

THERMOELECTRIC PROPERTIES OF GRAPHITE INTERCALATION COMPOUNDS

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Abstract

Graphite intercalation compounds, GICs, have high electrical conductivities, large Seebeck coefficients and low thermal conductivities; therefore their performance as thermoelectric materials is high compared with their host graphite. At present, although the electrical conductivities of GICs, as thermoelectric materials, are sufficiently high, their Seebeck coefficients are rather small and their thermal conductivities are too high. As a result, the thermoelectric performance of GICs is not high, as evaluated based on the figure of merit. However, they are comparable to those of other thermoelectric materials, as evaluated based on the power factor. In order to further improve the thermoelectric performance of GICs, it is necessary to increase their Seebeck coefficients and decrease their thermal conductivities.

Introduction

In recent years, interest in thermoelectric materials has been growing and there have been extensive efforts to develop more efficient materials. Thermoelectric materials can convert heat into electrical energy and are important materials for the future. To be an effective thermoelectric material, a material must possess a large Seebeck coefficient, a high electrical conductivity and a low thermal conductivity. A thermoelectric generator consists of n-type and p-type thermoelectric materials, as in thermocouples.

Graphite intercalation compounds (GICs) are graphite derivatives that contain other chemical species (intercalates) in their interlayer spaces. Since charge transfer occurs between the graphite planes and the intercalates, GICs usually have high electrical conductivities. In addition to the high electrical conductivity, GICs have relatively large 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 also have characteristics derived from their host graphites, such as light weight and anisotropy. 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.

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 ($\equiv \sigma \cdot \alpha^2$), where σ is the electrical conductivity, α is the Seebeck coefficient, and κ 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, so it is useful when the power conversion efficiency need not be considered. In this study, we evaluated the thermoelectric capabilities of GICs using the figure of merit and the power factor, because their thermoelectric properties were measured only at room temperature.

In this paper, we report the thermoelectric properties of GICs and discuss their potential as a thermoelectric material.

Experimental

Preparation of the GICs

Exfoliated graphite sheets prepared from natural graphite, Grafoil (GrafTech Co.), and well-oriented PGS graphite sheets (Matsushita Electric Industrial Co.) were used as the host graphite material. Grafoil sheets of 0.30 mm in thickness were cut into $3.0 \times 30 \text{ mm}^2$ rectangles and heat-treated under vacuum at $900 \text{ }^\circ\text{C}$ before use. PGS graphite sheets of 0.10 mm in thickness were cut into $2.0 \times 30 \text{ mm}^2$ rectangles. Alkali metals such as lithium, potassium and cesium, and metal chlorides such as FeCl_3 were used as the intercalate species.

GICs were prepared by allowing the graphite to react with the vapor of the intercalates at specific temperatures under vacuum. Ethylene or benzene was then absorbed into the vacant nano-space in the interlayer of the Cs-GICs for the improvement of their air stability and ternary GICs such as Cs-ethylene-GIC and Cs-benzene-GIC were formed.

Measurement of the thermoelectric properties

The in-plane electrical conductivities, Seebeck coefficients and thermal conductivities of the above GICs and their host graphites were measured at room temperature. Samples cut into 25-mm-long strips were used for these measurements. The electrical conductivities were measured by the four-terminal method in air. The thermal conductivities and Seebeck coefficients were measured under vacuum using almost the same system as that shown in **Figure 1**. The thermal conductivities were measured by the four-terminal method, in a way similar to the electrical conductivity measurement. That is, the electrical current was replaced by a heat flow and the voltage was replaced by a temperature difference. The Seebeck coefficients were measured by mounting voltage terminals on the samples after measuring the thermal conductivity. The reliability of this apparatus was confirmed using an isotropic graphite block as the standard, comparing the values determined by this method and applying the laser-flash method.

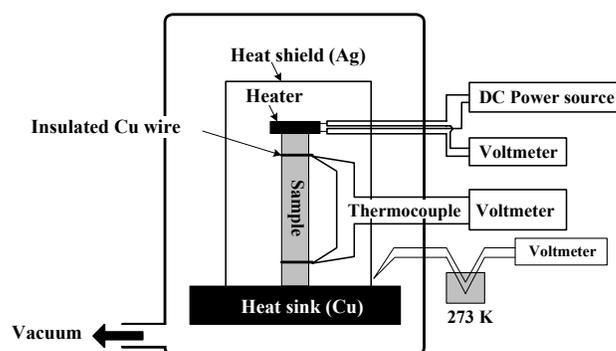


Figure 1. Experimental set-up for measuring thermal conductivity.

