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 (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\(_3\) in a single phase were obtained at Ru/Sr = 1.0 and 0.5, respectively. The second phases were identified, i.e., RuO\(_2\) and Ru at Ru/Sr > 1.0 and Sr\(_2\)RuO\(_3\); and Sr\(_2\)RuO\(_3\) at Ru/Sr < 1.0. The \(\sigma\) increased with increasing Ru/Sr, while the \(\kappa\) and \(S\) increased with increasing temperature at Ru/Sr = 0.5. The \(\kappa\) decreased with increasing temperature at Ru/Sr = 0.5. The \(S\) was around 25–40 \(\mu\)V K\(^{-1}\) at room temperature, almost independent of compositions. The \(\kappa\) decreased with temperature at Ru/Sr = 0.8 to 1.0, whereas the \(\kappa\) increased with temperature and showed a maximum around 500 to 600 K at Ru/Sr = 1.2. The \(S\) significantly decreased with increasing temperature at Ru/Sr = 0.5. The highest dimensionless figure of merit (ZT) value was 0.06 at 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 Ruddlesden-Popper series, \(\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}(n = 1, 2, 3, \text{and } \infty)\), 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 \(\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}\) has different electrical conductivity (\(\sigma\)) in \(c\) direction and \(ab\) plane. The anisotropy of \(\sigma\) decreases with increasing \(n\).\(^3\) The most widely studied compounds are infinite layered (\(n = \infty\)) \(\text{SrRuO}_3\) and single layered (\(n = 1\)) \(\text{Sr}_2\text{RuO}_3\). \(\text{SrRuO}_3\) has an orthorhombically distorted perovskite of the GdFeO\(_3\) type structure with a space group of \(Pbnm\) at 10 to 800 K.\(^2\) However, the orthorhombicity decreases significantly above room temperature showing a tetragonal structure until 950 K, and then transforms into a cubic perovskite structure.\(^2\)\(^-\)\(^4\) \(\text{SrRuO}_3\) shows a metallic electrical conduction. Capogna \textit{et al.}\(^5\) reported that the electrical conductivity of \(\text{SrRuO}_3\) increased from \(5 \times 10^5\) to \(90 \times 10^5\) Sm\(^{-1}\) with decreasing temperature from room temperature to 5 K. \(\text{SrRuO}_3\) has been used as a substrate for deposition of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) (\(\text{Y}123\)) film and high temperature superconductors due to its excellent electrical conductivity.\(^6\)\(^-\)\(^7\) \(\text{Sr}_2\text{RuO}_4\) has a body-centered tetragonal \(K\text{ZnF}_3\) structure\(^8\) having a superconduction below 1 K. \(\text{Sr}_2\text{RuO}_4\) 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).\(^9\) Chandrasekaran \textit{et al.}\(^10\) reported that \(\text{Sr}_2\text{RuO}_4\) exhibited semiconducting behavior between 15 and 300 K and the electrical conductivity changed with the oxygen defect of the \(\text{Sr}_2\text{RuO}_4\). \(\text{Sr}_2\text{RuO}_4\) has been applied as a lattice matching material of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) in a wide temperature range\(^7\)\(^-\)\(^11\) since its lattice parameters are almost independent of temperature.\(^2\)

Recently, strontium ruthenates have also been proposed as potential thermoelectric materials due to their high electrical conductivity and Seebeck coefficient. Maekawa \textit{et al.}\(^12\) reported \(\text{SrRuO}_3\) had high electrical conductivity and Seebeck coefficient. Zheng \textit{et al.}\(^13\) reported the Seebeck coefficient of single crystal \(\text{Sr}_2\text{RuO}_4\) 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 thermoelectric properties were studied mainly at low temperatures by using single crystals. No study on thermoelectric properties of polycrystalline \(\text{Sr-Ru-O}\) compounds was reported. This may be caused of the difficulty to obtain dense body by conventional sintering.\(^13\)

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

2. Experimental

\(\text{Sr-Ru-O}\) powders were synthesized by solid state reaction using \(\text{SrCO}_3\) (99.99%) and \(\text{Ru}_2\text{O}_3\) (99.99%) in the ratio of Ru to Sr (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 $R_{Ru/Sr} = 1.2$ (Fig. 1(a)) and $R_{Ru/Sr} = 1.1$ (Fig. 1(b)), respectively. A small amount of Sr$_3$Ru$_2$O$_7$ and/or Sr$_2$RuO$_4$ was detected at $R_{Ru/Sr} < 1.0$ (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 × 10⁵ 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 Sr₁Ru₂O₇ and Sr₂RuO₄ second phase (σ of Sr₁Ru₂O₇ and Sr₂RuO₄ were 3.5 × 10³ Sm⁻¹ 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 SPS in this study and that reported by Maekawa et al. had higher σ by factor of 3 than that prepared by pressureless sintering, probably 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 × 10⁵ 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⁻¹ K⁻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⁻¹ K⁻¹) and Sr₁Ru₂O₇ and Sr₂RuO₄. The κ of SrRuO₃ was ranged around 4.5 to 6.0 Wm⁻¹ K⁻¹ at 293 to 1020 K. Yamakawa et al. have studied many alkaline earth perovskites (e.g. SrTiO₃, SrZrO₃, SrHfO₂, 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 Wm$^{-1}$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 ($\kappa_{\text{ph}}$) and electronic thermal conductivity ($\kappa_{\text{el}}$). The relationship between electrical conductivity and thermal conductivity can be described by equations (1) to (3).

