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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 ($R_{Ru/Sr}$) from 0.5 to 1.2 were prepared by spark plasma sintering (SPS) and the effect of composition on the electrical conductivity (σ), thermal conductivity (κ) and Seebeck coefficient (S) was investigated. All compositions yielded dense sintered mass with around 90–100% of a theoretical density. $SrRuO_3$ and Sr_2RuO_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 $Sr_3Ru_2O_7$ and Sr_2RuO_4 at $R_{Ru/Sr} < 1.0$. The σ 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 σ showed a semiconducting behavior at $R_{Ru/Sr} = 0.5$. The κ 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 κ decreased 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. [doi:10.2320/matertrans.MRA2007230]

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1. Introduction

The strontium ruthenates can be considered as members of Ruddlesdon-Popper series, $Sr_{n+1}Ru_nO_{3n+1}$ ($n = 1$, 2, 3 and ∞), 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 $Sr_{n+1}Ru_nO_{3n+1}$ has different electrical conductivity (σ) in c direction and ab plane. The anisotropy of σ decreases with increasing n.[1)] The most widely studied compounds are infinite layered ($n = \infty$) $SrRuO_3$ and single layered ($n = 1$) Sr_2RuO_4. $SrRuO_3$ 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)] $SrRuO_3$ shows a metallic electrical conduction. Capogna *et al.*[5)] reported that the electrical conductivity of $SrRuO_3$ increased from 5×10^5 to 90×10^5 Sm^{-1} with decreasing temperature from room temperature to 5 K. $SrRuO_3$ has been used as a substrate for deposition of $YBa_2Cu_3O_{7-x}$ (Y123) film and high temperature electrodes due to its excellent electrical conductivity.[6,7)] Sr_2RuO_4 has a body-centered tetragonal K_2NiF_4 structure[8)] having a superconduction below 1 K. Sr_2RuO_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 *et al.*[10)] reported that Sr_2RuO_4 exhibited semiconducting behavior between 15 and 300 K and the electrical conductivity changed with the oxygen defect of the Sr_2RuO_4. Sr_2RuO_4 has been applied as a lattice matching material of $YBa_2Cu_3O_7$ in a wide temperature range[7,8,11)] 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 *et al.* reported $SrRuO_3$ had high electrical conductivity and Seebeck coefficient. Zheng *et al.*[12)] reported the Seebeck coefficient of single crystal Sr_2RuO_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 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 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 RuO_2 (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 (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.

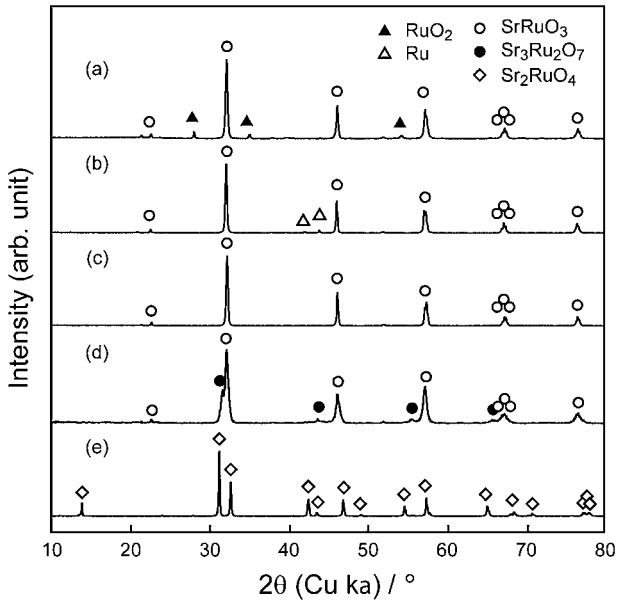

Fig. 1 XRD pattern of Sr-Ru-O compounds with various $R_{Ru/Sr} = 1.2$ (a), 1.1 (b), 1.0 (c), 0.8 (d) and 0.5 (e).

