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Author(s)	Kikuchi, Asami; Okinaka, Noriyuki; Akiyama, Tomohiro
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Large Thermoelectric Figure of Merit in La-Doped $SrTiO_3$ Prepared by Combustion Synthesis with post Spark Plasma Sintering

Asami Kikuchi[1, *], Noriyuki Okinaka[2] and Tomohiro Akiyama[2]

1. Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido, 060-8628 Japan

2. Center for Advanced Research of Energy Conversion Materials, Hokkaido University, Sapporo, Hokkaido, 060-8628 Japan

* Graduate student, Hokkaido University

* E-mail: oki@eng.hokudai.ac.jp

Abstract

We investigated figure of merit in La-doped $SrTiO_3$ prepared by Combustion Synthesis (CS) with post Spark Plasma Sintering (SPS), on which effect of sintering time was mainly examined. The samples of $Sr_{0.92}La_{0.08}TiO_3$, CSed from oxides, carbonate, metal and sodium perchlorate, was prepared by SPS at 1573 K for 1, 5, 15 and 30 min for measuring thermoelectric properties from RT to 1173K. In conclusion, only 5-min-sintered product recorded a maximum value of 0.37 in figure of merit at 1045 K.

Introduction

The last decade has seen a big surge in developing of thermoelectric oxides, with primary focus on improving the thermoelectric properties: electrical conductivity, σ [$S \cdot cm^{-1}$], Seebeck coefficient, α [$\mu V \cdot K^{-1}$], and thermal conductivity, κ [$W \cdot m^{-1} \cdot K^{-1}$]. $SrTiO_3$ [1–4], a typical transition-metal perovskite oxide, is one of the most important ceramics and many researchers have studied thermoelectric properties of $SrTiO_3$-based materials [5–10].

There have been many investigations on fabrication of $SrTiO_3$ ceramics: wet-chemical method [11], solid-state reaction method [12] and sol-gel method [13], which have already been used in the production of many materials. However, the conventional methods are quite time and energy-consuming because involving many procedures such as calcination and pulverization. To overcome this problem, L. Zhang et al. [1, 14-15] have proposed a combination of Combustion Synthesis (CS) [16] and Spark Plasma Sintering (SPS) [14, 16-22] for the synthesis of thermoelectric materials. The method proposed was suitable for synthesizing thermoelectric materials from many benefits of simple equipment, shorten operating time and relatively low operating temperature.

SPS is one of sintering methods using spark plasma phenomenon caused by charging high current between particles. Compared with conventional hot-pressed sintering method, SPS ensures a very rapid heating rate and mass transfer rate, allowing the samples sintered densely in a short period at a relatively lower temperature. Thus, grain growth of the sample might be suppressed, leading to small thermal conductivity. Consequently SPS looks more suitable for preparing thermoelectric materials [22]. Sintering conditions such as sintering temperature [23-25] and holding time during sintering affect its microstructures and properties seriously. Y. Zhao et al. [26] have reported that effects of different holding times and pressure on microstructure and mechanical properties. Significantly, they discovered that density increases with holding time and fracture toughness value depends on holding time.

A previous paper reported on the combination of CS with post SPS showed the

effect of sintering temperature on the thermoelectric properties of polycrystalline $Sr_{0.92}La_{0.08}TiO_3$ (SLTO) [15, 27] under the same condition of holding time. Key factors associated with SPS were not only sintering temperature but also holding time during sintering. However, the effect of holding time during sintering on the thermoelectric properties has never been well explained thus far. Therefore, the purpose of this paper was to investigate figure of merit in La-doped $SrTiO_3$ prepared by Combustion Synthesis (CS) with post Spark Plasma Sintering (SPS), on which effect of holding time during sintering was mainly examined. The new findings of this study will provide information to maximize figure of merit in not only $SrTiO_3$-based materials but other various oxide-based materials.