Results and Discussion

GICs prepared from Grafoil

The typical data obtained for the thermoelectric properties of the GICs prepared from Grafoil are listed in **Table 1**, together with the evaluated values of the power factors and figures of merit. For the GICs prepared from Grafoil, the highest electrical conductivity observed was $1.5 \times 10^6 \text{ } \Omega^{-1}\text{m}^{-1}$ in $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{x>1.0}$, over 10 times higher than that of pristine Grafoil. The Seebeck coefficient of the host graphite is nearly zero, since the number of electrons and number of holes (conductive carriers) in pristine graphite are almost equal. The Seebeck coefficients became negative in the alkali metal-GICs (AM-GICs) and positive in the metal chlorides-GICs, depending on their major conductive carriers. They were approximately $-30 \text{ } \mu\text{VK}^{-1}$; the maximum value was $-51 \text{ } \mu\text{VK}^{-1}$ in the partially decomposed LiC_x . These values are about one order of magnitude smaller than those of the other candidate thermoelectric materials. The thermal conductivities of the GICs were around $50 \sim 100 \text{ Wm}^{-1}\text{K}^{-1}$,

about 1/4 ~ 1/2 of that of pristine Grafoil. In graphite materials, the thermal conductivity is dominated by the lattice contribution. However, the lattice contribution in GICs is smaller than that in pristine graphite, because the intercalation process causes an increase in the number of lattice defects.

Although the Seebeck coefficients of the GICs prepared from Grafoil were appreciably smaller than those of the other candidate thermoelectric materials, the power factors of these GICs were relatively high because their electrical conductivities were sufficiently higher. The highest value for the GICs prepared from Grafoil was $1.2 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ in $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{x>1.0}$, which is comparable to the values of promising candidate thermoelectric materials.

The sample of $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{x>1.0}$ was stable in air, because the oligomerization of ethylene molecules occurred in the interlayer nano-space in CsC_{24} and the resulting ethylene oligomers blocked the diffusion of Cs atoms. Therefore, its electrical conductivity remained high. The electrical conductivity of a sample is strongly affected by its decomposition in air. The relatively low electrical conductivity of Cs-benzene-GIC, $\text{CsC}_{24}(\text{C}_6\text{H}_6)_{2.0}$, was attributed to its lower air stability.

On the other hand, the figures of merit of these GICs were one to two orders of magnitude lower than those of the other candidates, because the thermal conductivities of these GICs were about one order of magnitude higher.

Table 1. Electrical conductivity (σ), Seebeck coefficient (α), thermal conductivity (κ), power factor (P), and figure of merit (Z) for GICs prepared from Grafoil.

| Composition | $\sigma / \Omega^{-1}\text{m}^{-1}$ | $\alpha / \mu\text{VK}^{-1}$ | $\kappa / \text{Wm}^{-1}\text{K}^{-1}$ | $P / \text{Wm}^{-1}\text{K}^{-2}$ | Z / K^{-1} | |
|---|-------------------------------------|------------------------------|--|-----------------------------------|-----------------------|----------------------|
| Grafoil | 1.2×10^5 | -0.24 | 195 | 6.9×10^{-9} | 3.5×10^{-11} | |
| LiC_{18} | * | 2.0×10^6 | -21 | 88 | 8.8×10^{-4} | 1.0×10^{-5} |
| LiC_x | | 1.5×10^5 | -51 | 122 | 4.0×10^{-4} | 3.3×10^{-5} |
| KC_{24} | | 3.2×10^5 | -34 | 61 | 3.6×10^{-4} | 5.9×10^{-5} |
| $\text{CsC}_{12}(\text{C}_2\text{H}_4)_{0.32}$ | * | 1.1×10^6 | -27 | 50 | 8.4×10^{-4} | 1.7×10^{-5} |
| $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{1.1}$ | | 5.8×10^5 | -29 | 70 | 4.9×10^{-4} | 7.0×10^{-6} |
| $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{x<1.0}$ | * | 1.5×10^6 | -29 | 63 | 1.2×10^{-4} | 1.9×10^{-5} |
| $\text{CsC}_{30}(\text{C}_2\text{H}_4)_{0.95}$ | * | 1.0×10^6 | -32 | 93 | 9.9×10^{-4} | 1.1×10^{-5} |
| $\text{CsC}_{36}(\text{C}_2\text{H}_4)_{0.98}$ | * | 6.7×10^5 | -30 | 72 | 5.9×10^{-4} | 8.2×10^{-6} |
| $\text{CsC}_{39}(\text{C}_2\text{H}_4)_{0.99}$ | * | 9.2×10^5 | -29 | 80 | 7.8×10^{-4} | 9.7×10^{-6} |
| $\text{CsC}_{48}(\text{C}_2\text{H}_4)_{0.82}$ | * | 7.6×10^5 | -30 | 94 | 7.0×10^{-4} | 7.4×10^{-6} |
| $\text{CsC}_{24}(\text{C}_6\text{H}_6)_{2.0}$ | | 1.7×10^5 | -33 | 71 | 1.9×10^{-4} | 2.6×10^{-6} |
| $\text{C}_{8,8}\text{FeCl}_3$ | | 7.3×10^5 | 31 | 69 | 7.2×10^{-4} | 1.0×10^{-5} |