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_2RuO_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 $R_{Ru/Sr} \geq 1.2$ (Fig. 1(a)) and $R_{Ru/Sr} = 1.1$ (Fig. 1(b)), respectively. A small amount of $Sr_3Ru_2O_7$ and/or Sr_2RuO_4 were detected at $R_{Ru/Sr} < 1.0$ (Fig. 1(d)). Jacob *et al.*[14] have reported that $SrRuO_3$ formed at lower temperatures ($T < 1573$ K), and Sr_2RuO_4 and $Sr_3Ru_2O_7$ formed at higher temperature ($T > 1573$ K). $Sr_4Ru_3O_{10}$ would form at higher than 1723 K. In the present study, $Sr_4Ru_3O_{10}$ 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,[15] $SrRuO_3$ should be a stoichiometric compound. The lattice parameters of Sr_2RuO_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 (σ) of Sr-Ru-O compounds at various $R_{Ru/Sr}$. The relative densities of all specimens were around 96 to 99%. The σ decreased with increasing temperature at $R_{Ru/Sr} > 0.5$ showing a metallic conduction, whereas the σ 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 σ of 3×10^5 Sm^{-1} at 293 K, which was

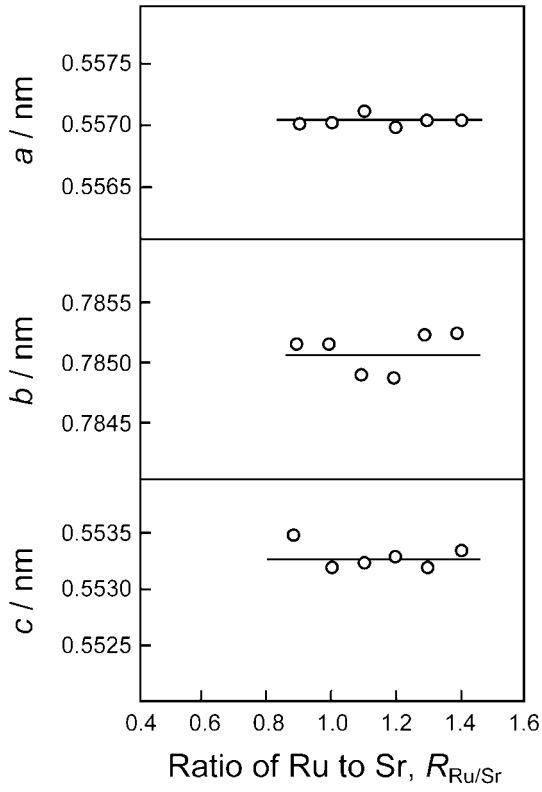

Fig. 2 Lattice parameters of $SrRuO_3$ compound.

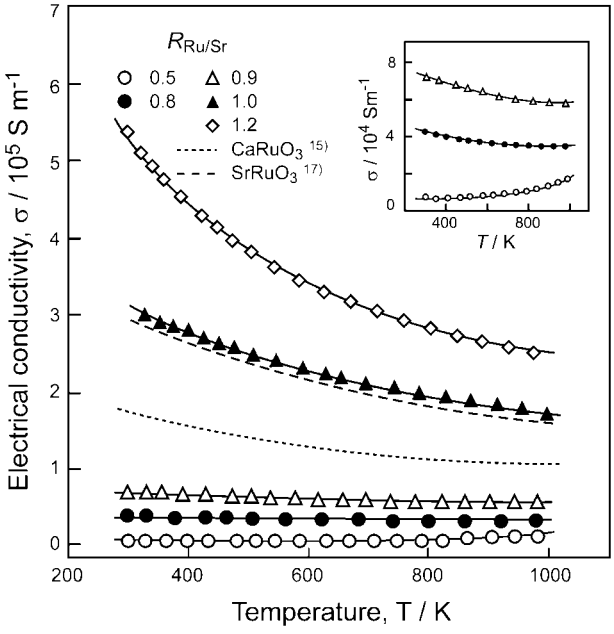

Fig. 3 Temperature dependence of electrical conductivity of Sr-Ru-O compounds.

almost the same as that reported by Maekawa.[17] The σ of $SrRuO_3$ was higher than that of $CaRuO_3$.[16] Cox *et al.*[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.*[19] have studied the relationship between crystal structure and electrical conductivity of $SrRuO_3$ and $CaRuO_3$ and reported that the distortion degree

