Thermoelectric properties of Sr-Ru-O compounds prepared by spark plasma sintering

| 著者 | 未 указан
| --- | ---
| 巻 | 49
| 号 | 3
| 項 | 600-604
| 年 | 2008
| URL | http://hdl.handle.net/10097/52385 |
Thermoelectric Properties of Sr-Ru-O Compounds Prepared by Spark Plasma Sintering

Nittaya Keawprak, Rong Tu and Takashi Goto

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Sr-Ru-O in the ratio of Ru to Sr ($R_{Ru/Sr}$) from 0.5 to 1.2 were prepared by spark plasma sintering (SPS) and the effect of composition on the electrical conductivity ($\sigma$), thermal conductivity ($\kappa$) and Seebeck coefficient ($S$) was investigated. All compositions yielded dense sintered mass with around 90–100% of a theoretical density. SrRuO$_3$ and Sr$_2$RuO$_4$ in a single phase were obtained at $R_{Ru/Sr} = 1.0$ and 0.5, respectively. The second phases were identified, i.e., RuO$_2$ and Ru at $R_{Ru/Sr} > 1.0$ and Sr$_2$RuO$_4$ and Sr$_2$RuO$_3$ at $R_{Ru/Sr} < 1.0$. The $\sigma$ increased with increasing $R_{Ru/Sr}$ in the $R_{Ru/Sr}$ range from 0.8 to 1.2 at room temperature exhibiting a metallic behavior, whereas the $\sigma$ showed a semiconducting behavior at $R_{Ru/Sr} = 0.5$. The $\kappa$ was around 2 to 7 Wm$^{-1}$K$^{-1}$ at $R_{Ru/Sr} = 0.8$ to 1.2 at room temperature and slightly increased with increasing temperature and $R_{Ru/Sr}$. The $S$ increased with increasing temperature at $R_{Ru/Sr} = 0.5$. The $S$ was around 25–40 $\mu$V/K$^{-1}$ at room temperature, almost independent of compositions. The $S$ slightly decreased with temperature at $R_{Ru/Sr} = 0.8$ to 1.0, whereas the $S$ increased with temperature and showed a maximum around 500 to 600 K at $R_{Ru/Sr} = 1.2$. The $S$ significantly decreased with increasing temperature at $R_{Ru/Sr} = 0.5$. The highest dimensionless figure of merit ($ZT$) was 0.06 at $R_{Ru/Sr} = 1.2$ at 600 K.

(Received October 2, 2007; Accepted December 4, 2007; Published January 23, 2008)

Keywords: Strontium ruthenate, thermoelectricity, spark plasma sintering

1. Introduction

The strontium ruthenates can be considered as members of Ruddlesdon-Popper series, $Sr_{n+1}Ru_{2/3}O_{n+1}$ ($n = 1, 2, 3$ and $\infty$), where $n$ is the number of corner sharing RuO$_6$ octahedra layers separated by SrO layers. The distortion degree of RuO$_6$ octahedra decreases with increasing $n$ due to the increase in the overlap of Ru-4d and O-2p orbitals. The $Sr_{n+1}Ru_{2/3}O_{n+1}$ has different electrical conductivity ($\sigma$) in $c$ direction and $ab$ plane. The anisotropy of $\sigma$ decreases with increasing $n$. The most widely studied compounds are infinite layered ($n = \infty$) SrRuO$_3$ and single layered ($n = 1$) Sr$_2$RuO$_3$. SrRuO$_3$ has an orthorhombically distorted perovskite of the GdFeO$_3$ type structure with a space group of $Pbnm$ at 10 to 800 K. However, the orthorhombicity decreases significantly above room temperature showing a tetragonal structure until 950 K, and then transforms into a cubic perovskite structure. SrRuO$_3$ shows a metallic electrical conduction. Capogna et al. reported that the electrical conductivity of SrRuO$_3$ increased from $5 \times 10^5$ to $90 \times 10^5$ Sm$^{-1}$ with decreasing temperature from room temperature to 5 K. SrRuO$_3$ has been used as a substrate for deposition of YBa$_2$Cu$_{3-x}$O$_7$ (Y123) film and high temperature superconductors due to its excellent electrical conductivity. Sr$_2$RuO$_4$ has a body-centered tetragonal K$_2$NiF$_3$ structure having a superconduction below 1 K. Sr$_2$RuO$_4$ single crystal shows metallic conduction behavior in the $ab$ plane and has a significant anisotropy in $ab$ plane and $c$ direction ($\sigma_{ab}/\sigma_c = 220$ at room temperature). Chandrasekaran et al. reported that Sr$_2$Ru$_2$O$_4$ exhibited semiconducting behavior between 15 and 300 K and the electrical conductivity changed with the oxygen defect of the Sr$_2$Ru$_2$O$_4$. Sr$_2$Ru$_2$O$_4$ has been applied as a lattice matching material of YBa$_2$Cu$_3$O$_7$ in a wide temperature range since its lattice parameters are almost independent of temperature.

