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## Synthesis and Structure of $\text{FeCl}_3\text{-CrO}_3$ -Graphite Bi-Intercalation Compound

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**Abstract** The paper deals with the synthesis and structure of  $\text{FeCl}_3\text{-CrO}_3$ -graphite bi-intercalation compound ( $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$ ) prepared during the subsequent intercalation of chromium trioxide into stage-2  $\text{FeCl}_3\text{-GIC}$ /graphite system. From the results of the X-ray diffraction measurements and the scanning electron microscopy coupled with energy dispersive X-ray analysis it was concluded that the product consists of a mixture of saturated  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  and stage-2  $\text{FeCl}_3\text{-GIC}$ . Based on the model of the transformation from stage-2  $\text{FeCl}_3\text{-GIC}$ /graphite system to  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$ , it can be understood that upon the subsequent intercalation process  $\text{CrO}_3$  is intercalated in the interlayer spacings of graphite both free and occupied by  $\text{FeCl}_3$ . Due to the latter invasion the double-layer co-intercalation domain is formed whereas a part of  $\text{FeCl}_3$  is displaced to the zone of the pristine graphite present in the host  $\text{FeCl}_3\text{-GIC}$ .

**Keywords:** graphite bi-intercalation compound;  $\text{FeCl}_3$ ;  $\text{CrO}_3$ ; XRD; EDX

## INTRODUCTION

Graphite bi-intercalation compounds (GBCs) are formed when the vacant interlayer spacings of graphite in graphite intercalation compounds (GICs)

with the stage number  $n \geq 2$  are successively filled with another intercalate. During the process of bi-intercalation the secondary intercalate can invade not only the vacant interspaces of GIC but also the interspaces occupied by the primary intercalate. As a result of the latter ingress the co-intercalation domains, intermediate or stable, are formed within GBC. Recently, GBCs have attracted considerable attention because of their novel properties arising from a variety of fascinating structures and compositions<sup>[1]</sup>. GBCs involving metal oxides are not numerous. Among them are those with  $\text{CrO}_3$  (e.g.  $\text{CrO}_3\text{-H}_2\text{SO}_4\text{-GBC}$  <sup>[2,3]</sup>,  $\text{CrO}_3\text{-HClO}_4\text{-GBC}$  <sup>[4,5]</sup>). Until now no GBC containing both transition metal chloride and oxide has been prepared.

In the present paper the synthesis of  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  is reported for the first time. The transformation from stage-2  $\text{FeCl}_3\text{-GIC}$  to  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  is discussed. From the results obtained the formation of the double-layer co-intercalation domain,  $\text{FeCl}_3\text{-CrO}_3$ , within GBC is suggested.

## EXPERIMENTAL

Anhydrous  $\text{FeCl}_3$  was intercalated into natural Sri Lanka graphite (flakes 30-100  $\mu\text{m}$  in diameter and 1-20  $\mu\text{m}$  in thickness) from a vapour phase at 300 °C for 20 hrs<sup>[6]</sup>. The intercalation reaction was carried out with excess of  $\text{FeCl}_3$  (52.12 wt.%) in the starting mixture. The obtained stage-2  $\text{FeCl}_3\text{-GIC}$  ( $I_c = 1.281\text{ nm}$ ) was then subjected to the subsequent intercalation with  $\text{CrO}_3$ <sup>[4,5,7]</sup>. A mixture of 5 g  $\text{FeCl}_3\text{-GIC}$  and 10 g  $\text{CrO}_3$  in 40  $\text{cm}^3$  glacial acetic acid was refluxed for 1.5 h. The product of intercalation was purified by washing with cold glacial acetic acid and acetone and then dried to a constant weight. The X-ray diffraction (XRD) patterns for the original  $\text{FeCl}_3\text{-GIC}$  and the resulting  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  are depicted in Fig. 1. For observing the concentration profiles of intercalates in both  $\text{CrO}_3\text{-GIC}$  and  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  the energy dispersive X-ray (EDX) analysis coupled with scanning electron microscopy (SEM) was used (Figs. 2 and 3).