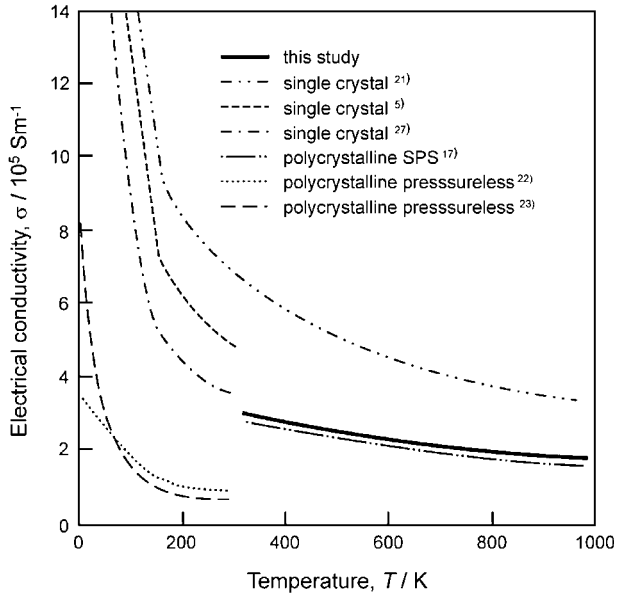

Fig. 4 Temperature dependence of single-crystalline and poly-crystalline $SrRuO_3$.

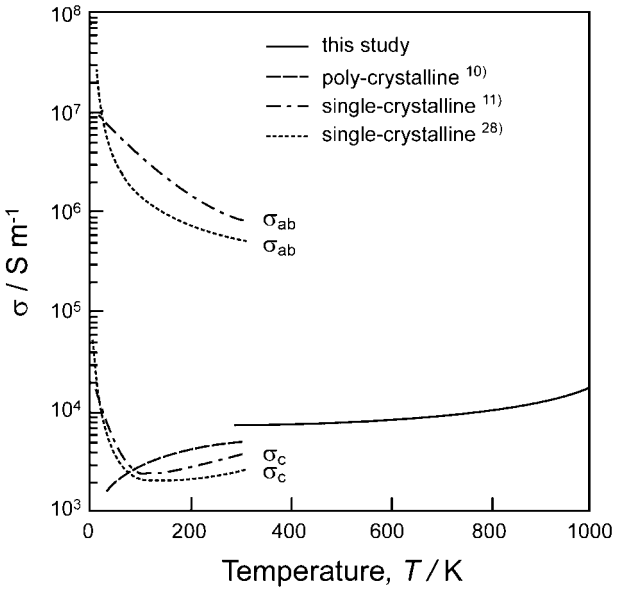

Fig. 5 Temperature dependence of single-crystalline and poly-crystalline Sr_2RuO_4.

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 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 RuO_2 ($\sigma_{RuO2} = 1.4 \times 10^6\,Sm^{-1}$ at 293 K).[15] The σ 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 σ of $Sr_3Ru_2O_7$ and Sr_2RuO_4 second phase (σ of $Sr_3Ru_2O_7$ and Sr_2RuO_4 were 3.5×10^3 Sm^{-1}[20] and $5 \times 10^3\,Sm^{-1}$[10] at RT, respectively). The σ of Sr_2RuO_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 σ 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 σ 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_2RuO_4 in literatures. The σ of Sr_2RuO_4 in this study exhibited a semiconducting behavior from RT to 1000 K (7×10^3 to $1.6 \times 10^4\,Sm^{-1}$). So far, no studies on the σ of Sr_2RuO_4 at high temperatures have been reported. The σ of single crystalline Sr_2RuO_4 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 Sr_2RuO_4 had intermediate values between *c* direction and *ab* plane. Chandrasekaran *et al.* reported that the σ of poly-crystalline Sr_2RuO_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.

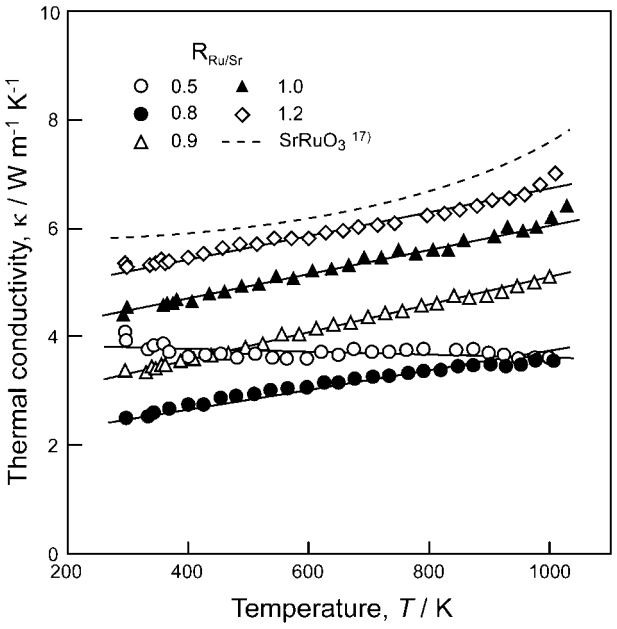

Fig. 6 Temperature dependence of thermal conductivity of Sr-Ru-O compounds.