Experimental Procedure

Polycrystalline samples of $Sr_{0.92}La_{0.08}TiO_3$ (SLTO) were prepared from $SrCO_3$ (99.9% purity, Kanto Chemical, Tokyo, Japan), TiO_2 (99.9% purity, Kanto Chemical, Sakado, Japan), Ti (99.9% purity, Kojundo Chemical, Sakado, Japan), $NaClO_4$ (98.0% purity, Sigma-Aldrich, St. Louis, US10), and La_2O_3 (99.9% purity, Kojundo Chemical, Sakado, Japan). The detailed explanations on the experimental procedure have been already published in the reference elsewhere [15]. Combustion-synthesized products were pulverized into powders in a planetary ball mill (Pulverisette 6, Fritsch, Idor-Oberstein, Germany) operated at 350 rpm for 40 min in air. The average particle size of the ground powders was measured by fiber optic dynamic light-scattering photometer (Otsuka Electronics Co.,Ltd.). The powders obtained were filled in a cylindrical graphite die and sintered by SPS (SPS-511S, Sumitomo Coal Mining, Tokyo, Japan) at a heating rate of 30 $K \cdot min^{-1}$ at 1573 K [27] in vacuum. In this study, the samples were sintered at different holding times; 1, 5, 15 and 30 min, under mechanically pressurized conditions of 34 MPa by using plungers. Sintered SLTOs of 10.0mg were heated up to 1373K at a heating rate of $3K \cdot min^{-1}$ and an air-flow rate of $50ml \cdot min^{-1}$ [28]. In preliminary test, the weight of the sample reached steady state after 12h, therefore the experimental time of 24h was enough for perfect oxidation of the sample. In the experiments, the sample was oxidized to be $Sr_{0.92}La_{0.08}TiO_{3.00}$ in the electric furnace. A value of δ, oxygen defect content, was determined by measuring the weight increase of the sample after being heated at 1373 K for 24 h in air. The phase composition and morphology of the products were analyzed by using an X-ray diffractometer (Miniflex, Rigaku, Tokyo, Japan) and a Scanning Electron Microscope (SEM) (JSM-7000F, JEOL, Tokyo, Japan). Electric conductivity and Seebeck coefficient were simultaneously measured by using a Seebeck coefficient/electric resistance measuring system (ZEM-3, ULVAC-RIKO, Yokohama, Japan) from room temperature to 1045 K in helium atmosphere. Thermal conductivity was calculated as:

$$\kappa = D\, C_p d. \qquad (1)$$

where D, C_p and d are the thermal diffusivity, heat capacity and experimental density, respectively. The densities of the samples were measured by Archimedes method, and the thermal diffusivity and heat capacity were measured by the laser flash thermal constant analyzer (TC-7000, ULVAC-RIKO, Yokohama, Japan) from room temperature to 1105 K in vacuum.

Results and Discussion

1) Crystal structure of the product

The equation of the CS reaction is generally given as follows [25]:

$$(1-x)S \quad {}_3 + (1-a)T + C \quad {}_2 + i(x/2)L O_2 O_3 + (4-4a-x)/8N \quad {}_4$$
$$\rightarrow Sr_{1-x}La_xTiO_3 + (1-x)CO_2 + (4-4a-x)/8NaCl. \qquad (2)$$

In Eq. (2), x denotes the La-doping content and a, the TiO_2 content. In our study, x and a are equal to 0.08 [1] and 0.25 [16], respectively. Figure 1 shows SEM images of cross-section of SLTO sintered at 1573 K for (a) 1 min, (b) 5 min, (c) 15 min, (d) 30 min, together with image of (e) powders before sintering. The average particle size of the ground powders was found to be 0.722 μm. As shown in Fig. 1, the grain of the sintered sample gradually increased with holding time up to 15 min. Even 30 min in holding time, the grain of the sample sintered did not grow larger in comparison to 15-min-sintered one. On 30-min-sintered sample the micro-size-particles attached to large grains grew well.

Table I lists comparisons of holding time during sintering, lattice parameters of synthesized powders before SPS, which were calculated from X-ray diffraction (XRD) data, bulk density after SPS and the value of δ for each sample prepared in various sintering times. Obviously, density of samples sintered for more than 5 min reached 96.8% of the theoretical density (T.D.) (T.D. = 5.24 $g \cdot cm^{-3}$). Density of 1-min-sintered one had only 66.2% of T.D. which was 46.2% lower than that of other ones. This fact showed that bulk SLTO were densely sintered over 5 min of sintering. Lattice parameter of CSed SLTO powders was 0.3902 [nm], which agreed well with the reported papers [1].

