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Thermoelectric Properties of Sr-Ru-O Compounds Prepared by Spark Plasma Sintering

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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 (σ), thermal conductivity (κ) and Seebeck coefficient (S) was investigated. All compositions yielded dense sintered mass with around 90–100% of a theoretical density. SrRuO₃ and Sr₂RuO₄ in a single phase were obtained at Ru/Srₐ=1 and 0.5, respectively. The second phases were identified, i.e., RuO₂ and Ru at Ru/Srₐ>1.0 and Sr₂RuO₄ and Sr₂RuO₄ at Ru/Srₐ<1.0. The σ increased with increasing Ru/Srₐ in the Ru/Srₐ range from 0.8 to 1.2 at room temperature exhibiting a metallic behavior, whereas the σ showed a semiconducting behavior at Ru/Srₐ=0.5. The κ was around 2 to 7 W m⁻¹ K⁻¹ at Ru/Srₐ=0.8 to 1.2 at room temperature and slightly increased with increasing temperature and Ru/Srₐ. The κ decreased with increasing temperature at Ru/Srₐ=0.5. The S was around 25–40 μV K⁻¹ at room temperature, almost independent of compositions. The S slightly decreased with temperature at Ru/Srₐ=0.8 to 1.0, whereas the S increased with temperature and showed a maximum around 500 to 600 K at Ru/Srₐ=1.2. The S significantly decreased with increasing temperature at Ru/Srₐ=0.5. The highest dimensionless figure of merit (ZT) was 0.06 at Ru/Srₐ=1.2 at 600 K. [doi:10.2320/matertrans.MRA2007230]

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1. Introduction

The strontium ruthenates can be considered as members of Ruddlesdon-Popper series, Srₙ₊₁RuO₃ₙ₋₁ (n = 1, 2, 3 and ∞), where n is the number of corner sharing RuO₆ octahedra layers separated by SrO layers. The distortion degree of RuO₆ octahedra decreases with increasing n due to the increase in the overlap of Ru-4d and O-2p orbitals. The Srₙ₊₁RuO₃ₙ₋₁ has different electrical conductivity (σ) in c direction and ab plane. The anisotropy of σ decreases with increasing n. The most widely studied compounds are infinite layered (n = ∞) SrRuO₃ and single layered (n = 1) Sr₂RuO₃. SrRuO₃ has an orthorhombically distorted perovskite of the GdFeO₃ type structure with a space group of Pbnnm 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. SrRuO₃ shows a metallic electrical conduction. Capogna et al. reported that the electrical conductivity of SrRuO₃ increased from 5 × 10⁵ to 90 × 10⁵ Sm⁻¹ with decreasing temperature from room temperature to 5 K. SrRuO₃ has been used as a substrate for deposition of YBa₂Cu₃O₇₋ₓ (Y123) film and high temperature superconductors due to its excellent electrical conductivity. Sr₂RuO₄ has a body-centered tetragonal K₂NiF₄ structure having a superconduction below 1 K. Sr₂RuO₄ single crystal shows metallic conduction behavior in the ab plane and has a significant anisotropy in ab plane and c direction (σab/σc = 220 at room temperature). Chandrasekaran et al. reported that Sr₂RuO₄ exhibited semiconducting behavior between 15 and 300 K and the electrical conductivity changed with the oxygen defect of the Sr₂RuO₄. Sr₂RuO₄ has been as a lattice matching material of YBa₂Cu₃O₇ 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 SrRuO₃ had high electrical conductivity and Seebeck coefficient. Zheng et al. reported the Seebeck coefficient of single crystal Sr₂RuO₄ of ab plane increased from 0.1 to 9.0 μV 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 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 (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 SrCO₃ (99.99%) and Ru₂O₃ (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 × 2 × 10 mm for the measurement of electrical conductivity by a d.c. 4-probe method and Seebeck coefficient by a thermoelectric power (ΔE)-temperature difference (ΔT) 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 \( R_{\text{Ru/Sr}} = 0.5 \) to 1.2. \( \text{SrRuO}_3 \) and \( \text{Sr}_2\text{RuO}_4 \) in a single phase were obtained at \( R_{\text{Ru/Sr}} = 1.0 \) (Fig. 1(c)) and 0.5 (Fig. 1(e)), respectively. Second phases of \( \text{RuO}_2 \) and Ru with the main phase of \( \text{SrRuO}_3 \) were identified at \( R_{\text{Ru/Sr}} = 1.1 \) (Fig. 1(b)) and \( R_{\text{Ru/Sr}} = 0.8 \) (Fig. 1(d)). Jacob et al.\(^{14}\) have reported that \( \text{SrRuO}_3 \) formed at lower temperatures (\( T < 1573 \) K), and \( \text{Sr}_2\text{RuO}_4 \) and \( \text{Sr}_2\text{Ru}_2\text{O}_7 \) formed at higher temperature (\( T > 1573 \) K). \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) would form at higher than 1723 K. In the present study, \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) was not identified due to the low sintering temperature.

