Thermoelectric Properties of Ca-Ir-O Compounds Prepared by Spark Plasma Sintering

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Ca-Ir-O compounds in various molar ratios of Ir to Ca ($R_{\text{Ir/Ca}}$) from 0.2 to 1.2 were synthesized by solid-state reaction and compacted by spark plasma sintering (SPS). Ca_4IrO_6 and CaIrO_3 with a small amount of second phase were obtained at $R_{\text{Ir/Ca}} = 0.25$ and 1.0, respectively, whereas Ca_2IrO_4 in a single phase was obtained at $R_{\text{Ir/Ca}} = 0.5$. The electrical conductivity was 4×10^{-4} to 150 Sm^{-1} at room temperature and exhibited a semiconducting behavior for all the samples. The Seebeck coefficient at $R_{\text{Ir/Ca}} = 0.4$ to 0.7 showed negative values whereas samples with $R_{\text{Ir/Ca}} = 0.25$ and 0.9 to 1.2 showed positive values. The thermal conductivity was 1.1 to $2.7 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature and slightly decreased with increasing temperature. The highest ZT value of p-type was 0.006 at 1023 K and $R_{\text{Ir/Ca}} = 1.1$ and 1.2, while that of n-type was 0.0022 at 800 K and $R_{\text{Ir/Ca}} = 0.5$. [doi:10.2320/matertrans.MRA2008377]

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1. Introduction

IrO_2 has been applied as electrodes and electrical conducting paste due to its excellent electrical conductivity. However, IrO_2 has a high volatility in an oxidizing atmosphere due to the formation of volatile IrO_3 . The volatile nature of IrO_3 can be depressed when it forms compounds with CaO, SrO and BaO. Among the IrO_2 -based compounds, calcium iridium oxides have received scant attention to date. An equilibrium phase diagram of the Ca-Ir-O system has been reported by McDaniel *et al.*¹⁾ They identified three stable compounds of Ca_4IrO_6 , Ca_2IrO_4 and CaIrO_3 and reported that the CaIrO_3 dissociated to Ir and Ca_2IrO_4 at 1408 K, Ca_2IrO_4 to Ir and Ca_4IrO_6 at 1443 K, and Ca_4IrO_6 to Ir and CaO at 1513 K. Figure 1 is a schematic of the crystal structures of CaIrO_3 , Ca_2IrO_4 and Ca_4IrO_6 . CaIrO_3 has a post-perovskite structure and a layered orthorhombic unit cell with a space group of $Cmcm$ and lattice parameters of $a = 0.31445$, $b = 0.98656$ and $c = 0.72986 \text{ nm}$. The post-perovskite structure of CaIrO_3 shares IrO_6 octahedral edges and form a chain, and the chain shares the octahedral corners, resulting in the formation of flat sheets (Fig. 1(a)).²⁾ This crystal structure is isostructural with MgSiO_3 ³⁾ and ThMnTe_3 ,⁴⁾ while the crystal habit of the latter has been reported to be platy (and needle-like). Ca_2IrO_4 has a hexagonal $P6_2m$ space group with lattice parameters of $a = 0.941$ and $c = 0.3195 \text{ nm}$ (Fig. 1(b)).⁵⁾ Its structure is built up by IrO_6 octahedral sharing edges, thus forming chains in the direction of the c axis. The crystal structure of Ca_4IrO_6 belongs to a hexagonal $R3c$ space group with lattice parameters of $a = 0.9330$ and $c = 1.1228 \text{ nm}$. This structure is identical to that reported for K_4CdCl_6 , forming isolated IrO_6 octahedra at the corner in the c direction (Fig. 1(c)). This is also the same structure as Sr_4PtO_6 and Sr_4IrO_6 which have been reported to be readily hydrolyzed on contact with water.⁶⁾

Thermodynamic properties of three stable compounds have been reported by Jacob *et al.*⁷⁾ Sarkozy *et al.*⁸⁾ have reported the electrical properties of calcium iridate prepared by a solid state reaction and a hydroxide precipitation

technique. Ca_4IrO_6 has been reported to be an insulator with resistance of 4×10^4 to $33 \times 10^6 \Omega$ at 300 to 400 K.⁸⁾ Ca_2IrO_4 has been observed to exhibit semiconducting behavior, and its resistance was found to decrease from 1.9×10^2 to 20Ω with an increase of temperature from 300 to 500 K.⁸⁾ However, the resistivity of the CaIrO_3 post-perovskite structure has not been reported.

