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 intercalating materials, such as alkali metals, metal chlorides, acids, and amalgams, to obtain GICs that display a range of different colors. Herein, we present a summary of the colored images of the GICs together with their synthesis procedures, structures, and selected physical properties.

1. INTRODUCTION

Graphite has a layered structure wherein each layer consists 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 a charge transfer between the graphite layers and the intercalated species, and the number of electronic carriers, i.e., electrons (n-type) or holes (p-type), increases by 102 to 103 times. As a result, GICs have higher electrical conductivities than their graphite hosts. Certain GICs have been reported to have electrical conductivities higher than those of metallic copper structures. Therefore, GICs are classified as synthetic metals.

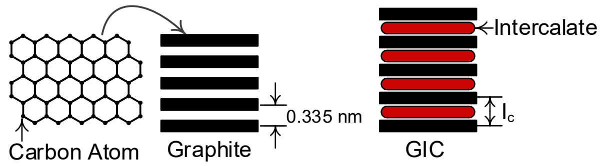

Fig.1 Graphite and GIC.

Another striking characteristic of a GIC is its color. The appearance of graphite is black or dark gray with luster. In contrast, 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, their color images have rarely been published. We believe these data to be necessary to advance the development of GICs.

In this study, we prepared color samples of several types of GICs and their color images together with their synthesis procedures, structures, and physical properties are presented. In this presentation, we e mainly provide the photographic images, Raman spectra, and reflectance spectra we recorded of the GIC samples.

2. EXPERIMENTAL

2.1 Samples

The graphite host we used were mainly 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 mainly synthesized using a vapor phase method under a vacuum. Specifically, the graphite and intercalate materials were sealed in a glass tube under a vacuum and heated.

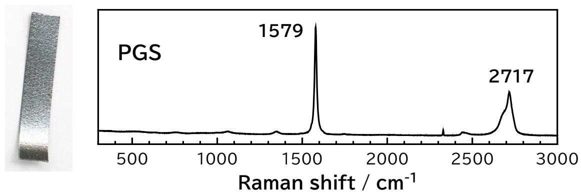

Fig.2 Image and Raman spectrum of PGS.

2.2 Photographic images

As GICs are unstable in air, the samples were kept encapsulated in the glass tube under vacuum. The images of the GIC samples were captured through the glass.

2.3 Measurements

Raman spectra of the GIC samples sealed in glass cells under a vacuum were recorded to determine their structure using an NRS-5500 instrument (Jasco, 532-nm laser line). Reflectance spectra were also measured using a thin-film measurement system F20 (FILMETRICS). 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.

3. RESULTS AND DISCUSSIONS

Table 1 presents a list of prepared GIC samples with their compositions [1] and colors.

3.1 Alkali-metal GICs

Alkali-metal GICs are the most widely-used GICs. Figure 3 shows samples of the stage 1 and 2 structures of K-GICs prepared from various graphite materials. Alkali-metal GICs have a golden color in stage 1 and a blue color in stage 2. The alkali-metal atoms intercalate all interlayers in the stage 1 structure and are present in every other interlayer in stage 2.

Figure 4 shows the reflectance spectra of stages 1 and 2 for AM-GICs with AM = K, Rb, and Cs. The golden color in stage 1 reflects wavelengths longer than 480 nm, while the blue stage 2 compounds reflect light with wavelengths longer than 750 nm.

Table 1 GIC samples prepared in the present study.