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 RuO_2 ($\kappa = 13\,Wm^{-1}\,K^{-1}$),[15] $Sr_3Ru_2O_7$ and Sr_2RuO_4. The κ of $SrRuO_3$ was ranged around 4.5 to 6.0 $Wm^{-1}\,K^{-1}$ at 293 to 1020 K. Yamanaka *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

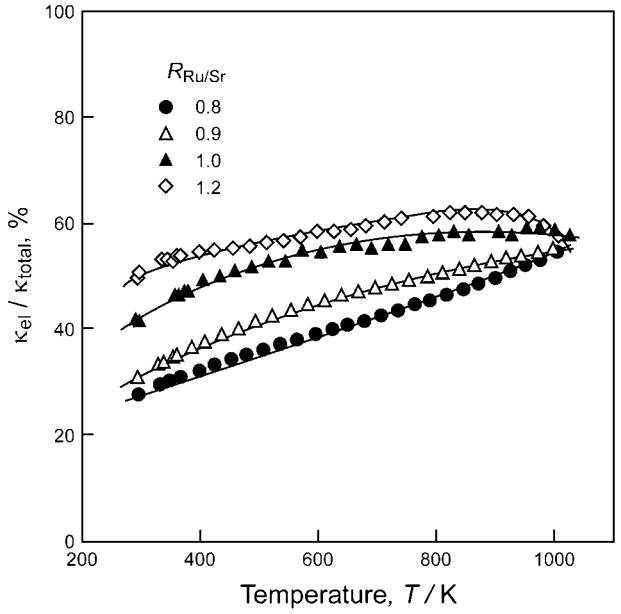

Fig. 7 Temperature dependence of fraction of electronic thermal conductivity of Sr-Ru-O compounds.

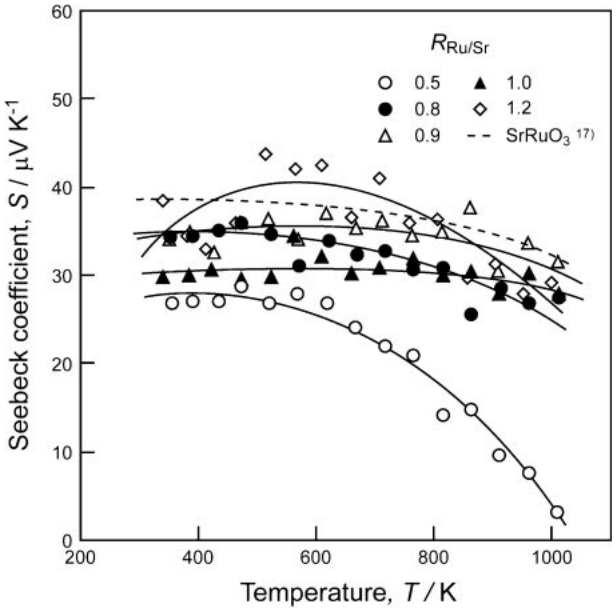

Fig. 8 Temperature dependence of Seebeck coefficient of Sr-Ru-O compounds.

with our study, which might be caused by the complicated electronic structure of $SrRuO_3$. Maekawa *et al.*[17] prepared $SrRuO_3$ by SPS, and the κ 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 (κ) is composed of the phonon thermal conductivity (κ_{ph}) and electronic thermal conductivity (κ_{el}). The relationship between electrical conductivity and thermal conductivity can be described by equations (1) to (3).

