD patterns between the samples before and after SPS; it indicated that there was no phase change during the sintering.

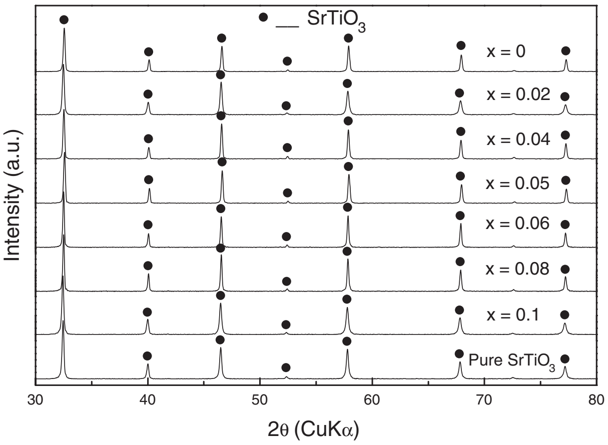

Fig. 1 X-ray diffraction patterns of the CSed $\mathrm{Sr}_{1-x}\mathrm{La}_x\mathrm{TiO_3}$ and the analytic reagent $SrTiO_3$ powders before sintering.

Figure 2 shows the SEM cross-section images of the CSed SLTO. In this paper, CSed SLTO implies the combustion-synthesized and spark plasma sintered SLTO. The samples were dense and had few voids. The bulk densities of all the samples were 98.0–99.6% of the true density of $SrTiO_3$ and the grain size of all the samples varied in the range 2–10 µm. In conclusion, dense SLTO were successfully prepared by CS combined with SPS.

3.2 Thermoelectric properties of CSed SLTO at room temperature

Figure 3 shows the doping amount dependence on the Seebeck coefficient, electric conductivity, and power factor of CSed SLTO at room temperature in comparison with those of the single crystal samples reported by Okuda *et al.*[8] The Seebeck coefficient of all the samples was negative, indicating that the materials were *n*-type. In the La-doped $SrTiO_3$, the carrier concentration is determined by the concentration of ionized La donors and the singly and doubly ionized oxygen vacancies. According to the reference,[20] La acts as a fully ionized donor down to 4.2 K or lower with a solubility between $x = 0$ and $x = 0.5$; in moderately reducing atmospheres, the formation of oxygen vacancies can be neglected, thus, the charge carrier density of the sintered ceramics is almost equal to the La concentration. Therefore, in our study, it was considered that the carrier density of the SLTO mainly depended on the La doing amount. With an increase in the La doping amount, the carrier density increased, which caused the decrease in the absolute value of the Seebeck coefficient and the increase in the electric conductivity, as a result, the power factor increased firstly and then decreased, indicating that the optimal La doping amount of $SrTiO_3$ was around 0.06 at room temperature, as shown in Fig. 3(a), (b), and (c). Compared with the reported single crystal samples, the absolute value of the Seebeck coefficient of the CSed SLTO

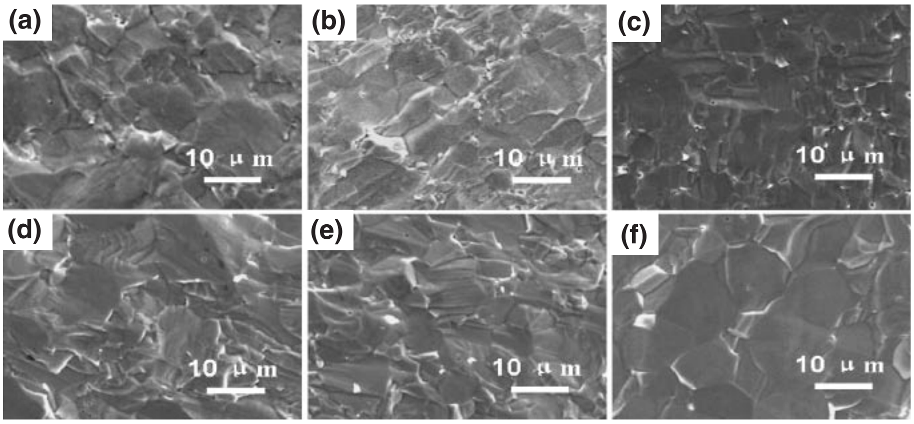

Fig. 2 Scanning electron microscopy images of the cross section of sintered $Sr_{1-x}La_xTiO_3$ (a) $x = 0.02$, (b) $x = 0.04$, (c) $x = 0.05$, (d) $x = 0.06$, (e) $x = 0.08$ and (f) $x = 0.1$.