We have been investigating crystal structures and electrical properties of $A\text{-}M\text{-}O$ (A : alkaline-earth element, M : Pt-group metal, O : oxygen) systems, and have reported moderate thermoelectric properties of Ca-Ru-O compounds.⁹⁾ Given their structural similarity with Ca-Ru-O compounds, Ca-Ir-O compounds may also have good thermoelectric properties. However, no studies on the Ca-Ir-O compounds have been published. In the present study, Ca-Ir-O compounds were compacted by spark plasma sintering (SPS), and the effect of the Ir/Ca ratio ($R_{\text{Ir/Ca}}$) on the crystal structure, electrical conductivity (σ), thermal conductivity (κ), Seebeck coefficient (S) and dimensionless figure of merit (ZT) value of Ca-Ir-O compounds was investigated.

2. Experimental

Ca-Ir-O compounds were synthesized by a solid state reaction using CaCO_3 (99.5%) and Ir (99.99%) in the molar ratio of Ir to Ca ($R_{\text{Ir/Ca}}$) of between 0.2 and 1.2. The powders were pressed into pellets after mixing with a small amount of ethanol and calcined at 1273 to 1473 K in air. The calcined pellets were reground and re-calcined until no phase change could be observed. The crushed powders were compacted by SPS at 1273 K for 0.18 ks in a vacuum at a pressure of 80 MPa. The compacted body was cut to a size of $2 \times 2 \times 10 \text{ mm}$ for the measurement of electrical conductivity by a d.c. 4-probe method and the Seebeck coefficient by a thermoelectric power (ΔE)-temperature difference (ΔT) method. Disk-shaped specimens 10 mm in diameter and 1 mm in thickness were employed to measure thermal conductivity by a laser flash method (ULVAC TC-7000) and electrical conductivity by a 2-probe method for high

Fig. 1 Schematic of structures of CaIrO_3 (a), Ca_2IrO_4 (b) and Ca_4IrO_6 (c).

resistivity specimens. All measurements were conducted from room temperature (RT) to 1023 K. The crystal phase was examined by X-ray diffraction (Rigaku Geigerflex). The lattice parameters were calculated by a program based on the least squares analysis and the standard deviation of d-values was less than 0.02%. The microstructure was observed by scanning electron microscopy (SEM) and transmission electron microscope (TEM). The composition of the crystals was examined by electron probe micro-analysis (EPMA). The density (d) was determined by an Archimedes' method.

3. Results and Discussion

Figure 2 demonstrates the relationship between the crystal phase and the compositions of calcinations. In the present study, calcium iridates were synthesized by using CaCO_3 and Ir metal powders as raw materials, whereas CaCO_3 and IrO_2 were employed as starting materials in the study by McDaniel and Schneider.¹⁾ The specimens at $R_{\text{Ir}/\text{Ca}} = 0.2$ to 0.4 were calcined at 1473 K, whereas at $R_{\text{Ir}/\text{Ca}} = 0.5$ to 1.2 they were calcined at 1273 K. The relationship between the phases of calcium iridates and $R_{\text{Ir}/\text{Ca}}$ was consistent with that reported by McDaniel and Schneider.¹⁾ Ca_4IrO_6 and Ca_2IrO_4 in a

Fig. 2 Relationship between phase compounds and compositions after calcination.

