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PREPARATION AND CHARACTERIZATION OF SODIUM-GRAPHITE INTERCALATION COMPOUNDS

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Preparation and characterization of sodium-graphite intercalation compounds were investigated. It was confirmed that the resulting compound (NaC_x) had the stage 8 structure with identity period of 2.8 nm. The Raman spectroscopy showed that the G-band signal of NaC_x was observed at 1582 cm^{-1} and at 1608 cm^{-1}, which is a typical indication of the formation of intercalation compounds. The g-value of NaC_x was determined to be 2.0018 by the ESR measurement, which was very close to the reported values for the other alkali metal-graphite intercalation compounds. The electrical resistivity of NaC_x was about 1/3 of that of host graphite at room temperature and showed metallic temperature dependence.

Keywords: intercalation; sodium; Raman; ESR; resistivity

INTRODUCTION

Alkali metals are able to intercalate graphite and modify it's structure and properties. Among alkali metal-graphite intercalation compounds (hereafter abbreviated as AM-GICs), the sodium-graphite intercalation compound is quite different from the others. The reaction of graphite and

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sodium results in the formation of dilute intercalation compounds such as NaC_{64} (stage 8) [1]. It has been also found that rich compounds are formed under high pressure [2] or existence of impurity such as oxygen [3]. In addition, the composition and stage structure depend largely on the graphitization degree of the host carbon material and rich compounds are prepared from less graphitized materials, in contrast to the other alkali metals [4]. This anomalous behavior of Na-graphite system is not well understood. Moreover, little information has been obtained about Na-GICs. This paper describes the change of structure of artificial graphite along with the reaction with metallic sodium and the characterization of the product. We used artificial graphite according to the report of A. Metrot and A. Herold where Na-GICs were easily prepared from artificial graphite [5].

EXPERIMENTAL

Materials

The host graphite materials were artificial graphites provided by SEC Corporation. The precursor, d value (d_{004}), Raman R-value and magnetoresistance of the graphite samples are shown in Table 1, where block specimen was used only for the measurement of magnetoresistance. For the other experiments, powders pulverized from the same block specimen was used.

Preparation of Sodium-graphite Intercalation Compounds

The graphite samples were kept in an evacuated glass tube, being contacted with sodium vapor at 593 K. The reaction tube was sometimes cooled down to room temperature during the reaction and the sample was transferred to the other part of the tube where Be window was attached for the transmittance of X-ray. The reaction tube was then set in the XRD apparatus. After XRD measurement the sample was moved back and the reaction was again continued. After completion of the reaction, the product was subdivided into several parts in sealed glass tubes for the characterization.

TABLE 1 Observed d Value (d_{004}), Raman R-value and Magnetoresistance ($\Delta\rho/\rho$) of Host Graphite Samples

Sample code	Precursor	d_{004}/nm	R-value	$\Delta\rho/\rho$
A	Petroleum needle coke	0.3359	0.22	0.040
B	Pitch coke (coal)	0.3360	0.23	0.026

Characterization of the Product by Raman, ESR and Electrical Resistivity Measurements

ESR spectra were measured using a conventional X-band spectrometer (JEOL, JES-TE100) with a rectangular TE_{102} microwave cavity. Raman spectra were measured with Jovin Yvon Ramanor T-64000 using Ar ion laser incident beam (514.5 nm). The host graphite samples (block specimen) were measured in open air and the product was measured being kept in an evacuated pyrex glass tube. The electrical resistivity was determined by the four-point technique.

RESULTS AND DISCUSSION

Structure Change of Graphite During Reaction with Sodium Vapor

Progress of XRD diagram of graphite (sample A) during reaction with sodium vapor at 593 K is shown in Figure 1, where several peaks from sample holder including beryllium window were also observed. Intensity of 002 and 004 lines of host graphite decreased along with the reaction and new peaks developed. These peaks were identified to be 008, 009 and 0017 lines of the stage 8 structure with identity period (I_c) of 2.8 nm in agreement with the reported value for NaC_{64} [1]. Although chemical analysis of the product have not yet been performed, its composition may be NaC_{64},

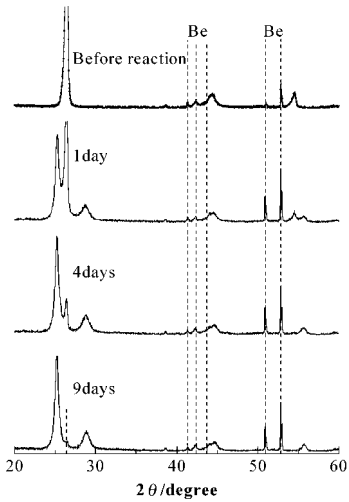

FIGURE 1 Progress of XRD diagram of graphite (sample A) in the course of reaction with sodium vapor at 593 K.

taking into account the report that petroleum cokes (HTT of 2000°C) gives NaC_{64} by the reaction with sodium vapor [5].

Characterization of NaC_x by ESR, Raman and Electrical Resistivity Measurements

The observed ESR spectra of the host graphite (sample B) and the derived NaC_x are comparatively shown in Figure 2, where 6 additional peaks of Mn^{2+} marker for magnetic field are also seen. The *g*-value was calculated to be 2.0018, which is very close to 2.0023 for the isolated spin. This is the same situation with other AM-GICs [6]. Temperature dependence of *g*-value and line width (ΔH) for the host graphite and NaC_x is shown in Figure 3. The *g*-value of NaC_x increases very slightly with increasing temperature, similarly to the behavior of KC_{60} [7]. The line width of NaC_x decreased with temperature in the range between 123 and 293 K.