* The measurements were performed just after the exposure to air.

GICs prepared from PGS graphite sheet

The thermoelectric properties of the GICs prepared from PGS graphite sheet are listed in **Table 2**. PGS graphite sheets have higher electrical and thermal conductivity than Grafoil. For the GICs prepared from PGS graphite sheet, the Seebeck coefficients were about 2/3 and the thermal conductivities were a few times higher than those of the GICs prepared from Grafoil. The electrical conductivities were, however, about 10 times higher than those of the GICs prepared from Grafoil. Therefore, the

power factors and the figures of merit were much higher than those of the GICs prepared from Grafoil. It should be noted that the power factor of the most of GICs prepared from PGS graphite sheet reached $10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$, which is comparable to those of other promising candidate thermoelectric materials.

Table 2 Electrical conductivity (σ), Seebeck coefficient (α), thermal conductivity (κ), power factor (P), and figure of merit (Z) for GICs prepared from PGS graphite sheets.

| Composition | $\sigma / \Omega^{-1}\text{m}^{-1}$ | $\alpha / \mu\text{VK}^{-1}$ | $\kappa / \text{Wm}^{-1}\text{K}^{-1}$ | $P / \text{Wm}^{-1}\text{K}^{-2}$ | Z / K^{-1} |
|---|-------------------------------------|------------------------------|--|-----------------------------------|----------------------|
| PGS graphite sheet | 4.3×10^5 | -4.6 | 500 | 9.1×10^{-6} | 1.8×10^{-8} |
| LiC ₆ * | 4.6×10^6 | -18 | 110 | 1.4×10^{-3} | 1.3×10^{-5} |
| KC ₂₄ | 3.1×10^6 | -27 | 150 | 2.2×10^{-3} | 1.5×10^{-5} |
| KC ₂₄ | 1.2×10^6 | -22 | 140 | 6.1×10^{-4} | 4.5×10^{-6} |
| KC ₂₄ | 2.6×10^6 | -34 | 140 | 3.0×10^{-3} | 2.1×10^{-5} |
| CsC ₂₄ | 1.3×10^7 | -22 | 300 | 6.2×10^{-3} | 2.1×10^{-5} |
| CsC ₂₄ | 6.8×10^6 | -22 | 270 | 3.2×10^{-3} | 1.2×10^{-5} |
| CsC ₂₄ (C ₂ H ₄) _{1.4} | 1.2×10^7 | -23 | 240 | 6.5×10^{-3} | 2.7×10^{-5} |

* The measurements were performed just after the exposure to air.

Thermoelectric performance of GICs

At present, although the electrical conductivities of the GICs are sufficiently high compared with those of the other candidates, their Seebeck coefficients are rather small and their thermal conductivities are high. As a result, the figures of merit of GICs are not comparable to those of the other candidate thermoelectric materials, although their 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. Indeed, it is also important to improve their air stability, because the performance of GICs as thermoelectric materials is governed mainly by their electrical conductivity.

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