The thermoelectric properties of cesium–graphite intercalation compounds (Cs-GICs) and some other GICs were studied. The electrical conductivities of the Cs-GICs prepared from Grafoil were around $10^6 \, \Omega^{-1} \, m^{-1}$, about 10 times higher than that of the host graphite, and the thermal conductivities were 50–100 Wm$^{-1}$K$^{-1}$, about 1/4–1/2 of that of the host graphite. While the Seebeck coefficient of the host graphite was nearly zero, those of the Cs-GICs were found to be around $-30 \, \mu V \, K^{-1}$. These properties were determined also for the Cs-GICs prepared from well-oriented PGS graphite sheets. Consequently, the figures of merit of the Cs-GICs were of the order of $10^{-2}$, approximately 10 times higher than that of the host graphite. The power factor of the Cs-GICs reached the order of $10^{-3}$ Wm$^{-1}$K$^{-2}$, with the best datum at $6.5 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$. The carrier density of the GICs increased as the concentration of intercalated species increased, whereas their lattice thermal conductivities decreased. It is suggested that highly concentrated GICs might be promising candidate thermoelectric materials.

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1. Introduction

Recently, interest in thermoelectric materials has been growing and there have been extensive efforts to discover excellent materials. Many candidate thermoelectric materials; such as oxides, silicides, heuslers, chalcogenides, skutterudites, and clathrates etc., have been investigated. In this paper, a novel candidate thermoelectric material, a graphite intercalation compound, is introduced.

Graphite intercalation compounds (GICs) are graphite derivatives that contain other chemical species (intercalates) in their interlayer spaces, as shown in Fig. 1. More than 100 intercalate species have been found so far, such as alkali metals, halogens, metal chlorides, etc. As charge transfer occurs between the graphite planes and the intercalates, GICs usually have high electrical conductivities. GICs have attracted much attention for many years as lightweight conductive materials. In addition to the high electrical conductivity, GICs have relatively high Seebeck coefficients and low thermal conductivities compared with their host graphite materials. It is quite likely that GICs can be used as thermoelectric materials. GICs have characteristics derived from their host graphite materials; thus, GICs are lightweight and anisotropic, and come in arbitrary shapes, such as sheets, blocks and powders. Also, both n-type and p-type GICs are available depending on the types of intercalates. We feel that these characteristics make GICs particularly attractive as thermoelectric materials.

However, since GICs have rarely been investigated as thermoelectric materials, there are only a few reports of thermoelectric data on GICs. Generally, it is very difficult to obtain thermoelectric data on GICs due to their instability in air. In this study, relatively air-stable GICs were chosen and their thermoelectric properties were measured; then, their potential as thermoelectric materials was discussed.

Usually, the thermoelectric performance of a material is evaluated using the figure of merit, $Z \equiv \sigma \cdot \alpha^2 / \kappa$, the dimensionless figure of merit, $ZT \equiv Z \cdot T$, or the power factor, $P \equiv \sigma \cdot \alpha^3$, where $\alpha$ is the electrical conductivity, $\kappa$ is the thermal conductivity. Since the working temperature is important for the practical use of thermoelectric materials, the dimensionless figure of merit, $ZT$, is often used. The power factor, $P$, expresses only the electronic contribution among the thermoelectric properties, so it is effective when the power conversion efficiency need not be considered. In this study, we evaluated the ability of Cs-GICs using the figure of merit and power factor, because their thermoelectric properties were measured only at room temperature.

In this paper, we report the thermoelectric properties of some GICs, mainly Cs-GICs, and their potential as thermoelectric materials. First, we discuss the thermoelectric properties of Cs-GICs and the dependence of these thermoelectric properties on the intercalates and host graphite materials; then we show their dependence on the intercalate concentration. Finally, we propose a method of producing GICs as promising thermoelectric materials.

2. Experimental

2.1 Preparation of GICs

Exfoliated graphite sheets prepared from natural graphite, Grafoil (UCAR Co.), were mainly used as the host graphite material. Grafoil sheets, 0.30mm thick, were cut into $3.0 \times 30$-mm$^2$ rectangles, and were heat-treated under vacu-
Thermoelectric Properties of Cesium–Graphite Intercalation Compounds

3. Results and Discussion

3.1 Thermoelectric properties of Cs-GICs

3.1.1 Cs-GICs prepared from Grafoil

The typical data obtained for the thermoelectric properties of the Cs-GICs prepared from Grafoil are listed in Table 1, together with the evaluated values of the power factors and figures of merit.