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

$$\kappa_{\text{el}} = L \sigma T$$  \hspace{1cm}  (2)

$$\kappa = L \sigma T + \kappa_{\text{ph}}$$  \hspace{1cm}  (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. The Lorenz number was calculated by the slope of $\kappa$ vs. $\sigma T$ plot as shown in eq. (3). The $L$ at $R_{\text{Ru/Sr}} = 0.8, 0.9, 1.0$ and 1.2 were $5.58 \times 10^{-8}, 4.89 \times 10^{-8}, 2.09 \times 10^{-8}$ and $1.68 \times 10^{-8}$ WSK$^{-2}$, respectively, and decreased with increasing $R_{\text{Ru/Sr}}$. The difference of $L$ in this study may be resulted from the effect of secondary phases. The high $\sigma$ of secondary phase of RuO$_2$ at $R_{\text{Ru/Sr}} > 1.0$ may result in the low $L$ whereas the low $\sigma$ of secondary phase of Sr$_2$RuO$_4$ and Sr$_3$Ru$_2$O$_7$ at $R_{\text{Ru/Sr}} < 1.0$ may result in the high $L$. The $L$ of single-crystalline SrRuO$_3$ was reported to be $1.63 \times 10^{-8}$ WSK$^{-2}$\textsuperscript{25} at low temperatures from 8 to 250 K. The Lorenz number of common metallic material is $2.43 \times 10^{-8}$ WSK$^{-2}$\textsuperscript{26}. This value was almost coincided with that of SrRuO$_3$ in this study. Figure 7 shows the fraction of electronic thermal conductivity ($\kappa_{\text{el}}$) in the total thermal conductivity of Sr-Ru-O compounds at $R_{\text{Ru/Sr}} = 0.8$ to 1.2. The $\kappa_{\text{el}}$ of all specimens increased with increasing temperature. Although the $\sigma$ decreased with increasing temperature, the increase in $\kappa_{\text{el}}$ with $T$ can be understood from eq. (2). The $\kappa_{\text{el}}$ also increased with increasing $R_{\text{Ru/Sr}}$ due to the increase in $\sigma$. The fraction of $\kappa_{\text{el}}$ in $\kappa$ at $R_{\text{Ru/Sr}} = 1.0$ increased from 42 to 59% with increasing temperature from RT to 1000 K. The fraction of $\kappa_{\text{el}}$ at $R_{\text{Ru/Sr}} = 1.2$ increased gradually from 50% at RT to 62% at 930 K, indicating the heat can be dominantly transported with holes. The fraction of $\kappa_{\text{el}}$ at $R_{\text{Ru/Sr}} < 1.0$ were less than 30% at room temperature implying the heat can be transported with phonons. 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 $\kappa_{\text{el}}$ 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 $R_{\text{Ru/Sr}}$. All specimens showed positive Seebeck coefficient from RT to 1000 K, consistent with the p-type conduction. The $S$ at $R_{\text{Ru/Sr}} = 1.0$ was 30 $\mu$V K$^{-1}$, almost independent of temperature. The $S$ at $R_{\text{Ru/Sr}} < 1.0$ decreased with increasing temperature and increased with increasing $R_{\text{Ru/Sr}}$. At $R_{\text{Ru/Sr}} = 1.2$, 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$_4$ ($R_{\text{Ru/Sr}} = 0.5$) 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).

$$ZT = S^2 \sigma T / \kappa$$  \hspace{1cm}  (4)

The ZT at $R_{\text{Ru/Sr}} = 0.8$ to 1.0 slightly increased with increasing temperature, whereas that at $R_{\text{Ru/Sr}} = 0.5$ decreased with increasing temperature. The ZT at $R_{\text{Ru/Sr}} = 1.2$ increased with increasing temperature and showed the highest value of...
0.06 at 600 K. This value could be the highest among those of alkaline-earth ruthenate compounds, which was resulted from the combined effect of highest $\sigma$ and highest $S$ among these compositions. The $ZT$ was around 0.001 at $R_{Ru/Sr} = 0.5$ and around 0.02–0.025 at $R_{Ru/Sr} = 1.0$. The value of SrRuO$_3$ was slightly higher than that reported by Maekawa et al.

4. Conclusion

Sr-Ru-O compounds in various 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 electrical conductivity ($\sigma$), thermal conductivity ($\kappa$) and Seebeck coefficient ($S$) was investigated. SrRuO$_3$ and Sr$_2$RuO$_4$ in a single phase were obtained at $R_{Ru/Sr} = 1.0$ and 0.5, respectively. The $\sigma$ increased with increasing $R_{Ru/Sr}$ at room temperature, exhibiting a metallic behavior at $R_{Ru/Sr} > 0.5$ whereas that at $R_{Ru/Sr} = 0.5$ slightly increased with temperature. The $S$ of Sr-Ru-O was around 20–40 $\mu$V K$^{-1}$ and increased with increasing $R_{Ru/Sr}$. The $S$ was almost independent of temperature at $R_{Ru/Sr} \geq 1.0$, whereas that at $R_{Ru/Sr} < 1.0$ decreased significantly with increasing temperature. The $\kappa$ was around 2 to 7 W m$^{-1}$ K$^{-1}$ at room temperature and slightly increased with increasing temperature and $R_{Ru/Sr}$, whereas the $\kappa$ decreased with 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.

Acknowledgements

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

REFERENCES