Figure 2 shows XRD patterns of SLTO before and after sintering for different holding times, together with the data of raw materials before combustion synthesis. All peaks of the products corresponded to those of $SrTiO_3$ very well. The result shows that SLTO with high purity was well prepared. With increasing holding time, the position of

all peaks shifted to lower angle. This was probably because more oxygen defects were introduced with prolonging sintering. In contract, no appearance of other peaks in the XRD patterns of samples after SPS was observed. This means that secondary-phase has not emerged during sintering.

2) Temperature dependence of thermoelectric properties

Fig. 3 (a), (b) and (c) show the temperature dependence of electric conductivity, Seebeck coefficient and thermal conductivity of the products sintered in various times, respectively. With increasing temperature, electric conductivity decreased and the absolute value of Seebeck coefficient increased, like a metal. With increasing sintering time, electric conductivity increased and the absolute value of Seebeck coefficient decreased, except 15-min-sintered sample. Remember that the sample powder of SLTO was charged into cylindrical graphite die and sintered by SPS, in which carbon can reduce SLTO at high temperatures gradually. As a result, the product obtained after prolonged sintering changed into the nonstoichiometric compound of $Sr_{0.92}La_{0.08}TiO_{3-\delta}$, where δ is the oxygen defect content. Oxygen defects generate electrons as carriers. Therefore, the value of δ can be treated as the carrier density in this paper. Electric conductivity and Seebeck coefficient [29] can be expressed in the following equations:

$$\sigma = ne\mu. \tag{3}$$

$$\alpha = -\frac{k_B}{e}\left\{ r + 2 + \ln\frac{nh^3}{2(2\pi m^* k_B T)^{3/2}} \right\}. \tag{4}$$

In Eqs. (3) and (4), n, e, μ, k_B, r, h, m^* and T are the carrier density, the elementary charge, the mobility, Boltzmann constant, the scattering factor, Planck's constant, the effective mass and the absolute temperature, respectively. According to Eqs. (3) and (4), it is obvious that electric conductivity and Seebeck coefficient are proportion to the carrier density, in other words, they are proportion to the value of δ because the elementary charge and Seebeck coefficient have negative values in n-type semiconductor. Looking at Table 1, the amount of the δ value is 30-min- > 5-min- > 15-min- > 1-min-sintered SLTO and the δ value of 5-min-sintered sample is slightly

higher than that of 15-min-sintered sample. This tendency is very well accorded with Figs. 3 (a) and (b). As shown in Figs. 3 (a) and (b), the amount of the electric conductivity and Seebeck coefficient is 30-min- > 5-min- > 15-min- > 1-min-sintered SLTO, which is the same order as that of the value of δ. With an increase in holding time, the δ value of CSed and SPSed SLTO increased, which caused the increase of the electric conductivity and Seebeck coefficient. Thus, an increase in the holding time leads to an increase in the oxygen defect content, thereby resulting in high electric conductivity and Seebeck coefficient. The δ value of 5-min-sintered sample was larger than that of 15-min-one, which resulted in higher electric conductivity and Seebeck coefficient.

Thermal conductivity of CSed and SPSed SLTO decreased with temperature. 15-min-sintered sample and 30-min-sintered sample show a systematic decrease of the thermal conductivity with increasing temperature, indicating that the phonon-phonon scattering is dominant in the experimental temperature range. The thermal conductivities of the 1-min-sintered and 5-min-sintered samples are lower and less dependant on the temperature. This is caused by relative increase of the temperature-independent phonon-impurity scattering. The amount of the thermal conductivities is 30-min- ≈ 15-min- > 5-min- > 1-min-sintered SLTO, which is the same sequence as that of the average grain size. With an increase in holding time, average grain size of CSed and SPSed SLTO increased, which caused the decrease of the effect of phonon scattering at grain boundaries. Density of the samples also affected the thermal conductivity. 1-min-sintered sample with 66.2 %T.D. showed the smallest thermal conductivity at respective temperatures. Therefore, longer holding time during sintering made average grain size of sintered sample larger and densified, as a result, thermal conductivity of sintered sample increased with holding time during sintering.