Recently, strontium ruthenates have also been proposed as potential thermoelectric materials due to their high electrical conductivity and Seebeck coefficient. Maekawa et al. reported SrRuO$_3$ had high electrical conductivity and Seebeck coefficient. Zheng et al. reported the Seebeck coefficient of single crystal Sr$_2$RuO$_3$ of $ab$ plane increased from 0.1 to 9.0 $\mu$V/K$^{-1}$ with increasing temperature from 9 to 260 K. However, the electrical and thermolectric properties were studied mainly at low temperatures by using single crystals. No study on thermoelectric properties of polycrystalline Sr-Ru-O compounds was reported. This may be caused of the difficulty to obtain dense body by conventional sintering.

Spark plasma sintering (SPS) has been demonstrated as an effective method to densify hardly sinterable powder. In the present study, dense Sr-Ru-O body was prepared by spark plasma sintering (SPS), and the effect of Ru/Sr ratio ($R_{Ru/Sr}$) on the crystal structure, electrical conductivity, thermal conductivity, Seebeck coefficient and $ZT$ value of Sr-Ru-O compounds was investigated.

2. Experimental

Sr-Ru-O powders were synthesized by solid state reaction using SrCO$_3$ (99.99%) and Ru$_2$O$_3$ (99.99%) in the ratio of Ru to Sr ($R_{Ru/Sr}$) between 0.5 and 1.4. The powder mixtures were calcined at 1273 K for 43.2 ks in air. The calcined powder was pressed in a graphite die and sintered by SPS at 1523 K for 0.3 ks in a vacuum at a load of 80 MPa. The sintered body was cut to $2 \times 2 \times 10$ mm for the measurement of electrical conductivity by a d.c. 4-probe method and Seebeck coefficient by a thermoelectric power ($\Delta E$)-temperature difference ($\Delta T$) method. A disk shape specimen of 10 mm in diameter and 1 mm in thickness was employed to measure thermal conductivity by a laser flash method (ULVAC TC-7000). All electrical and thermal measurements were conducted from room temperature (RT) to 1023 K. The crystal phase was examined by X-ray diffraction (Rigaku Geigerflex). The density (d) was determined by an Archimedes method.
3. Results and Discussion

Figure 1 shows the XRD patterns of Sr-Ru-O compounds at $R_{Ru/Sr}$ = 0.5 to 1.2. SrRuO$_3$ and Sr$_2$RuO$_4$ in a single phase were obtained at $R_{Ru/Sr}$ = 1.0 (Fig. 1(c)) and 0.5 (Fig. 1(e)), respectively. Second phases of RuO$_2$ and Ru with the main phase of SrRuO$_3$ were identified at $R_{Ru/Sr}$ = 1.1 (Fig. 1(b)) and 1.0 (Fig. 1(d)). Jacob et al.\textsuperscript{14} have reported that SrRuO$_3$ formed at lower temperatures ($T < 1573$ K), and Sr$_2$RuO$_4$ and Sr$_3$Ru$_2$O$_7$ formed at higher temperature ($T > 1573$ K). Sr$_4$Ru$_3$O$_{10}$ would form at higher than 1723 K. In the present study, Sr$_4$Ru$_3$O$_{10}$ was not identified due to the low sintering temperature.

