Preparation of Color Samples of Graphite Intercalation Compounds: Analysis and Use of Colors

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ABSTRACT

Graphite intercalation compounds (GICs) exhibit various colors depending on the materials used for intercalation and their concentrations. The color of a GIC, which suggests its electrical properties, is the most important characteristic of a GIC. In this study, we synthesized graphite compounds with many different types of intercalated materials, such as alkali metals, metal chlorides, acids, and amalgams to obtain GICs that display a range of striking colors. Here we present a summary of the color images of the GICs together with their synthetic procedures, structures, and selected physical properties.

1. INTRODUCTION

Graphite has a layered structure, with each layer consisting of a sheet of hexagons, each of which contains six carbon atoms. These layers form a stack of horizontal sheets that are held together by weak bonds. This structure therefore enables other chemical species to enter the space between consecutive graphite interlayers to form graphite intercalation compounds (GICs), as shown in Fig.1. The intercalation process is accompanied by charge transfer between the graphite layers and the intercalated species and the number of electronic carriers, i.e., electrons or holes, increases to 10^2-10^3 times. As a result, the GICs have higher electrical conductivities than the graphite host. Certain GICs have been reported to have electrical conductivities higher than those of metallic copper. Therefore, GICs are classified as synthetic metals.

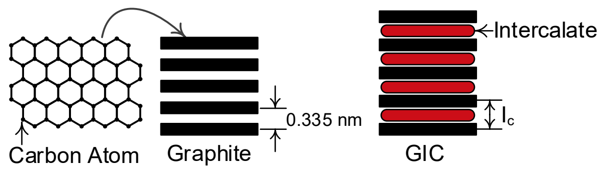

Fig.1 Graphite and GIC.

Another striking characteristic of a GIC is its color. The appearance of graphite is black or dark gray with luster. On the other hand, the color of a GIC depends on the intercalated species and its concentration. The color change is also derived from charge transfer. Even though the color of a GIC is one of its most important characteristics, investigations of the color, especially color images, have rarely been published. We believe these data and results to be necessary to advance the development of GICs.

In this study, we prepared color samples of a few types of GICs and here we summarize their color images together with their synthetic procedures, structures, and physical properties. In this presentation, we mainly introduce the photographic images and Raman spectra we recorded of the GIC samples.

2. EXPERIMENTAL

2.1 Samples

The graphite host we used mainly comprised PGS graphite sheets (Fig.2), which are flexible and highly oriented thin graphite sheets (Panasonic, 0.1 mm depth). In addition, other types of graphite such as natural graphite powder were also used. The GIC samples were synthesized by a vapor phase method under vacuum. Specifically, the graphite and reagents were sealed in a glass tube under vacuum and heated. Table 1 is the list of prepared GIC samples with their reaction conditions.

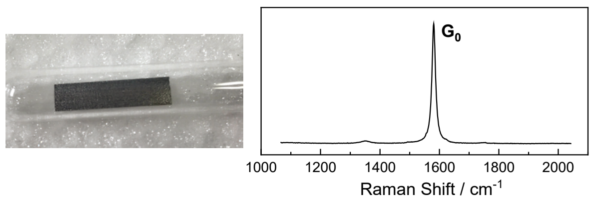

Fig.2 Image and Raman spectrum of PGS.

Table 1 GIC samples and their reaction conditions.

Type	Reagents	Heating
K-GIC	K	200 °C, 24-72h
Rb-GIC	Rb	200 °C, 24-72h
K-Hg-GIC	K, Hg	210 °C, 7d
$FeCl_3$-GIC	$FeCl_3$	300 °C, 15-72h
$MoCl_5$-GIC	$MoCl_5$, MoO_3	300 °C, 24-72h
$CuCl_2$-GIC	$CuCl_2$, $AlCl_3$	500 °C, 15h
$AlCl_3$-GIC	$AlCl_3$, $C_4H_4ClNO_2$	115 °C, 24h
H_2SO_4-GIC*	H_2SO_4, HNO_3	r.t., >3d

* Prepared by liquid method.

2.2 Photographic images

As GICs are unstable in air, the GIC samples were kept encapsulated in the glass tube under vacuum. The images of the GIC samples were captured through the glass by using the camera of an i-Phone 7 mobile device.

2.3 Measurements

Raman spectra of the GIC samples sealed in glass cells under vacuum were recorded to determine their stage structure by using an NRS-5500 instrument (Jasco, 532 nm laser line). After each sample was exposed to air, its

X-ray diffraction patterns were recorded to detect the period (I_c) in which the GIC could be identified. In addition, electrical properties such as the electrical conductivity were also measured.