(1) Electrical conductivity \( \sigma \)

For the Cs-GICs, the highest electrical conductivity observed was \( 1.5 \times 10^6 \, \Omega^{-1} \, \text{m}^{-1} \), over 10 times higher than that of Grafoil. Table 2 shows our previous results \(^{11,21}\) for the carrier densities and mobilities estimated from the values of the Hall coefficients, magnetoresistances, and electrical conductivities of Grafoil and Cs-ethylene-GIC prepared from Grafoil. Since the magnetoresistance of Cs-ethylene-GIC was too small to be detected, it was concluded that the carriers of electrical conduction on Cs-ethylene-GIC were almost exclusively electrons. The electron density of Cs-ethylene-GIC was \( 5.7 \times 10^{20} \, \text{cm}^{-3} \), which is approximately 700 times that of Grafoil, and its electron mobility was approximately 1/60. This remarkable enhancement of the electron density is due to the electron transfer from the Cs atoms to the graphite planes. It has also been observed that the electrical resistivity of Cs-ethylene-GIC has a metallic temperature dependence, as shown in Fig. 5—this is a typical feature of GICs \(^{22-24}\).—while Grafoil has a semiconductive dependence \(^{14,25,26}\).

The relatively low electrical conductivities of Cs-benzene-GIC and Cs-acrylonitril-GIC shown in Table 1 were attributed to their lower air stability, because the electrical conductivity of a sample is strongly affected by its decomposition in air. \(^{10,21}\)
Table 1 Electrical conductivity ($\sigma$), Seebeck coefficient ($\alpha$), thermal conductivity ($\kappa$), power factor ($P$), and figure of merit ($Z$) for Cs-GICs prepared from Grafoil.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma$/$\Omega^{-1}$ m$^{-1}$</th>
<th>$\alpha$/$\mu$V K$^{-1}$</th>
<th>$\kappa$/Wm$^{-1}$ K$^{-1}$</th>
<th>$P$/Wm$^{-1}$ K$^{-2}$</th>
<th>$Z$/K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Grafoil)</td>
<td>1.2 x 10$^5$</td>
<td>-0.24</td>
<td>195</td>
<td>6.9 x 10$^{-9}$</td>
<td>3.5 x 10$^{-11}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{0.32}$</td>
<td>1.1 x 10$^6$</td>
<td>-27</td>
<td>50</td>
<td>8.4 x 10$^{-4}$</td>
<td>1.7 x 10$^{-5}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{1.1}$</td>
<td>5.8 x 10$^6$</td>
<td>-29</td>
<td>70</td>
<td>4.9 x 10$^{-4}$</td>
<td>7.0 x 10$^{-6}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{&lt;1.0}$</td>
<td>1.5 x 10$^6$</td>
<td>-29</td>
<td>63</td>
<td>1.2 x 10$^{-3}$</td>
<td>1.9 x 10$^{-6}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{95}$</td>
<td>1.0 x 10$^6$</td>
<td>-32</td>
<td>93</td>
<td>9.9 x 10$^{-4}$</td>
<td>1.1 x 10$^{-6}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{0.88}$</td>
<td>6.7 x 10$^5$</td>
<td>-30</td>
<td>72</td>
<td>5.9 x 10$^{-4}$</td>
<td>8.2 x 10$^{-6}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{0.75}$</td>
<td>9.2 x 10$^5$</td>
<td>-29</td>
<td>80</td>
<td>7.8 x 10$^{-4}$</td>
<td>9.7 x 10$^{-6}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{0.82}$</td>
<td>7.6 x 10$^5$</td>
<td>-30</td>
<td>94</td>
<td>7.0 x 10$^{-4}$</td>
<td>7.4 x 10$^{-6}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{2.0}$</td>
<td>1.7 x 10$^5$</td>
<td>-33</td>
<td>71</td>
<td>1.9 x 10$^{-4}$</td>
<td>2.6 x 10$^{-6}$</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$CN)$</em>{1.2}$</td>
<td>2.1 x 10$^5$</td>
<td>-41</td>
<td>75</td>
<td>3.5 x 10$^{-4}$</td>
<td>4.7 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