Fig. 3 XRD patterns of Ca-Ir-O compound sintered bodies at $R_{\text{Ir}/\text{Ca}} = 0.25$ (a), 0.3 (b), 0.5 (c), 0.8 (d), 1.0 (e) and 1.2 (f).

single phase were identified at $R_{\text{Ir}/\text{Ca}} = 0.25$ and 0.5, respectively, whereas CaIrO_3 in a single phase was not obtained at $R_{\text{Ir}/\text{Ca}} = 1.0$, always containing with a trace of Ca_2IrO_4 . Ca_2IrO_4 appeared at $R_{\text{Ir}/\text{Ca}} = 0.3$ and increased with increasing $R_{\text{Ir}/\text{Ca}}$. CaIrO_3 appeared at $R_{\text{Ir}/\text{Ca}} = 0.7$ and increased with increasing $R_{\text{Ir}/\text{Ca}}$. The main phase of CaIrO_3 with a small amount of IrO_2 was obtained at $R_{\text{Ir}/\text{Ca}} > 1.0$.

Figure 3 shows the effect of $R_{\text{Ir}/\text{Ca}}$ on the crystal phase of the compacted body. A sintering temperature of 1273 K was selected to achieve as high a densification as possible prior to decomposition. The crystal phases were almost the same as that of calcined powders, but Ir metal was identified to be an additional phase after SPS. Ca_2IrO_4 in a single phase was identified at $R_{\text{Ir}/\text{Ca}} = 0.5$ (Fig. 3(c)). The main phase of CaIrO_3 with a small amount of Ir was obtained at $R_{\text{Ir}/\text{Ca}} = 1.2$ (Fig. 3(f)). The lattice parameters of CaIrO_3 were $a = 0.315$, $b = 0.987$ and $c = 0.730$ nm, and those of Ca_4IrO_6 and

Fig. 4 SEM images of fracture surface observation of Ca-Ir-O compound sintered bodies at $R_{\text{Ir/Ca}} = 0.25$ (a), 0.5 (b), 0.7 (c) and 1.0 (d).

Ca_2IrO_4 were $a = 0.933$, $c = 1.124$ and $a = 0.943$, $c = 0.319$ nm, respectively. They were almost the same as those reported by McDaniel *et al.*¹⁾ However, the Ca_4IrO_6 compacted body was gradually decayed by contact with moisture. This is consistent with the decay of Sr_4PtO_6 ⁶⁾ having the identical structure. The identification of Ir metal in the present study might result from the reducing atmosphere in the vacuum and by the graphite die. We confirmed that Ir metal still appeared after sintering in argon gas; however, no Ir phase was identified in air.

Figure 4 shows the fractural microstructure of Ca-Ir-O compounds compacted by SPS at $R_{\text{Ir/Ca}} = 0.25$ to 1.0. The relative densities of these specimens were 60 to 70% due to the use of a low sintering temperature (1273 K) to minimize the formation of Ir metal. At higher than 1273 K, a large amount of Ir metal with an even higher density was obtained. At $R_{\text{Ir/Ca}} = 0.25$, Ca_4IrO_6 had a granular microstructure with a grain size of about 3 μm (Fig. 4(a)). At $R_{\text{Ir/Ca}} = 0.5$, Ca_2IrO_4 showed fine grains 1 μm in diameter (Fig. 4(b)). At $R_{\text{Ir/Ca}} = 0.7$, fine gains 1 μm in diameter and elongated grains about 10 μm in length and 2 μm in width were observed (Fig. 4(c)). These grains were identified as Ca_2IrO_4 and CaIrO_3 by EPMA, respectively. The rod-like grains of CaIrO_3 were predominantly observed at $R_{\text{Ir/Ca}} = 1.0$ (Fig. 4(d)).

Figure 5 shows a TEM microstructure image and selected area electron diffraction (SAED) pattern and the projection of the crystal structure of CaIrO_3 . The electron diffraction pattern of the elongated grain had a [011] zone axis and the normal line of the (200) plane in electron diffraction pattern paralleled with the elongated direction of the CaIrO_3 grain, implying a preferred growth along [100] direction. The relationship between the crystalline planes of (100), ($1\bar{1}1$) and ($02\bar{2}$) crystallographic structure was consistent with those in the electron diffraction pattern. The direction of the rod-like CaIrO_3 crystal was confirmed to grow in the [100] direction, the direction of the edge-sharing octahedral chain. Since the sheet structure of post-perovskite can be compressed in the [010] direction higher than that of the [100] and [001] directions,¹⁰⁾ the anisotropy of the crystal structure may yield a platy morphology parallel to the (010) plane, i.e., parallel to the sheet structure.