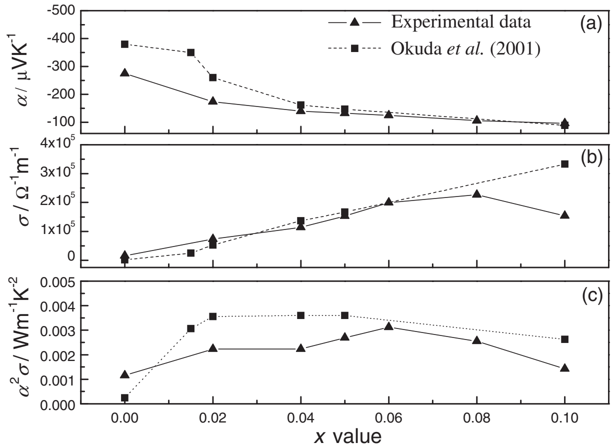

Fig. 3 La doping amount dependence on (a) Seebeck coefficient, (b) electric conductivity, and (c) power factor of $Sr_{1-x}La_xTiO_3$ at room temperature, together with the data on single crystals from Okuda *et al.*[8)]

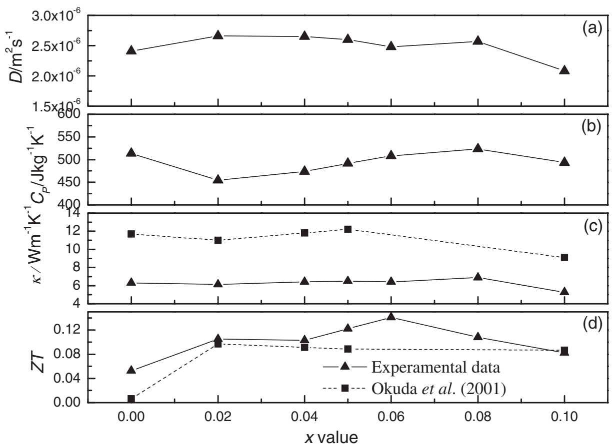

Fig. 4 La doping amount dependence on (a) thermal diffusivity, (b) heat capacity, (c) thermal conductivity, and (d) *ZT* value of $Sr_{1-x}La_xTiO_3$ at room temperature, together with the thermal conductivity and *ZT* value on single crystals from Okuda *et al.*[8)]

was slightly lower and the electric conductivity was close to that reported by Okuda *et al.*;[8)] this resulted in the lower power factor of the CSed samples.

Figure 4(a) and (b) show the doping amount dependence on the thermal diffusivity and heat capacities respectively. The thermal conductivity was calculated by eq. (2) from the above data and the densities. Figure 4(c) and (d) show the doping amount dependence on the thermal conductivity and *ZT* of CSed SLTO at room temperature in comparison with that reported by Okuda *et al.*[8)] In Fig. 4(c), the thermal conductivity of the CSed SLTO was about half of the reported single crystal samples; this was mainly caused by the phonon scattering of the grain boundary in polycrystal. At room temperature, the thermal conductivity of $Sr_{0.9}La_{0.1}TiO_3$ sample is the lowest, which was a little lower than that of the reported data[13)] prepared by conventional SSR method; the relatively lower thermal conductivity of our sample was considered to be caused by the small grain size obtained by CS and SPS, because CSed powders had small grain size, which helped the acceleration of sintering at relatively lower temperature, and the grain size increasing could also be controlled by SPS sintering method. As shown in Fig. 4(d), *ZT* of La doped $SrTiO_3$ was higher than that of $SrTiO_3$, indicating that La doping can definitely improve thermoelectric properties. Although the power factor of CSed SLTO was lower than that reported by Okuda *et al.*,[8)] the *ZT* was higher because of the low thermal conductivity. When the doping amount was increased, *ZT* initially increased and then decreased very slightly; finally, it showed a maximum value at the doping amount of 0.06. This was in accordance with the power factor of Fig. 3(c).

