ELECTRICAL AND THERMAL PROPERTIES OF GRAPHITE INTERCALATION COMPOUNDS CONTAINING CALCIUM AND LITHIUM

Rika Matsumoto[1], Mutsuki Nakajima[1], and Noboru Akuzawa[2]

[1] Faculty of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan
[2] Dept. of Chemical Science and Engineering, Tokyo National College of Technology, 1220-2 Kunugida, Hachioji, Tokyo 193-0997, Japan

Introduction

Recently, Ca-graphite intercalation compounds (Ca-GICs; CaC_6) have attracted considerable attention because of their superconductivity and transition temperature, Tc = 11.5 K, which is the highest among the GICs [1]. In addition, the structure of Ca-GICs differs from that of other GICs with alkali metals and alkali earth metals.

In most of the studies on Ca-GICs, highly oriented pyrolytic graphite (HOPG) was used as the host graphite material. We attempted to synthesis Ca-GICs by using graphite sheets that can be easily handled [2]. We found that the mixture of CaC_6, LiC_6, and Ca-Li-ternary GIC can be easily prepared, while pure CaC_6 is difficult to prepare. In addition, GICs containing CaC_6 partly exhibit superconductivity at Tc = 11.5 K, similar to pure CaC_6. However, despite possessing such interesting properties, the physical properties of Ca-GICs have not yet been clarified in detail.

In this study, we investigated the electrical and thermal properties of GICs containing Ca and Li.

Experimental

The host graphite materials used in this study were Grafoil sheets (GrafTech Co.) and PGS graphite sheets (Panasonic Co.). Grafoil sheets with a thickness of 0.10 mm were cut into 5 × 20-30 mm^2 rectangles and heat-treated under vacuum at 900 °C before use. PGS graphite sheets with a thickness of 0.10 mm were also cut into 5 × 20-30 mm^2 rectangles. Ca metal (99.5% purity) and Li metal (>99.9% purity) were used without further purification.

First, Ca was added to Li in the ratio 1:3 and heated to 350 °C under an Ar atmosphere to obtain a molten Ca-Li alloy in a reaction tube. Then, the graphite materials were soaked in the molten Ca-Li alloy, and the reaction tube was heated to 350 °C between 1 h to 15 days. In some cases, the reaction tube was evacuated before heating. For comparison with GICs containing CaC_6, pure Li-GIC (LiC_6) was also prepared. Li and graphite materials was placed in a stainless reaction tube, and the tube was evacuated and heated to 450 °C for about 2 days.

The structure of the product was examined by X-ray structural analysis and Raman spectroscopy. The electrical conductivity, thermal conductivity, and Seebeck coefficient of the products were measured at room temperature [3]. The temperature dependence of electrical conductivity was measured from 77 K to 300 K. The Hall coefficient and magnetoresistance of the products were measured to determine their conducting carrier density and mobility [3].

Results and Discussion

The electrical conductivity (σ), thermal conductivity (κ) and Seebeck coefficient (α) of the reaction products and their host graphite materials at room temperature are listed in Table 1. For comparison, the values of the parameters of Li-GIC (LiC_6) and K-GIC (KC_{24}) were also listed.

The amount of CaC_6 in the products denoted as 07Ca-8, 07Ca-10, and 06Ca-3 was quite small; the relative intensity of the peaks of CaC_6 (Ic = 0.45 nm) in XRD profiles was around 1%. The amount of CaC_6 in the products denoted as 07Ca-GB-1 and 07Ca-GB-2 was relatively large, and their electrical conductivity was 10 times that of their host graphite materials. These electrical conductivity are almost equal to those of pure LiC_6 and other alkali metal-GICs.

The thermal conductivity of 07Ca-GB-1 and 07Ca-GB-3 was 24 and 32 $Wm^{-1}K^{-1}$, respectively; these values are rather small as compared to those of other GICs. The Seebeck coefficient of 07Ca-GB-1 was –3.2 μVK^{-1}; this small value indicated that this product is similar to simple metals. In addition, the Seebeck coefficient of 07Ca-GB-3 was positive, which implies that it is a p-type material with hole conduction.

Figure 1 shows the temperature dependence of the electrical resistivity of 07Ca-GB-3, Cs-ethylene-ternary GIC, and their host graphite material (Grafoil). These two types of GICs show metallic temperature dependence, while Grafoil shows semi-conductive behavior. However, the temperature dependence of 07Ca-GB-3 is quite strong as compared to $CsC_{24}(C_2H_4)_{1.4}$. This implies that GICs containing CaC_6 are more metallic than alkali metal-GICs.