## RESULTS AND DISCUSSION

As seen from the XRD pattern illustrated in Fig. 1a, the host stage-2  $\text{FeCl}_3\text{-GIC}$  is admixed with the phase of unreacted graphite. The identity period of the compound,  $I_c = 1.28$  nm, is consistent with the estimates reported elsewhere for  $\text{FeCl}_3\text{-GIC}$ <sup>[8,9]</sup>. The EDX profiles for Fe and Cl (Fig. 2) show the island-like distribution of intercalate within a whole flake of  $\text{FeCl}_3\text{-GIC}$ . The decreased concentration of intercalate at the most outer regions of flake arises from the washing procedure used to remove unreacted  $\text{FeCl}_3$  from the product of intercalation. Due to such a treatment some intercalate is extruded from the compound. It was expected that glacial acetic acid used as a solvent during the subsequent intercalation of  $\text{CrO}_3$  brings about further deintercalation of  $\text{FeCl}_3$  from the edge regions of the flake. The released  $\text{FeCl}_3$  present at the

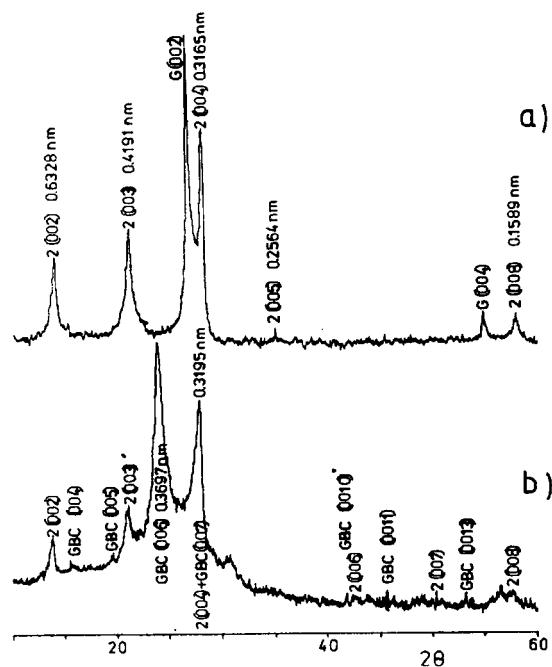


FIGURE 1 XRD patterns recorded for (a) the original  $\text{FeCl}_3\text{-GIC}$  and (b)  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$ .  $\text{CuK}\alpha$  radiation.

graphite-solution interface might play the role of a strong oxidizer promoting intercalation of  $\text{CrO}_3$  into the occupied graphite galleries of stage-2  $\text{FeCl}_3$ -GIC. Furthermore, the mechanism of intercalation of  $\text{CrO}_3$  into the vacant galleries of the host  $\text{FeCl}_3$ -GIC was assumed to resemble that reported for the process occurring for the pristine graphite<sup>[4,5,7]</sup>. The XRD pattern obtained for the product of the subsequent intercalation of  $\text{CrO}_3$  into stage-2  $\text{FeCl}_3$ -GIC (Fig. 1b) confirms the above prediction and provides the evidence for the

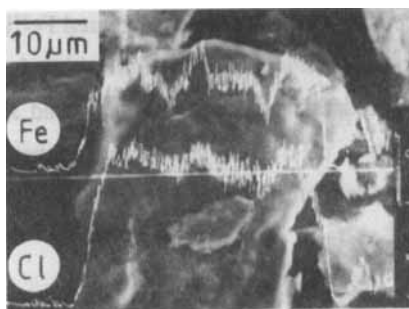


FIGURE 2 SEM micrograph with superimposed EDX distribution lines for  $\text{FeCl}_3$ -GIC.

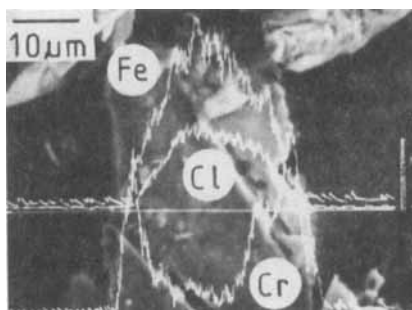


FIGURE 3 SEM micrograph with superimposed EDX distribution lines for  $\text{FeCl}_3$ - $\text{CrO}_3$ -GIC.

formation of bi-intercalation compound with the c-axis identity period  $I_c = 2.231$  nm.