Table 2 Values of electrical conductivity ($\sigma$), Hall coefficients ($R_H$), magnetoresistance ($\Delta \rho/\rho$), electron and hole densities ($n_e$, $n_h$), and, electron and hole mobilities ($\mu_e$, $\mu_h$) for Grafoil and Cs-ethylene-GIC prepared from Grafoil at 77 K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma$/$\Omega^{-1}$ m$^{-1}$</th>
<th>$R_H$/cm$^2$ C$^{-1}$ (at 1T)</th>
<th>$\Delta \rho/\rho$ (at 1T)</th>
<th>$n_e$/cm$^{-3}$</th>
<th>$n_h$/cm$^{-3}$</th>
<th>$\mu_e$/cm$^2$ V$^{-1}$ s$^{-1}$</th>
<th>$\mu_h$/cm$^2$ V$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grafoil</td>
<td>7.5 x 10$^7$</td>
<td>-0.12</td>
<td>0.084</td>
<td>8.3 x 10$^{17}$</td>
<td>7.8 x 10$^{17}$</td>
<td>2900</td>
<td>2900</td>
</tr>
<tr>
<td>CsC$_2$(C$_2$H$<em>4$)$</em>{1.4}$</td>
<td>4.6 x 10$^5$</td>
<td>-0.011</td>
<td>—</td>
<td>5.7 x 10$^{20}$</td>
<td>—</td>
<td>51</td>
<td>—</td>
</tr>
</tbody>
</table>

(2) Seebeck coefficient $\alpha$

The Seebeck coefficient of the host graphite is nearly zero since the number of electrons and number of holes (conductive carriers) are almost equal. Since Cs-GICs are n-type materials, their Seebeck coefficients became negative, approximately $-30 \mu$V K$^{-1}$. The absolute values of the Seebeck coefficients of GICs at around room temperature are similar, $25-40 \mu$V K$^{-1}$, although the reported values for the Seebeck coefficients are considerably fewer than the reported electrical conductivity values. These values are of the order of 1/10 times smaller than those of the other candidate thermoelectric materials.

(3) Thermal conductivity $\kappa$

The thermal conductivities of the Cs-GICs were $50-100$ Wm$^{-1}$ K$^{-1}$, about $1/4-1/2$ of that of Grafoil. The thermal conductivity of GICs has been investigated in detail as described below.

Although the thermal conduction in host graphite is dominated by the lattice contribution, that in GICs is the result of both the lattice and carrier contribution. While the carrier contribution of GICs is higher than that of the host graphite, the lattice contribution is smaller, because the intercalation process causes an increase in the number of lattice defects, as well as an increase in the carrier density. It has also been found that the lattice contribution dominates in GICs at around room temperature. As a result, the thermal conductivities of GICs at around room temperature are low as compared to those of the host graphite.

(4) Power factor $P$, and figure of merit $Z$

Although the Seebeck coefficients of the Cs-GICs were appreciably smaller than those of the other candidate thermoelectric materials, the electrical conductivities were sufficiently higher; therefore, the power factors of the Cs-GICs were relatively high. The highest value for the Cs-GICs prepared from Grafoil was $1.2 \times 10^{-7}$ Wm$^{-1}$ K$^{-2}$, which is comparable to the values of promising candidate thermoelectric materials.

On the other hand, the figures of merit of the Cs-GICs were one to two orders of magnitude lower than those of the other candidates, because the thermal conductivities of the Cs-GICs were of the order of 10 times higher than those of the other candidates. The figures of merit of the Cs-GICs were of the order of $10^{-5}$ K$^{-1}$, $10^5$ times higher than that of Grafoil.

Thus, in order to improve the thermoelectric performance...
of Cs-GICs, it is necessary to increase the Seebeck coefficients and decrease the thermal conductivities.