3. RESULTS AND DISCUSSIONS

3.1 Alkali-metal GICs

Alkali-metal GICs are the most popular GICs with Li, K, Rb, and Cs easily being intercalated into the interlayers of the graphite structure. Figure 3 shows samples of the stage 1 and 2 structures of K-GIC prepared from PGS. Alkali-metal GICs have a golden color in stage 1 (the composition is KC_8) and appear blue in stage 2 (KC_{24}). The higher stage structures appear more dark blue to black.

Figure 4 shows the Raman spectra of stage 1 and 2 for Rb-GIC. The G_0 band at 1580 cm^{-1} of the graphite structure shifts as a result of intercalation, and the G_1 and G_2 bands appear at 1600 cm^{-1} and 1620 cm^{-1}, respectively. However, stage 1 alkali-metal GICs are known to exhibit quite different Raman shifts, caused by an in-plane structure that differs from those of the higher stages [1].

Stage 1 Stage 2

Fig.3 Photographic images of stage 1 and 2 K-GICs.

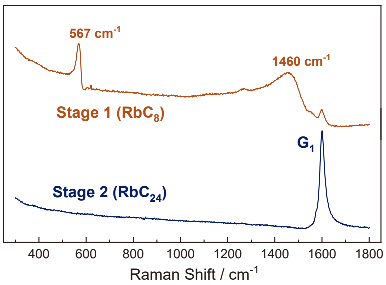

Fig.4 Raman spectra of stage 1 and 2 Rb-GICs.

3.2 Metal Chloride GICs

Many kinds of metal chlorides can be intercalated to form GICs. We selected $FeCl_3$, $CuCl_2$, $MoCl_5$, and $AlCl_3$ GICs for our work, because these are easily synthesized and form the stage 1 structure. Images of these GiCs are shown in Fig.5. The colors of metal chloride GICs, which are darker compared with those of alkali-metal GICs, are mostly blueish green with a slight metallic luster, while $AlCl_3$-GIC is dark blue. The surface morphology is uneven because of bubbles of chlorine gas generated during the reaction. The three GICs, $FeCl_3$-, $MoCl_5$-, and $AlCl_3$-GICs, almost have the same I_c values and electrical conductivity.

Figure 6 shows the Raman spectra of the stage 1 and 2 $MoCl_5$-GIC. Stage 1 exhibits only the G_2 band, whereas stage 2 mainly exhibits the G_1 band. The stage 2 $MoCl_5$ -GIC is gray in color.

Fig.5 Images of stage 1 $FeCl_3$-, $MoCl_5$-, and $AlCl_3$-GICs.

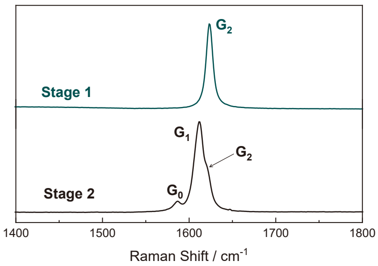

Fig.6 Raman spectra of stage 1 and 2 $MoCl_5$-GICs.

3.3 Other GICs

The molecules of certain acids can intercalate with graphite. Here, we prepared H_2SO_4-GIC. The GIC structure containing H_2SO_4 was obtained by simply submerging a piece of graphite into a liquid mixture of H_2SO_4 and HNO_3 in ambient atmosphere. The resulting GIC was blue-green in color with a slight metallic luster as shown in Fig.7 and the structure was stage 1.

Amalgams with alkali metals are also well-known intercalates of GICs, with K amalgams reported to be pink in color. In this work, we attempted to prepare the K-Hg GIC with the composition $KHgC_4$ and succeeded in confirming the bronze-pink color, as shown in Fig.7.

H_2SO_4-GIC K-Hg-GIC

Fig.7 Images of H_2SO_4- and K-Hg-GIC.

4. SUMMARY

GICs with alkali metals, metal chlorides, acids, and amalgams were synthesized by using PGS graphite sheets and color photographic images of these GICs were taken. In addition, their structures and properties were investigated. The study is presently continuing and we aim to conduct various measurements in future. We plan to prepare additional beautiful GIC samples with HOPG (highly oriented pyrolytic graphite) and to capture images and carry out color measurements. We also aim to estimate the magnitude of electron transfer by measuring the magnetoelectric properties to briefly assess the relationship between the color and these properties.

ACKNOWLEGEMENTS

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REFERENCES

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