3.3 Dependences of temperature and doping amount on the thermoelectric properties of CSed SLTO

The temperature and La doping amount dependencies on the Seebeck coefficient and electric conductivity of CSed SLTO are shown in Figs. 5 and 6, respectively. With an increase in the temperature, the absolute value of the Seebeck coefficient increased and the electric conductivity decreased, indicating a metallic behavior. In the experimental temperature range, with an increase in the doping amount, the carrier density increased, therefore, the absolute value of the Seebeck coefficient decreased and electric conductivity increased. However, the electric conductivity of the sample with the doping amount of 0.1 was between that of the

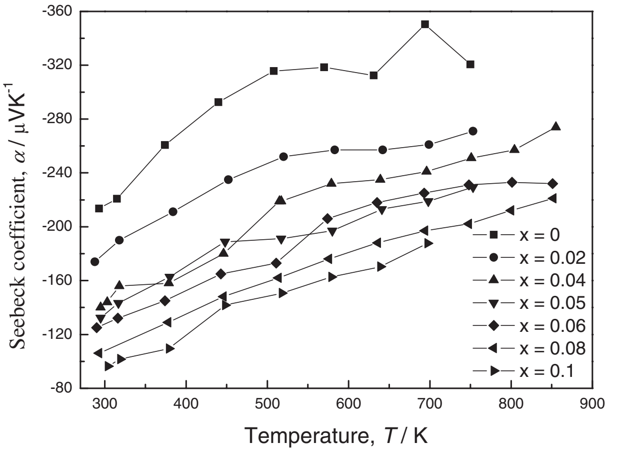

Fig. 5 Temperature and La doping amount dependence on Seebeck coefficient.

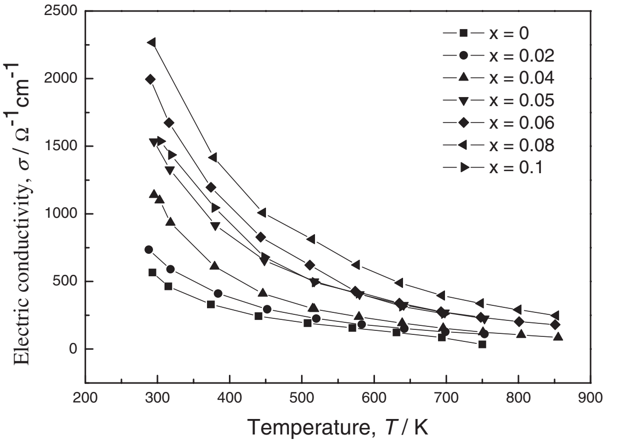

Fig. 6 Temperature and La doping amount dependence on electric conductivity.

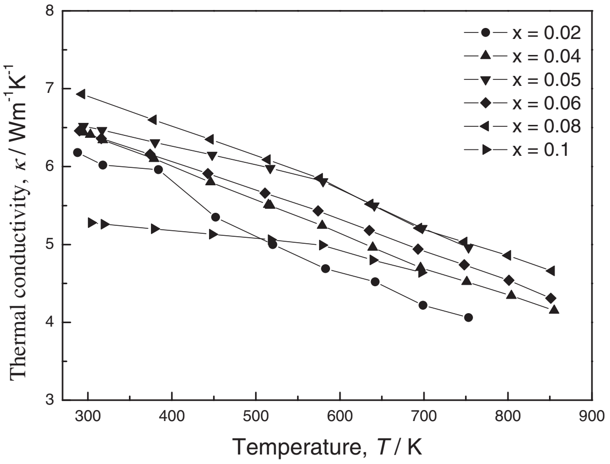

Fig. 7 Temperature and La doping amount dependence on thermal conductivity.