Fig. 4 shows temperature dependence on dimensionless figure of merit with various holding times during sintering. We compared our data with reference data [1, 10] of polycrystalline $SrTiO_3$-based bulk ceramics reported by L. Zhang et al. and S. Ohta et al., respectively. In the temperature range considered, ZT of sample sintered for

1 min showed very low values due to its low electric conductivity shown in Fig. 3 (a). ZT of 5-min-sintered sample increased with temperature and it has a tendency to increase at even higher temperatures; this showed this sample is suitable for high-temperature application. Among our samples, SLTO sintered for 5 min showed the maximum ZT of 0.37 at 1045 K. This value is the largest value among $SrTiO_3$-based bulk semiconductors ever reported, along with that of Nb-doped $SrTiO_3$ epitaxial films reported by S. Ohta et al [9]. Generally, thermoelectric modules are composed of bulk polycrystalline materials, our sample can be adapted for application due to the high ZT value and suitability for high-temperature usage. The most optimum holding time during sintering was 5 min at 1573 K [27]. All of these results proved that CS with post SPS is a promising method for fabrication of thermoelectric materials.

Conclusions

We studied the effect of sintering time on figure of merit of La-doped $SrTiO_3$ which was prepared by the combination of CS with post SPS. The following results were obtained:

(1) Prolonged sintering charged more oxygen defects into the sample, which can produce electrons as carriers. Thus, samples sintered for longer time, except 15-min-sintered one, showed higher electric conductivity.

(2) Prolonged sintering grew the grain size of the sample, which caused larger thermal conductivity.

(3) The sample sintered for only 5 min recorded the maximum ZT of 0.37 at 1045 K. This is the largest value among previously reported $SrTiO_3$-based bulk semiconductors.

The results also appealed a possibility that the combination of CS with post SPS can produce commercial-available thermoelectric oxides to generate electricity efficiently.

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Caption list of figures

Fig. 1 SEM images of cross-section of SLTO sintered at 1573 K for (a) 1 min, (b) 5 min, (c) 15 min, (d) 30 min and together with image of (e) powders before sintering.

Fig. 2 X-ray diffraction patterns of SLTO before and after sintering for different holding times, together with the data of raw materials before combustion synthesis.

Fig. 3 Temperature dependence of (a) electric conductivity, (b) Seebeck coefficient and (c) thermal conductivity of CSed and SPSed SLTO with various holding times, respectively

Fig. 4 Temperature dependence on dimensionless figure of merit with various holding times during sintering, in comparison with ZT data of the heavily Nb-doped $SrTiO_3$ ceramic and La-doped $SrTiO_3$ reported by S. Ohta et al. [10] and L. Zhang et al. [1], respectively.

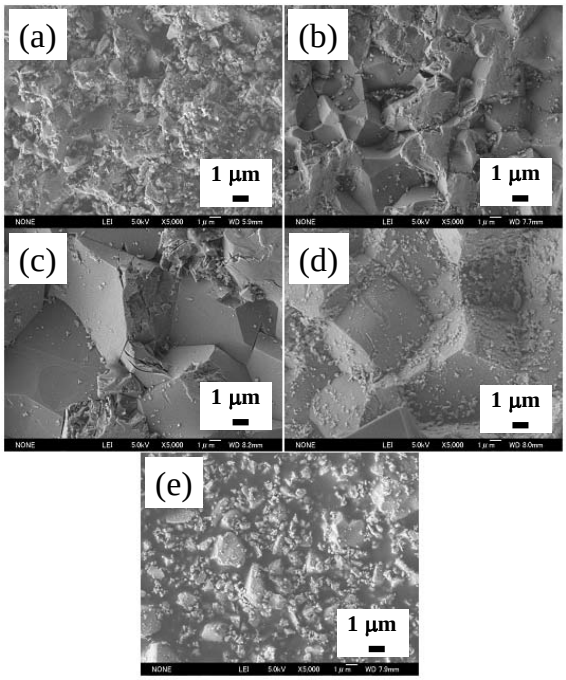
Table

Table I Lattice parameters of synthesized powders before SPS calculated from X-ray diffraction (XRD) data and comparison of sintering temperatures and bulk density after SPS. The values of δ in samples sintered at various sintering temperatures are also given.