Type	Intercalate	Composition	Color
n	Li	LiC_6	Gold
		LiC_{18}	Blue
	AM = K, Rb, Cs	AMC_8	Gold
		AMC_{24}	Blue
	Ca	CaC_6	Silver
	K-Hg	$KHgC_4$	Gold ~ Pink
p	$FeCl_3$	$C_{6.1}FeCl_3$	Blue-green
	$MoCl_5$	C_xMoCl_5	Blue-green
	$CuCl_2$	$C_{4.9}CuCl_2$	?
	$AlCl_3$	$C_{8.3}AlCl_3$	Blue
	$AlCl_3$-$CuCl_2$	---	Blue-green
	H_2SO_4	---	Blue-green
	Br_2	---	Black

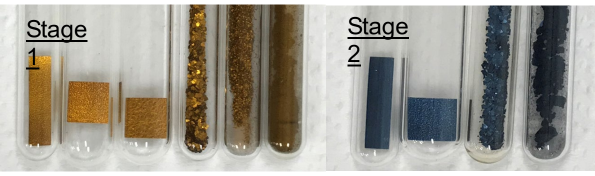

Fig.3 Photographic images of stage 1 and 2 K-GICs.

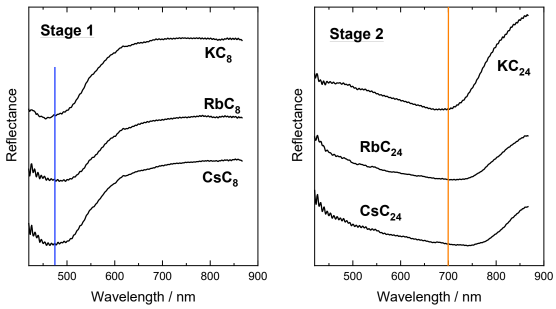

Fig.4 Reflectance spectra of stage 1 and 2 AM-GICs.

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 in this study because they are easily synthesized and form stage 1 structures. Figure 5 shows their Raman spectra. The GICs with a stage 1 structure exhibit only the G_2 band around 1620 cm^{-1}.

Images of these GICs are shown in Fig. 6. The colors of the 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. Therefore, their reflectance spectra measurements were difficult to obtain. In addition, the surface morphology is uneven due to bubbles of chlorine gas that were generated during the reaction. The three GICs, namely $FeCl_3$-, $MoCl_5$-, and $AlCl_3$-GICs, have almost identical I_c values and electrical conductivities.

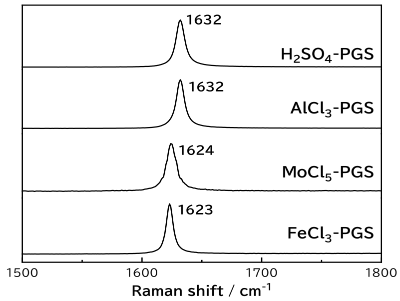

Fig.5 Raman spectra of p-type GICs.

Fig.6 Photographic images of p-type GICs.

3.3 Other GICs

The molecules of certain acids can intercalate with graphite. Here, we prepared H_2SO_4-GIC using a liquid method. 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 an ambient atmosphere. The resulting GIC was blue-green in color with a slight metallic luster as shown in Fig. 6, and the structure was stage 1 considering the Raman spectrum shown in Fig. 5.

Amalgams with alkali metals are also well-known intercalates of GICs, and K amalgams have been reported to be pink in color. In this work, we attempted to prepare the stage 1 structure of K-Hg-GIC with the composition $KHgC_4$ and succeeded in confirming its bronze-pink color.

4. SUMMARY

GICs with alkali metals, metal chlorides, acids, and amalgams were synthesized using PGS graphite sheets and colored photographic images of these GICs were obtained. In addition, their structures and properties were investigated. This study is still ongoing, and we plan to prepare additional GIC samples with highly oriented pyrolytic graphite (HOPG) and to obtain images of these samples. We also aim to estimate the magnitude of electron transfer to briefly assess the relationship between the color and these properties.

ACKNOWLEGEMENTS

The authors thank Dr. N. Akuzawa for his support in synthesizing of K-Hg-GIC samples.

REFERENCES

[1] M.S. Dresselhaus, G. Dresselhaus, “Intercalation compounds of graphite,” Adv. Phys. 30, 139-326 (1981).