### 3.1.2 Other GICs prepared from Grafoil

In Fig. 6, the thermal conductivities, Seebeck coefficients, and figures of merit are plotted against the electrical conductivity, for Cs-ethylene-GIC, Cs-benzene-GIC, Cs-


As seen in Fig. 6(a), the Seebeck coefficients remain almost constant with increasing electrical conductivity above \( \sigma = 5.8 \times 10^5 \text{ \Omega}^{-1} \text{m}^{-1} \), and the absolute values of the Seebeck coefficients are somewhat larger below \( \sigma = 5.1 \times 10^2 \text{ \Omega}^{-1} \text{m}^{-1} \). As seen in Fig. 6(b), the thermal conductivities appear to decrease slightly with increasing electrical conductivity.

As mentioned in section 3.1.1, the electrical conductivity is strongly affected by the decomposition of the sample in air, unlike the Seebeck coefficient and thermal conductivity. Thus, the effect of the difference in the air stability of each sample is more or less reflected in the results shown in Figs. 6(a) and (b).

It should be noted that the power factor and figure of merit generally increased linearly with increasing electrical conductivity, as shown in Figs. 6(c) and (d). This suggests that the performance of GICs as thermoelectric materials is governed mainly by their electrical conductivity.

### 3.1.3 Cs-GICs prepared from PGS graphite sheet

The thermoelectric properties of Cs-GICs prepared from PGS graphite sheets, instead of Grafoil, are listed in Table 3. PGS graphite sheets\(^{28}\) have higher electrical and thermal conductivity than Grafoil.

For the Cs-GICs prepared from the PGS graphite sheet, the Seebeck coefficients were about 2/3 and the thermal conductivities were a few times higher than those of the Cs-GICs prepared from Grafoil. The electrical conductivities were, however, about 10 times higher than those of the Cs-GICs prepared from Grafoil, and thus the figures of merit were much higher than those of the Cs-GICs prepared from Grafoil.

It should be noted that the power factor of the Cs-GICs prepared from the PGS graphite sheet reached \( 6.5 \times 10^{-3} \text{ Wm}^{-1} \text{K}^{-2} \), which is comparable to those of promising candidate thermoelectric materials.

It is considered that the most effective way of improving the figure of merit and power factor of Cs-GICs, is to increase the electrical conductivity of the sample, because it is apparently difficult to control the Seebeck coefficient.

### 3.2 Dependence of the thermoelectric properties of Cs-GICs on the intercalate concentration

Figure 7 shows the dependence of the electrical conductivity, Seebeck coefficient, and thermal conductivity on the Cs concentration in Cs-ethylene-GICs prepared from Grafoil. In this figure, an increase in \( x \) implies a decrease in the Cs concentration.

As shown in Fig. 7(a), the electrical conductivity tends to

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**Table 3**  
Electrical conductivity (\( \sigma \)), Seebeck coefficient (\( \alpha \)), thermal conductivity (\( \kappa \)), power factor (\( P \)), and figure of merit (\( Z \)) for Cs-GICs prepared from PGS graphite sheet.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( \sigma/\Omega^{-1} \text{m}^{-1} )</th>
<th>( \alpha/\mu \text{V K}^{-1} )</th>
<th>( \kappa/\text{Wm}^{-1} \text{K}^{-1} )</th>
<th>( P/\text{Wm}^{-1} \text{K}^{-2} )</th>
<th>( Z/\text{K}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PGS graphite sheet)</td>
<td>( 4.3 \times 10^5 )</td>
<td>( -4.6 )</td>
<td>( 500 )</td>
<td>( 9.1 \times 10^{-6} )</td>
<td>( 1.8 \times 10^{-8} )</td>
</tr>
<tr>
<td>CsC(_{24})</td>
<td>( 1.3 \times 10^7 )</td>
<td>( -22 )</td>
<td>( 300 )</td>
<td>( 6.2 \times 10^{-3} )</td>
<td>( 2.1 \times 10^{-5} )</td>
</tr>
<tr>
<td>CsC(_{24})</td>
<td>( 6.8 \times 10^6 )</td>
<td>( -22 )</td>
<td>( 270 )</td>
<td>( 3.2 \times 10^{-3} )</td>
<td>( 1.2 \times 10^{-5} )</td>
</tr>
<tr>
<td>CsC(_{24})(C(_3)H(<em>4))(</em>{1-x})</td>
<td>( 1.2 \times 10^7 )</td>
<td>( -23 )</td>
<td>( 240 )</td>
<td>( 6.5 \times 10^{-3} )</td>
<td>( 2.7 \times 10^{-5} )</td>
</tr>
</tbody>
</table>
increase slightly with increasing the Cs concentration. We have reported previously that the electrical conductivities of K-GICs prepared from Grafoil increase with increasing K concentration. 13)