Figure 2 demonstrates the effect of $R_{Ru/Sr}$ on the lattice parameters of SrRuO$_3$ phase. At $R_{Ru/Sr}$ = 0.9 to 1.4, the lattice parameters of $a$, $b$, and $c$ were independent of $R_{Ru/Sr}$ and were constant values of 0.5570, 0.7851 and 0.5533 nm, respectively. The lattice parameters at $R_{Ru/Sr}$ = 0.7 and 0.8 were not clearly determined, due to too broad XRD peaks. It is difficult to keep the standard deviation of d-values within 0.1% by using broad peaks. Then, lattice parameters at $R_{Ru/Sr}$ = 0.7 and 0.8 was not presented. Although CaRuO$_3$ has a solid solution range of the ratio of Ru to Ca ($R_{Ru/Ca}$) = 0.7 to 1.0,\textsuperscript{15} SrRuO$_3$ should be a stoichiometric compound. The lattice parameters of Sr$_2$RuO$_4$ were $a = b = 0.3869$ and $c = 1.2742$ nm, almost the same as the reference ($a = b = 0.38694$ and $c = 1.2746$ nm).\textsuperscript{16}

Figure 3 presents the temperature dependence of the electrical conductivity ($\sigma$) of Sr-Ru-O compounds at various $R_{Ru/Sr}$. The relative densities of all specimens were around 96 to 99%. The $\sigma$ decreased with increasing temperature at $R_{Ru/Sr} > 0.5$ showing a metallic conduction, whereas the $\sigma$ at $R_{Ru/Sr} = 0.5$ slightly increased with temperature showing a semiconducting conduction. SrRuO$_3$ in a single phase ($R_{Ru/Sr} = 1.0$) had a $\sigma$ of $3 \times 10^5$ S m$^{-1}$ at 293 K, which was almost the same as that reported by Maekawa.\textsuperscript{17} The $\sigma$ of SrRuO$_3$ was higher than that of CaRuO$_3$.\textsuperscript{16} Cox et al.\textsuperscript{18} have studied the electrical conduction of SrRuO$_3$ and CaRuO$_3$ by photoelectron spectroscopy. SrRuO$_3$ showed higher electrical conductivity because of higher density of states at Fermi energy ($E_F$). Kobayashi et al.\textsuperscript{19} have studied the relationship between crystal structure and electrical conductivity of SrRuO$_3$ and CaRuO$_3$ and reported that the distortion degree.
and the angle of Ru-O-Ru bond of CaRuO₃ was higher than those of SrRuO₃, resulting in the lower electrical conductivity of CaRuO₃. The σ of Sr-Ru-O increased with increasing R_{Ru/Sr}. The high electrical conductivity at R_{Ru/Sr} > 1.0 might be caused by the second phase of RuO₂ (σ_{RuO₂} = 1.4 × 10⁴ Sm⁻¹ at 293 K). The σ at R_{Ru/Sr} < 1.0 presented a much lower values comparing with that of R_{Ru/Sr} ≥ 1.0. This might be caused by the low σ of Sr₃Ru₂O₇ and Sr₂RuO₄ second phase (σ of Sr₃Ru₂O₇ and Sr₂RuO₄ were 3.5 × 10³ Sm⁻¹ at 293 K and 5 × 10³ Sm⁻¹ at RT, respectively). The σ of Sr₂RuO₄ at room temperature was 7.2 × 10³ Sm⁻¹ and much lower than that of SrRuO₃.

Figure 4 shows the temperature dependence of electrical conductivity of single- and poly-crystalline SrRuO₃ reported in literatures. All data exhibited a metallic behavior at the whole temperature. The σ of the single-crystalline SrRuO₃ was higher than that of poly-crystalline in the present study by a factor of 2. The poly-crystalline SrRuO₃ prepared by pressureless sintering (SPS) in this study and that reported by Maekawa et al. had higher σ by factor of 3 than that prepared by pressureless sintering possibly due to the high density.

Figure 5 shows the temperature dependence of the electrical conductivity of single- and poly-crystalline Sr₂RuO₄ in literatures. The σ of Sr₂RuO₄ in this study exhibited a semiconducting behavior from RT to 1000 K (7 × 10³ to 1.6 × 10⁴ Sm⁻¹). So far, no studies on the σ of Sr₂RuO₄ at high temperatures have been reported. The σ of single-crystalline Sr₂RuO₄ sharply decreased with increasing temperature at less than 100 K, and showed significant anisotropic electrical conductivity between ab plane and c axis. The σ of poly-crystalline Sr₂RuO₄ had intermediate values between c direction and ab plane. Chandrasekaran et al. reported that the σ of poly-crystalline Sr₂RuO₄ prepared by a conventional sintering method increased with increasing temperature from 15 K to room temperature (σ = 4.8 × 10³ Sm⁻¹ at RT). This value was lower than our results.