Figure 6 presents the temperature dependence of the electrical conductivity (σ) of Ca-Ir-O compounds at various $R_{\text{Ir/Ca}}$. The σ of all specimens increased with increasing temperature, showing a semiconducting behavior. Since the σ at $R_{\text{Ir/Ca}} = 0.25$ showed low values, the conductivity was measured by a 2-probe method. At $R_{\text{Ir/Ca}} = 0.25$, the σ increased rapidly by more than 5 orders of magnitude from 4×10^{-4} to 15 S m^{-1} with increasing temperature

Fig. 5 TEM diffraction patterns of CaIrO_3 at $R_{\text{Ir}/\text{Ca}} = 1.0$.

from RT to 1023 K. At $R_{\text{Ir}/\text{Ca}} = 0.25$ to 0.6, the σ increased from 4×10^{-4} to 140 Sm^{-1} at RT and increased with increasing $R_{\text{Ir}/\text{Ca}}$ (Fig. 6(a) and 6(b)), implying that Ca_4IrO_6 ($R_{\text{Ir}/\text{Ca}} = 0.25$) had a lower σ than Ca_2IrO_4 ($R_{\text{Ir}/\text{Ca}} = 0.5$). The σ at $R_{\text{Ir}/\text{Ca}} = 0.6$ was higher than that at $R_{\text{Ir}/\text{Ca}} = 0.5$. This might have been caused by the second phase of Ir. At $R_{\text{Ir}/\text{Ca}} = 0.7$ to 1.2, the σ decreased with increasing $R_{\text{Ir}/\text{Ca}}$, implying that Ca_2IrO_4 ($R_{\text{Ir}/\text{Ca}} = 0.5$) had a higher σ than CaIrO_3 ($R_{\text{Ir}/\text{Ca}} = 1.0$). The σ slightly increased from RT to 600 K and then rose significantly over 600 K (Fig. 6(c)).

The σ of Ca_4IrO_6 at $R_{\text{Ir}/\text{Ca}} = 0.25$ can be fitted by eq. (1):

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \quad (1)$$

where σ_0 is a constant, E_a is the activation energy and k_B is the Boltzmann's constant. A slope change was observed in two temperature regions of 500 to 1010 K and 300 to 500 K in Fig. 6(a). The activation energies calculated from the slopes were 0.24 and 0.11 eV, respectively. The σ of Ca_2IrO_4 at $R_{\text{Ir}/\text{Ca}} = 0.5$ can be fitted by eq. (1) in the temperature ranges of 350 to 450 K and 620 to 1010 K (Fig. 6(b)). The activation energies were 0.029 and 0.055 eV, respectively. The σ at $R_{\text{Ir}/\text{Ca}} = 1.0$ was fitted to an Arrhenius-type eq. (1) at only high temperatures of 800 to 1010 K (Fig. 6(c)). The E_a was calculated to be 0.15 eV, which is consistent with the value reported by Ohgushi *et al.*, i.e., E_a of 0.17 eV.¹¹⁾ This activation energy may represent the intrinsic conduction of CaIrO_3 since the σ increased significantly with increasing temperature at high temperatures.