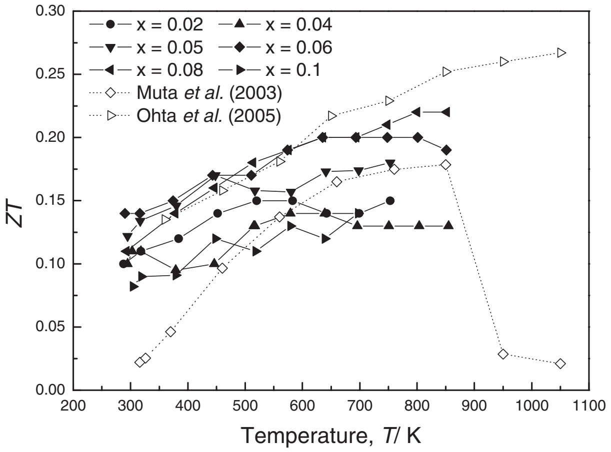

Fig. 8 Temperature and La doping amount dependence on ZT value, together with recently reported data.[13,15)]

samples with the doping amount of 0.05 and 0.06 (also as shown in Fig. 3(b)); it was probably caused by the small quantity of impurities in the sample that were not detected by the XRD. For all the samples, the electric conductivity decreased with temperature proportionally to T^{-M}, and M is in the range from 1.9 to 2.4, which showed a lattice scattering mechanism. The power of $-M$ is intermediate to the reported values: -2.7 to -3.2 at 100–300 K and -1.6 at high temperature.[21,22)]

Figure 7 shows the temperature dependencies on the thermal conductivity of CSed SLTO. The thermal conductivity decreased with the increasing temperature; this was caused by the decrease in the thermal diffusivity. Figure 8 shows the temperature dependencies on *ZT* in comparison with those of the polycrystalline samples synthesized by SSR and the single crystal samples reported by Muta *et al.*[13)] and Ohta *et al.*,[15)] respectively; the *ZT* of La-doped $SrTiO_3$ reported by Ohta *et al.*[15)] is the highest thus far. 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. The optimal La doping amount for maximizing *ZT* was 0.06 from room temperature to 500 K and 0.08 from 500 K to 850 K. Among all the CSed SLTO, the $Sr_{0.92}La_{0.08}TiO_3$ sample showed the largest *ZT* 0.22 at 800 K; this value was close to that reported by Ohta *et al.*[15)] at the same temperature. Compared with the reference data, the thermoelectric properties of the materials synthesized by CS were as good as that of the single crystals, and most samples were even better than those samples synthesized by the SSR method. These results indicated that CS was 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 the perovskite-oxide thermoelectric material La-doped $SrTiO_3$ for high-temperature application. The following results were obtained:

(1) The desired products with various doping amount ratios were successfully combustion synthesized.
(2) At room temperature, La doping increased the *ZT* of the products and the CSed SLTO had a relatively higher *ZT* compared with the reported single crystal samples.

(3) With increasing temperature, the *ZT* of the CSed SLTO showed an increasing tendency. The maximum *ZT* of 0.22 was obtained from the sample with a doping amount of 0.08 at 800 K.
(4) Under the experimental conditions, the optimal La doping amount to maximize *ZT* ranged from 0.06 to 0.08. Compared with the thermoelectric properties of the materials synthesized by the conventional method, the CSed samples had a relatively higher *ZT*.

All the results proved that combustion synthesis was a promising method to produce perovskite-oxide thermoelectric materials without deterioration in the thermoelectric properties.

Acknowledgment

This work was financially supported in part by the 21st Century COE Program "Topological Science and Technology". And we would like to express our appreciation to Prof. S. Tanda, leader of the 21st Century COE Program "Topological Science and Technology", for his technical assistance in the experiments and Mr. K. Ohkubo for his help in the thermal conductivity measurement.

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