Figure 6 shows the temperature dependence of thermal conductivity (κ) of Sr-Ru-O compounds with various R_{Ru/Sr}. The κ at R_{Ru/Sr} = 0.8 to 1.2 increased with increasing temperature whereas that of R_{Ru/Sr} = 0.5 slightly decreased with increasing temperature. The κ at room temperature increased from 2.5 to 5.3 Wm⁻¹K⁻¹ with increasing R_{Ru/Sr} from 0.8 to 1.2. This might be resulted from the second phase of RuO₂ (κ = 13 Wm⁻¹K⁻¹). Sr₃Ru₂O₇ and Sr₂RuO₄. The κ of SrRuO₃ was ranged around 4.5 to 6.0 Wm⁻¹K⁻¹ at 293 to 1020 K. Yamanaka et al. have studied many alkaline earth perovskites (e.g. SrTiO₃, SrZrO₃, SrHfO₃, BaZrO₃ and SrRuO₃) and only SrRuO₃ showed the increase of thermal conductivity with increasing temperature. This is consistent...
with our study, which might be caused by the complicated electronic structure of SrRuO$_3$. Maekawa et al.\textsuperscript{17} prepared SrRuO$_3$ by SPS, and the $\kappa$ increased from 6 to 8 W m$^{-1}$ K$^{-1}$ with increasing temperature from RT to 1200 K. These values were higher than those of the present study.

The total thermal conductivity ($\kappa$) is composed of the phonon thermal conductivity ($\kappa_{ph}$) and electronic thermal conductivity ($\kappa_{el}$). The relationship between electrical conductivity and thermal conductivity can be described by equations (1) to (3).

$$\kappa = \kappa_{el} + \kappa_{ph}$$  
(1)

$$\kappa_{el} = L\sigma T$$  
(2)

$$\kappa = L\sigma T + \kappa_{ph}$$  
(3)

where $L$ is a Lorenz number, $\sigma$ is the electrical conductivity and $T$ is an absolute temperature. According to eq. (2), at a specific temperature the ratio of the electrical and thermal conductivity is constant for a metallic conductor, called the Wiedemann-Franz law would not be applicable to Sr$_2$RuO$_3$. Shepard et al.\textsuperscript{24} have measured the $\kappa$ and $\sigma$ of Sr$_{1-x}$Ca$_x$RuO$_3$ ($x = 0$ to 1), and reported the $\kappa_{el}$ at $x = 0$ (SrRuO$_3$) was around 50% at room temperature. This was almost consistent with our results. Sr$_2$RuO$_4$ showed a semiconducting behavior, and then the Wiedemann-Franz law would not be applicable to Sr$_2$RuO$_4$.

Figure 8 shows the temperature dependence of Seebeck coefficient ($S$) of Sr-Ru-O compounds at various $R_{Ru/Sr}$. All specimens showed positive Seebeck coefficient from RT to 1000 K, consistent with the p-type conduction. The $S$ at $R_{Ru/Sr} = 1.0$ was 30 $\mu$V K$^{-1}$, almost independent of temperature. The $S$ at $R_{Ru/Sr} < 1.0$ decreased with increasing temperature and increased with increasing $R_{Ru/Sr}$. At $R_{Ru/Sr} = 1.2$, the $S$ increased with temperature and showed the highest value of 42 $\mu$V K$^{-1}$ at 600 K. The $S$ of Sr$_2$RuO$_3$ ($R_{Ru/Sr} = 0.5$) significantly decreased from 28 to 3 $\mu$V K$^{-1}$ with increasing temperature from RT to 1000 K. The $S$ of Sr$_2$RuO$_4$ showed common temperature dependence of semiconductors.

Figure 9 shows the temperature dependence of dimensionless thermoelectric figure of merit (ZT) calculated from eq. (4).

$$ZT = S^2\sigma T/\kappa$$  
(4)

The ZT at $R_{Ru/Sr} = 0.8$ to 1.0 slightly increased with temperature, whereas that at $R_{Ru/Sr} = 0.5$ decreased with increasing temperature. The ZT at $R_{Ru/Sr} = 1.2$ increased with increasing temperature and showed the highest value of...
dimensionless figure of merit ($ZT$) was 0.06 at $R_{Ru/Sr} = 1.2$ at 600 K.

Acknowledgements

The authors are grateful to global COE program, JSPS Asian CORE program, Furuya Metal Co., Ltd. and Lonmin Plc. for financial support.

REFERENCES