Figure 7 shows the temperature dependence of the Seebeck coefficient (S) of Ca-Ir-O compounds at various $R_{\text{Ir}/\text{Ca}}$. The S of the specimen having the main phase of Ca_4IrO_6 ($R_{\text{Ir}/\text{Ca}} = 0.25$) showed positive values and decreased from 800 to $300 \mu\text{VK}^{-1}$ with increasing temperature from 400 to 1000 K, implying that Ca_4IrO_6 is a p-type semi-

conductor (Fig. 7(a)). The S of the main phase of Ca_2IrO_4 ($R_{\text{Ir}/\text{Ca}} = 0.4$ –0.5) showed negative values of about $-110 \mu\text{VK}^{-1}$ at RT and increased to around $-50 \mu\text{VK}^{-1}$ with increasing temperature (Fig. 7(b)). The S at $R_{\text{Ir}/\text{Ca}} = 0.8$ showed a negative value of $-20 \mu\text{VK}^{-1}$ at room temperature and decreased to $-50 \mu\text{VK}^{-1}$ with increasing temperature to around 500 K, and then increased with increasing temperature and finally changed from negative to positive values. Since the specimen at $R_{\text{Ir}/\text{Ca}} = 0.8$ consisted of Ca_2IrO_4 and CaIrO_3 , this complicated behavior may have been due to the sum effect of n-type Ca_2IrO_4 and p-type CaIrO_3 . The S of the specimens mainly consisting of CaIrO_3 ($R_{\text{Ir}/\text{Ca}} = 1.0$ –1.2) showed p-type semiconduction which decreased significantly from 700 to $60 \mu\text{VK}^{-1}$ with increasing temperature from room temperature to 600 K and then became almost temperature independent at $T > 600$ K (Fig. 7(a)). The temperature where the σ increased significantly was almost the same as that where the S remained as a constant, implying CaIrO_3 may show intrinsic properties at $T > 600$ K.

Figure 8 presents the temperature dependence of thermal conductivity (κ) at various $R_{\text{Ir}/\text{Ca}}$. The κ at $R_{\text{Ir}/\text{Ca}} = 0.25$ and 0.5 (Ca_4IrO_6 main phase and Ca_2IrO_4 in a single phase) had almost the same value of $1.08 \text{ Wm}^{-1}\text{K}^{-1}$ at RT and slightly decreased to $0.8 \text{ Wm}^{-1}\text{K}^{-1}$ at 620 K and then slightly increased with increasing temperature. At $R_{\text{Ir}/\text{Ca}} > 0.7$, the κ significantly decreased with increasing temperature from RT to 650 K and then slightly increased with increasing temperature from 800 K. The κ at $R_{\text{Ir}/\text{Ca}} = 1.0$ having the CaIrO_3 main phase decreased from 2.7 to $1.2 \text{ Wm}^{-1}\text{K}^{-1}$ with increasing temperature from RT to 800 K, and then slightly increased to $1.25 \text{ Wm}^{-1}\text{K}^{-1}$ at 1023 K. Thermal conductivity usually decreases with increasing temperature due to the decrease in electron mobility and keeps almost constant or slowly increases due to an increase in electron energy and lattice vibration.

Fig. 6 Temperature dependence of electrical conductivity of various compositions.

Figure 9 shows the temperature dependence of the dimensionless thermoelectric figure of merit (ZT) calculated from eq. (2):

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

The ZT at $R_{\text{Ir}/\text{Ca}} = 0.25$ (main phase of Ca_4IrO_6) was about 0.003 at RT and slightly decreased with increasing temperature (Fig. 9(a)). The ZT at $R_{\text{Ir}/\text{Ca}} = 0.5$ (Ca_2IrO_4 in a single phase) slightly increased with increasing temperature and showed a maximum value at 800 K. The ZT at $R_{\text{Ir}/\text{Ca}} = 0.8$ showed the lowest values because of the lowest absolute Seebeck coefficient. The ZT at $R_{\text{Ir}/\text{Ca}} = 1.0$ (main phase of CaIrO_3) decreased from 0.0011 to 0.0002 with increasing temperature from RT to 600 K and significantly increased with increasing temperature above 600 K, showing the highest value of 0.004 at 1023 K. The ZT at $R_{\text{Ir}/\text{Ca}} = 1.1$ and 1.2 showed the same trend as that of $R_{\text{Ir}/\text{Ca}} = 1.0$. The p-type compounds showed the highest ZT of 0.003 at RT and

Fig. 7 Temperature dependence of Seebeck coefficient of Ca-Ir-O compounds.