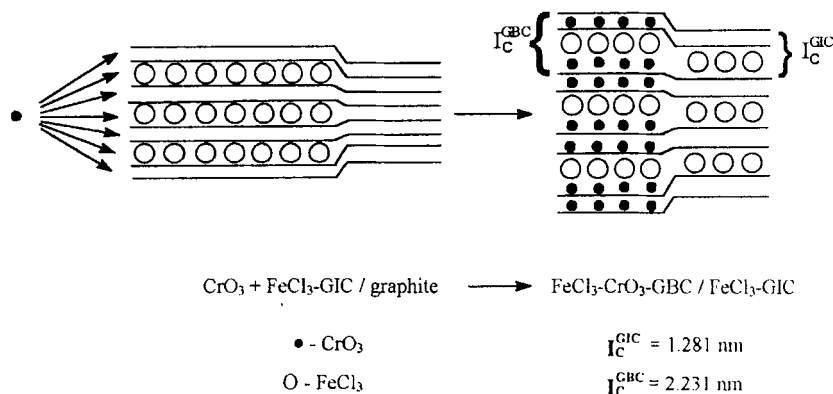


FIGURE 4 The model of the transformation from stage-2  $\text{FeCl}_3\text{-GIC}$ /graphite system to  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$ .

To approach to the structural description of  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  the thickness of the  $\text{FeCl}_3$  layer in the host  $\text{FeCl}_3\text{-GIC}$ ,  $\Delta d = 0.611 \text{ nm}$ , and the thickness of the  $\text{CrO}_3$  layer in  $\text{CrO}_3\text{-GIC}$ ,  $\Delta d = 0.474 \text{ nm}$ <sup>[3,5]</sup> is taken into account.  $l_c = 2.231 \text{ nm}$  calculated for  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  is nearly equal to the sum of  $d_{i(1)} = 0.810 \text{ nm}$  and  $d_{i(2)} = 1.421 \text{ nm}$  (the  $d_{i(1)}$  value being the thickness of the interlayer spacing of graphite filled with  $\text{CrO}_3$  whereas the  $d_{i(2)}$  value corresponding to the interlayer spacing in which the intercalate is accommodated in the double-layer sandwich comprising the  $\text{FeCl}_3$  and  $\text{CrO}_3$  layers). From this calculation, it may be inferred that during the subsequent intercalation the invasion of  $\text{CrO}_3$  occurs into the empty graphite galleries as well as those occupied by the primary intercalate. This conclusion is supported by the distribution lines recorded for  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  (Fig. 3). As can be seen from this figure, the lines for Fe and Cr overlap to each other at the peripheral regions of the graphite flake whereas the graphite core is preferably filled with  $\text{FeCl}_3$  and almost completely free of  $\text{CrO}_3$ . This result agrees with the XRD pattern for  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  (Fig. 1b) in which the peaks responsible for the original  $\text{FeCl}_3\text{-GIC}$  are observed besides those corresponding to the new phase of

$\text{FeCl}_3\text{-CrO}_3\text{-GBC}$ . According to the proposed model of bi-intercalation (Fig. 4), the subsequent intercalation of  $\text{CrO}_3$  occurs into both the vacant interlayer spacings of graphite in  $\text{FeCl}_3\text{-GIC}$  and the interspaces occupied with  $\text{FeCl}_3$ . During the latter process the co-intercalation domain is formed following the displacement of the  $\text{FeCl}_3$  islands into the regions free of intercalate. Such an explanation account for why the graphite peaks recorded on the XRD pattern for the host material (Fig. 1a) disappear in the final product with  $\text{CrO}_3$  (Fig. 1b). In the light of this, the final product of the reaction with  $\text{CrO}_3$  may be recognized as a mixture of saturated  $\text{FeCl}_3\text{-CrO}_3\text{-GBC}$  and stage-2  $\text{FeCl}_3\text{-GIC}$ . The depth of intercalation noted for  $\text{CrO}_3$  in GBC, not exceeding 15  $\mu\text{m}$ , (Fig. 3), is comparable with that reported for  $\text{CrO}_3\text{-GIC}^{[10,11]}$ ,  $\text{CrO}_3\text{-H}_2\text{SO}_4\text{-GBC}^{[11]}$  and  $\text{CrO}_3\text{-Br}_2\text{-GIC}^{[12]}$ .

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