Holding time [min]	Lattice parameter before SPS [nm]	Bulk density after SPS [g･cm^{-3}]	(%T.D.)	The value of δ [–]
1	0.3902	3.47	66.2	0.019
5		5.12	97.7	0.031
15		5.14	98.5	0.030
30		5.07	96.8	0.061

T.D.: Theoritical dencity
T.D.=5.24 [g･cm^{-3}]

Figures



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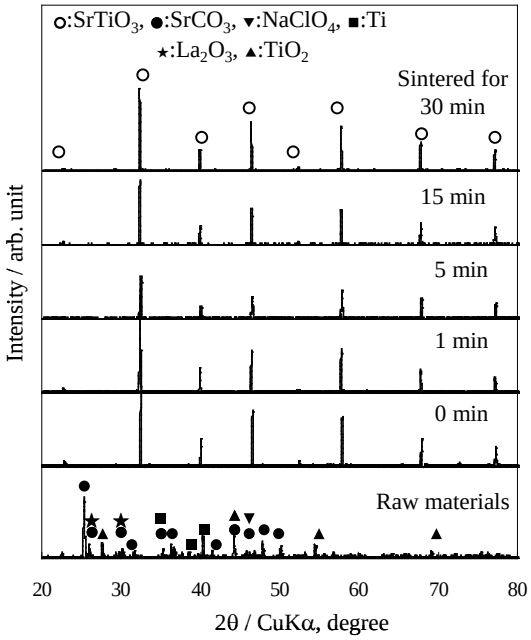

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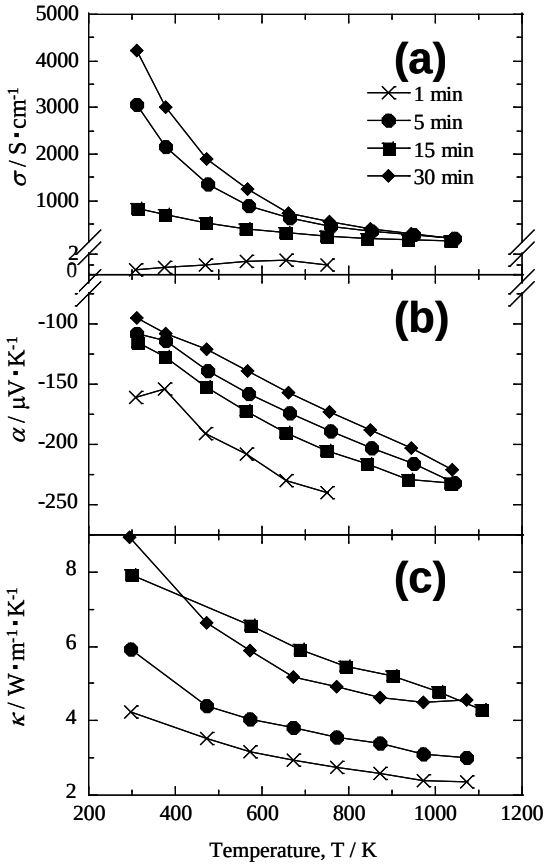

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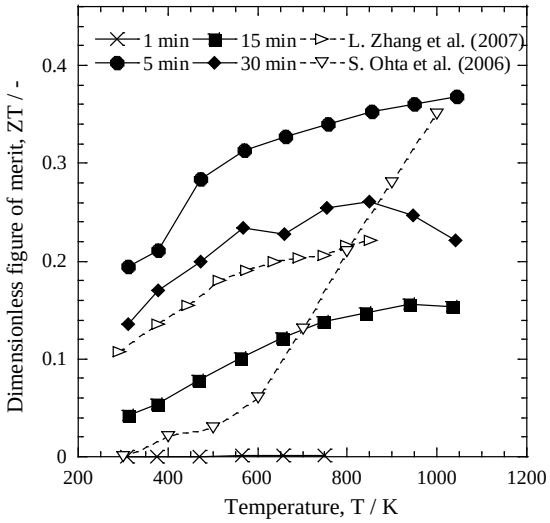

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