Raman spectra of the host graphite (sample B) and derived NaC_x are shown in Figure 4. The G-band signal of NaC_x was observed at 1582 cm^{-1}, the same position with that of the host graphite and 1608 cm^{-1}. This is a clear indication of the formation of higher stage GICs [6]. It must be noted that the D-band signal observed for the host graphite disappeared for NaC_x, similarly to the case of CsC_{24} derived from petroleum cokes [8].

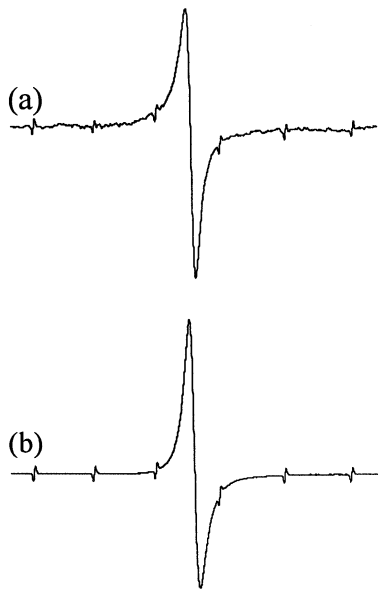

FIGURE 2 ESR spectra of (a) graphite (sample B) and (b) derived NaC_X.

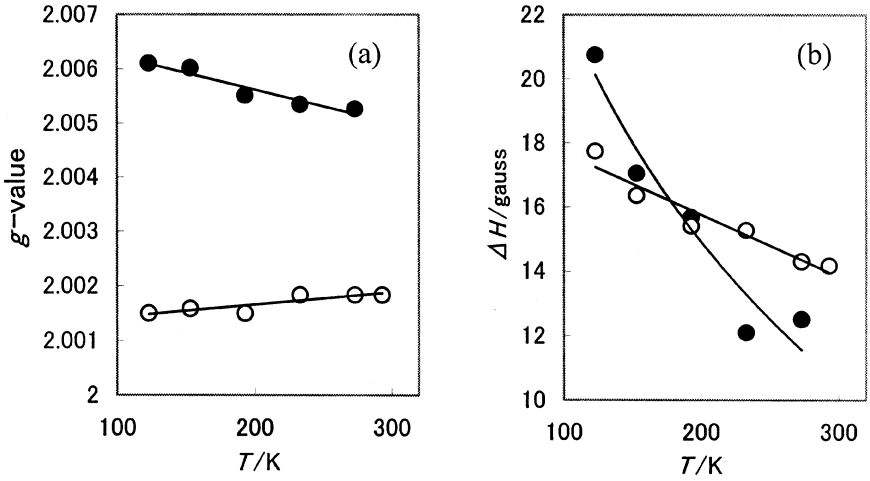

FIGURE 3 Temperature dependence of (a) g-values and (b) line width (ΔH) of host graphite (sample B) (●) and derived NaC_x (○).

Temperature dependence of the electrical resistivity of graphite (sample A) and derived NaC_x was determined. The NaC_x sample was prepared by placing graphite block specimen in powder sample of NaC_x and heat-treated at 473 K. This procedure made possible to obtain block specimen of NaC_x without deposition of sodium on the surface. The resistivity was determined by the four-point technique with iron wires for the electrical

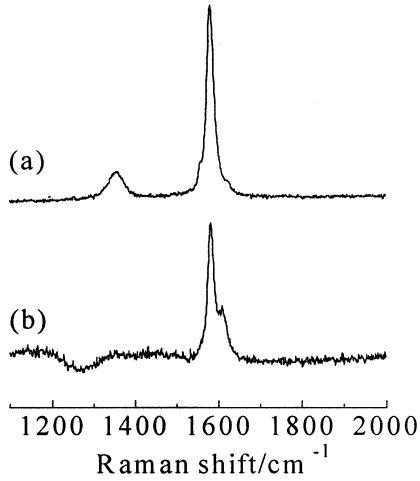

FIGURE 4 Raman spectra of (a) graphite (sample B) and (b) derived NaC_x.

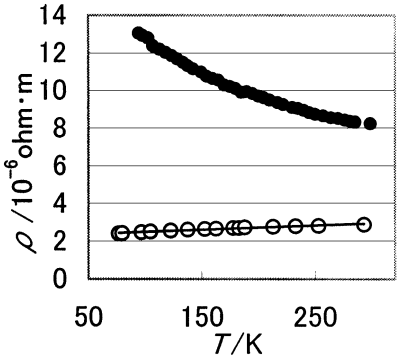

FIGURE 5 Temperature dependence of resisitivity of graphite (sample A) (●) and derived NaC_x (○).

contact. Temperature dependence of the resistivity of graphite and NaC_x is shown in Figure 5. It shows clearly that the absolute value of the resistivity decreased by the intercalation of sodium and that NaC_x shows metallic temperature dependence rather than semi-conductive character observed for the host graphite.

It must be noted that no difference was observed for NaC_x specimens prepared from the two artificial graphites except resistivity. The resistivity of sample B was larger than that of A due to low density of the block.

CONCLUSIONS

Artificial graphite was allowed to react with sodium. The structure change of graphite was followed by XRD measurement during reaction. The product (NaC_x) had stage 8 structure with identity period of 2.8 nm. The ESR measurement of NaC_x showed that the *g*-value was 2.0018, comparable to those for other AM-GICs. Raman experiment showed the splitting of G-band signal indicative of the intercalation of sodium. The electrical resistivity of NaC_x was determined to be 3×10^{-6} ohm·m at room temperature, which was about 1/3 of that of host graphite.

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