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

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

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

where L is a Lorenz number, σ 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 κ vs. σT plot as shown in eq. (3). The L at $R_{Ru/Sr} = 0.8$, 0.9, 1.0 and 1.2 were 5.58×10^{-8}, 4.89×10^{-8}, 2.09×10^{-8} and 1.68×10^{-8} WSK^{-2}, respectively, and decreased with increasing $R_{Ru/Sr}$. The difference of L in this study may be resulted from the effect of secondary phases. The high σ of secondary phase of RuO_2 at $R_{Ru/Sr} > 1.0$ may result in the low L whereas the low σ of secondary phase of Sr_2RuO_4 and $Sr_3Ru_2O_7$ at $R_{Ru/Sr} < 1.0$ may result in the high L. The L of single-crystalline $SrRuO_3$ was reported to be 1.63×10^{-8} WSK^{-2} [25] at low temperatures from 8 to 250 K. The Lorenz number of common metallic material is 2.43×10^{-8} WSK^{-2}.[26] This value was almost coincided with that of $SrRuO_3$ in this study. Figure 7 shows the fraction of electronic thermal conductivity (κ_{el}) in the total thermal conductivity of Sr-Ru-O compounds at $R_{Ru/Sr} = 0.8$ to 1.2. The κ_{el} of all specimens increased with increasing temperature. Although the σ decreased with increasing temperature, the increase in κ_{el} with T can be understood from eq. (2). The κ_{el} also increased with increasing $R_{Ru/Sr}$ due to the increase in σ. The fraction of κ_{el} in κ at $R_{Ru/Sr} = 1.0$ increased from 42 to 59% with increasing temperature from RT to 1000 K. The fraction of κ_{el} at $R_{Ru/Sr} = 1.2$ increased gradually from 50% at RT to 62% at 930 K, indicating the heat can be dominently transported with holes. The fraction of κ_{el} at $R_{Ru/Sr} < 1.0$ were less than 30% at room temperature implying the heat can be transported with phonons. Shepard *et al.*[24] have measured the κ and σ of $Sr_{1-x}Ca_xRuO_3$ ($x = 0$ to 1), and reported the κ_{el} at $x = 0$ ($SrRuO_3$) was around 50% at room temperature. This was almost consistent with our results. Sr_2RuO_4 showed a semiconducting behavior, and then the Wiedemann-Franz law would not be applicable to Sr_2RuO_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 μV 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 μV K^{-1} at 600 K. The S of Sr_2RuO_4 ($R_{Ru/Sr} = 0.5$) significantly decreased from 28 to 3 μV K^{-1} with increasing temperature from RT to 1000 K. The S of Sr_2RuO_4 showed common temperature dependence of semiconductors.

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

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

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

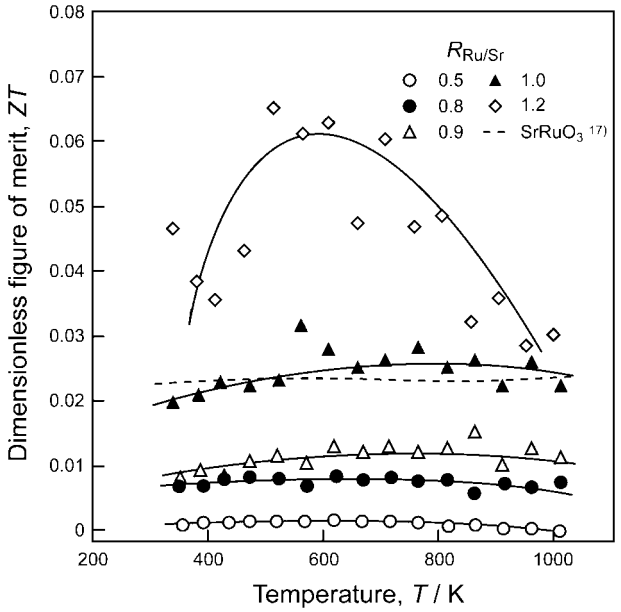

Fig. 9 Temperature dependence of dimensionless figure-of-merit (ZT) of Sr-Ru-O compounds.

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 $R_{Ru/Sr} = 0.5$ 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 (σ), thermal conductivity (κ) and Seebeck coefficient (S) was investigated. $SrRuO_3$ and Sr_2RuO_4 in a single phase were obtained at $R_{Ru/Sr} = 1.0$ and 0.5, respectively. The σ 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 κ was around 2 to 7 $Wm^{-1} K^{-1}$ at room temperature and slightly increased with increasing temperature and $R_{Ru/Sr}$, whereas the κ 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.

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