Figure 2 demonstrates the effect of \( R_{\text{Ru/Sr}} \) on the lattice parameters of \( \text{SrRuO}_3 \) phase. At \( R_{\text{Ru/Sr}} = 0.9 \) to 1.4, the lattice parameters of \( a \), \( b \) and \( c \) were independent of \( R_{\text{Ru/Sr}} \) and were constant values of 0.5570, 0.7851 and 0.5533 nm, respectively. The lattice parameters at \( R_{\text{Ru/Sr}} = 0.7 \) 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 \( R_{\text{Ru/Sr}} = 0.7 \) and 0.8 was not presented. Although \( \text{CaRuO}_3 \) has a solid solution range of the ratio of Ru to Ca (\( R_{\text{Ru/Ca}} \)) = 0.7 to 1.0,\(^{15}\) \( \text{SrRuO}_3 \) should be a stoichiometric compound. The lattice parameters of \( \text{Sr}_2\text{RuO}_4 \) 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).\(^{16}\)

Figure 3 presents the temperature dependence of the electrical conductivity (\( \sigma \)) of Sr-Ru-O compounds at various \( R_{\text{Ru/Sr}} \). The relative densities of all specimens were around 96 to 99%. The \( \sigma \) decreased with increasing temperature at \( R_{\text{Ru/Sr}} > 0.5 \) showing a metallic conduction, whereas the \( \sigma \) at \( R_{\text{Ru/Sr}} = 0.5 \) slightly increased with temperature showing a semiconducting conduction. \( \text{SrRuO}_3 \) in a single phase (\( R_{\text{Ru/Sr}} = 1.0 \)) had a \( \sigma \) of \( 3 \times 10^5 \) Sm\(^{-1} \) at 293 K, which was almost the same as that reported by Maekawa.\(^{17}\) The \( \sigma \) of \( \text{SrRuO}_3 \) was higher than that of \( \text{CaRuO}_3 .^{16} \) Cox et al.\(^{18}\) have studied the electrical conduction of \( \text{SrRuO}_3 \) and \( \text{CaRuO}_3 \) by photoelectron spectroscopy. \( \text{SrRuO}_3 \) showed higher electrical conductivity because of higher density of states at Fermi energy (\( E_F \)). Kobayashi et al.\(^{19}\) have studied the relationship between crystal structure and electrical conductivity of \( \text{SrRuO}_3 \) and \( \text{CaRuO}_3 \) and reported that the distortion degree
and the angle of Ru-O-Ru bond of CaRuO$_3$ was higher than those of SrRuO$_3$, resulting in the lower electrical conductivity of CaRuO$_3$. The $\sigma$ 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 RuO$_2$ ($\sigma_{RuO_2} = 1.4 \times 10^6$ Sm$^{-1}$ at 293 K).\(^{13}\) The $\sigma$ at $R_{Ru/Sr} < 1.0$ presented a much lower values comparing with that of $R_{Ru/Sr} \geq 1.0$. This might be caused of the low $\sigma$ of Sr$_2$Ru$_2$O$_7$ and Sr$_2$RuO$_4$ second phase ($\sigma$ of Sr$_2$Ru$_2$O$_7$ and Sr$_2$RuO$_4$ were $3.5 \times 10^3$ Sm$^{-1}$\(^{20}\) and $5 \times 10^3$ Sm$^{-1}$\(^{10}\) at RT, respectively). The $\sigma$ of Sr$_2$RuO$_4$ at room temperature was $7.2 \times 10^3$ Sm$^{-1}$ and much lower than that of SrRuO$_3$.

Figure 4 shows the temperature dependence of electrical conductivity of single- and poly-crystalline SrRuO$_3$ reported in literatures. All data exhibited a metallic behavior at the whole temperature. The $\sigma$ of the single-crystalline SrRuO$_3$\(^{21}\) was higher than that of poly-crystalline in the present study by a factor of 2. The poly-crystalline SrRuO$_3$ prepared by SPS in this study and that reported by Maekawa et al.\(^{17}\) had higher $\sigma$ by factor of 3 than that prepared by pressureless sintering.\(^{22,23}\) probably due to the high density.