Fig. 8 Temperature dependence of thermal conductivity of Ca-Ir-O compounds.

$R_{\text{Ir}/\text{Ca}} = 0.25$ (Ca_4IrO_6), and the highest ZT of 0.006 at 1023 K and $R_{\text{Ir}/\text{Ca}} = 1.1$ and 1.2. The n-type compounds showed the highest ZT of 0.0022 at 800 K and $R_{\text{Ir}/\text{Ca}} = 0.5$. Table 1 summarizes the crystal structure and properties of the Ca-Ir-O compounds.

Table 1 Properties of Ca-Ir-O compounds.

Compound	$R_{\text{Ir/Ca}}$	Space group	Crystal system	Lattice parameters (nm)			Ref.	Microstructure	Electrical property	Seebeck coefficient	Highest ZT value
				a	b	c					
Ca_4IrO_6	0.25	$R3c$	Hexagonal	0.9334		1.1237	*)	Coarse grain	Semiconduction	p-type	0.003 at RT
				0.9330		1.1228					
Ca_2IrO_4	0.5	$P6_2m$	Hexagonal	0.9431		0.3196	*)	Fine grain	Semiconduction	n-type	0.002 at 800 K
				0.9421		0.3195					
CaIrO_3	1.0	Cmcm	Orthorhombic	0.3148	0.9866	0.7300	*)	Rod-like	Semiconduction	p-type	0.004 at 1023 K
				0.3144	0.9866	0.7299					

*)the present study

Fig. 9 Temperature dependence of dimensionless figure of merit of Ca-Ir-O compounds.

4. Conclusions

Ca-Ir-O compounds at various molar ratios of Ir to Ca ($R_{\text{Ir/Ca}}$) from 0.2 to 1.2 were synthesized by a solid-state reaction and compacted by spark plasma sintering. The specimens had a theoretical density of around 70%. Ca_4IrO_6 with a trace of Ir metal was obtained at $R_{\text{Ir/Ca}} = 0.25$. Ca_2IrO_4 in a single phase was obtained at $R_{\text{Ir/Ca}} = 0.5$. CaIrO_3 accompanied by a trace of Ca_2IrO_4 and Ir metal was

prepared at $R_{\text{Ir/Ca}} = 1.0$. The σ increased with increasing temperature independent of $R_{\text{Ir/Ca}}$, exhibiting semiconducting behavior. The σ at room temperature was around 4×10^{-4} to 150 Sm^{-1} and increased with increasing $R_{\text{Ir/Ca}}$ from 0.25 to 0.6 and then decreased with increasing $R_{\text{Ir/Ca}}$. The σ of Ca_2IrO_4 was higher than that of CaIrO_3 and Ca_4IrO_6 . The temperature dependence of σ of Ca_4IrO_6 , Ca_2IrO_4 and CaIrO_3 showed activation energies of 0.24, 0.55 and 0.15 eV, respectively, at high temperatures. Ca_4IrO_6 and CaIrO_3 were p-types, whereas Ca_2IrO_4 was a n-type semiconductor. The absolute values of S decreased with increasing temperature. Ca_4IrO_6 had the highest S of around $800 \mu\text{VK}^{-1}$ at RT. The κ of Ca_4IrO_6 , CaIrO_3 and Ca_2IrO_4 at room temperature were 1.1, 1.1 and $2.7 \text{ Wm}^{-1}\text{K}^{-1}$, respectively. The ZT of p-type Ca_4IrO_6 was of 0.003 at RT, whereas those of n-type Ca_2IrO_4 and p-type CaIrO_3 were 0.002 and 0.004 at 800 and 1023 K, respectively. The highest ZT of p-type was 0.006 at $R_{\text{Ir/Ca}} = 1.1$ and 1.2 and 1023 K and that of n-type was 0.0022 at $R_{\text{Ir/Ca}} = 0.5$ and 800 K.

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