Some reports2–4) have indicated that the Seebeck coefficients of GICs depend slightly on their stage structure, that is, on the intercalate concentration. For example, in the case of SbCl3-GIC at room temperature, 2) the Seebeck coefficients of the stage-2 and stage-3 compounds are almost equal (≈ 25 μV K⁻¹), and that of the stage-10 compound is approximately 40 μV K⁻¹. The stage structure dependence of the Seebeck coefficient appears weak compared with that of the electrical and thermal conductivity. In this study, the Seebeck coefficients (Fig. 7(b)) were almost constant with increasing Cs concentration, except in one of the samples, CsC₄₈(C₂H₄)₉.

On the other hand, the thermal conductivity clearly correlated with the Cs concentration, as shown in Fig. 7(c). The increase in the Cs concentration causes a decrease in the thermal conductivity in a manner similar to that described in section 3.1.1: The intercalation process causes an increase in the number of lattice defects, as well as an increase in the carrier density. Therefore, with the increase in the Cs concentration, the increase in electrical conductivity and the decrease in thermal conductivity occurred simultaneously in the Cs-GICs. In this case, the Wiedemann-Franz rule, which represents one of the difficulties in finding an excellent thermoelectric material, apparently does not apply.

The figure of merit showed a similar dependence on the electrical conductivity, as shown in Fig. 7(d). This indicates that the performance of Cs-GICs as thermoelectric materials is principally regulated by their electrical conductivity, as has been pointed out.

The same trend as that in the Cs-GICs was also observed in the FeCl₃-GICs prepared from Grafoil; the experimental results are given in Table 4. Since FeCl₃-GICs are p-type materials, the electrons of the graphite planes are transferred to the FeCl₃ intercalates. With the increase in the FeCl₃ concentration, the electrical conductivity increased and the thermal conductivity decreased, resulting the increase of the figure of merit.

4. Conclusion

The thermoelectric properties of Cs-GICs and other GICs were investigated and their potential as thermoelectric materials was discussed. At present, although the electrical conductivities of Cs-GICs are sufficiently high compared with those of the other candidates, their Seebeck coefficients are rather small and thermal conductivities are high. As a result, the figures of merit of these GICs are not comparable to those of the other candidate thermoelectric materials, although the power factors are comparable. In order to improve the thermoelectric performance of GICs, it is necessary to increase their Seebeck coefficients and decrease their thermal conductivities. However, it appears difficult to control the Seebeck coefficients of GICs.

The simultaneous increase in the carrier density and decrease in the lattice thermal conductivity were caused by the increase in the intercalate concentration. We consider this to be a great advantage for improving the thermoelectric performance of GICs. In particular, it is important to devise a method to decrease the thermal conductivity by increasing the intercalate concentration—this is one of the most important subjects for further study.

![Fig. 7 Cs concentration dependence of (a) electrical conductivity σ, (b) Seebeck coefficient α, (c) thermal conductivity κ, and (d) figure of merit Z for Cs-GICs prepared from Grafoil.](image-url)

Table 4 Electrical conductivity (σ), Seebeck coefficient (α), thermal conductivity (κ), and figure of merit (Z) for FeCl₃-GICs prepared from Grafoil.

<table>
<thead>
<tr>
<th>Composition</th>
<th>σ/Ω⁻¹ m⁻¹</th>
<th>α/μV K⁻¹</th>
<th>κ/W m⁻¹ K⁻¹</th>
<th>Z/K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₃FeCl₃</td>
<td>1.7 × 10⁵</td>
<td>23</td>
<td>200</td>
<td>4.4 × 10⁻⁷</td>
</tr>
<tr>
<td>C₄₈FeCl₃</td>
<td>7.3 × 10⁵</td>
<td>31</td>
<td>69</td>
<td>1.0 × 10⁻⁵</td>
</tr>
</tbody>
</table>
REFERENCES