Figure 5 shows the temperature dependence of the electrical conductivity of single- and poly-crystalline Sr$_2$RuO$_4$ in literatures. The $\sigma$ of Sr$_2$RuO$_4$ in this study exhibited a semiconducting behavior from RT to 1000 K ($7 \times 10^3$ to $1.6 \times 10^4$ Sm$^{-1}$). So far, no studies on the $\sigma$ of Sr$_2$RuO$_4$ at high temperatures have been reported. The $\sigma$ of single crystalline Sr$_2$RuO$_4$ sharply decreased with increasing temperature at less than 100 K, and showed significant anisotropic electrical conductivity between $ab$ plane and $c$ axis. The $\sigma$ of poly-crystalline Sr$_2$RuO$_4$ had intermediate values between $c$ direction and $ab$ plane. Chandrasekaran et al.\(^{18}\) reported that the $\sigma$ of poly-crystalline Sr$_2$RuO$_4$ prepared by a conventional sintering method increased with increasing temperature from 15 K to room temperature ($\sigma = 4.8 \times 10^3$ Sm$^{-1}$ at RT).\(^{10}\) This value was lower than our results.

Figure 6 shows the temperature dependence of thermal conductivity ($\kappa$) of Sr-Ru-O compounds with various $R_{Ru/Sr}$. The $\kappa$ 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 $\kappa$ 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 RuO$_2$ ($\kappa = 13$ Wm$^{-1}$K$^{-1}$)\(^{15}\) Sr$_3$Ru$_2$O$_7$ and Sr$_2$RuO$_4$. The $\kappa$ of SrRuO$_3$ was ranged around 4.5 to 6.0 Wm$^{-1}$K$^{-1}$ at 293 to 1020 K. Yamana et al.\(^{24}\) have studied many alkaline earth perovskites (e.g. SrTiO$_3$, SrZrO$_3$, SrHfO$_3$, BaZrO$_3$ and SrRuO$_3$) and only SrRuO$_3$ 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).

\begin{equation}
\kappa = \kappa_{\text{el}} + \kappa_{\text{ph}}
\end{equation}

\begin{equation}
\kappa_{\text{el}} = \sigma T
\end{equation}

\begin{equation}
\kappa = \sigma T + \kappa_{\text{ph}}
\end{equation}

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$_3$ 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$_3$ ($R_{\text{Ru/Sr}} = 0.5$) significantly decreased from 28 to 3 $\mu$V K$^{-1}$ with increasing temperature from RT to 1000 K. The $S$ of Sr$_2$RuO$_3$ showed common temperature dependence of semiconductors.

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

\begin{equation}
ZT = S^2 \sigma T / \kappa
\end{equation}

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
Sr-Ru-O was around 20–40 m these compositions. The ZT/C0 to 7 Wm
R increased with increasing 4. Conclusion was slightly higher than that reported by Maekawa et al. from the combined effect of highest /C27 alkaline-earth ruthenate compounds, which was resulted 0.06 at 600 K. This value could be the highest among those of SrRuO
3 Sr-Ru-O compounds.

Fig. 9 Temperature dependence of dimensionless figure-of-merit (ZT) of Sr-Ru-O compounds.

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 σ and highest S among these compositions. The ZT was around 0.001 at Ru/Sr = 0.5 and around 0.02–0.025 at Ru/Sr = 1.0. The value of SrRuO3 was slightly higher than that reported by Maekawa et al.

4. Conclusion

Sr-Ru-O compounds in various 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 electrical conductivity (σ), thermal conductivity (κ) and Seebeck coefficient (S) was investigated. SrRuO3 and Sr2RuO4 in a single phase were obtained at Ru/Sr = 1.0 and 0.5, respectively. The σ increased with increasing Ru/Sr at room temperature, exhibiting a metallic behavior at Ru/Sr > 0.5 whereas that at Ru/Sr = 0.5 slightly increased with temperature. The S of Sr-Ru-O was around 20–40 μV K⁻¹ and increased with increasing Ru/Sr. The S was almost independent of temperature at Ru/Sr ≥ 1.0, whereas that at Ru/Sr < 1.0 decreased significantly with increasing temperature. The κ was around 2 to 7 W m⁻¹ K⁻¹ at room temperature and slightly increased with increasing temperature and Ru/Sr, whereas the κ decreased with temperature at Ru/Sr = 0.5. The highest dimensionless figure of merit (ZT) was 0.06 at Ru/Sr = 1.2 at 600 K.

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