Figure 2 shows Raman spectra of the product CaC_6-rich product, 07Ca-GB-5, and its host graphite material (Grafoil). A large D-band peak attributed to the disordered structure is observed at around 1330 cm^{-1}. However, a large D-band peak is also observed in the spectra of LiC_6.

Conclusions

The electrical and thermal properties of GICs containing Ca and Li were investigated. The electrical conductivity of GICs containing Ca and Li were almost the same as that of alkali metal-GICs. The thermal conductivity of GICs containing Ca and Li was only rather small. However, the temperature dependence of the electrical conductivity and the value of Seebeck coefficient of GICs containing Ca and Li were remarkably different from those of other alkali metal-GICs. GICs containing CaC_6 were found to be more metallic than alkali metal-GICs.

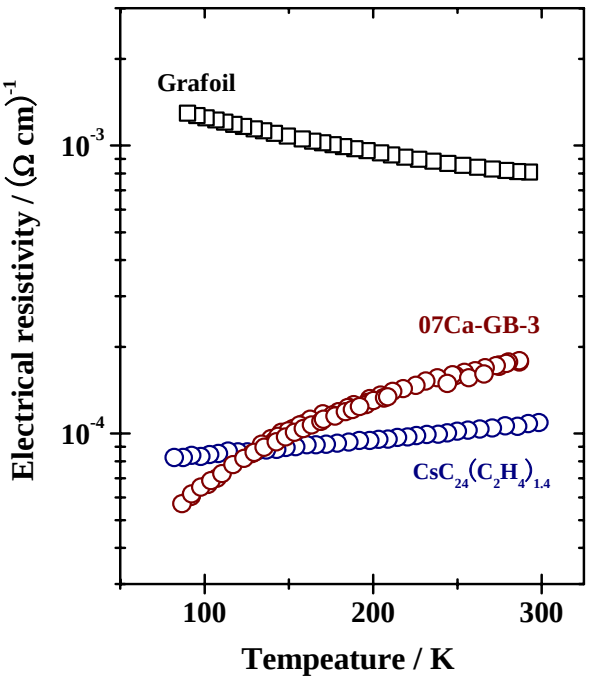

Fig.1 Temperature dependence in electrical resistivity of 07Ca-GB-3, Cs-ethylene-GIC and Grafoil.

References

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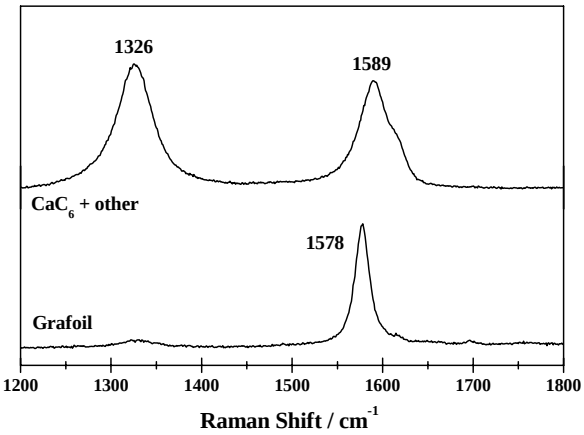

Fig.2 Raman spectra of 07Ca-GB-5 and Grafoil.

Table 1. Electrical conductivity (σ), thermal conductivity (κ) and Seebeck coefficient (α) of GICs and hosts.

Sample code		Composition ・ Structure	σ / Scm^{-1}	κ / $Wm^{-1}K^{-1}$	α / μVK^{-1}
HOST	Grafoil	C	1.2×10^3	200	–0.24
	07Ca-GB-1	CaC_6 + LiC_6 + others	1.0×10^4	24	–3.2
	07Ca-GB-3		1.2×10^4	32	+3.4
	07Ca-8	LiC_6 (+ CaC_6)	1.1×10^4	---	---
	07Ca-10		9.0×10^3	---	---
	07Ca-2	LiC_6	1.4×10^4	120	–44
	K-37 after 1day in air	KC_{24}	6.5×10^3	130	–36
HOST	PGS	C	4.3×10^3	500	–4.6
	06Ca-3	LiC_6 + LiC_{18} (+ CaC_6)	4.6×10^4	110	–18
	after 1day in air	LiC_6 + LiC_{18} + C	---	250	–46
	Li-29	LiC_6	2.9×10^4	130	–18