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Bi-intercalation of ICl into a stage-5 $FeCl_3$ graphite intercalation compound

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X-ray diffraction (XRD) has been used for the study of bi-intercalation of ICl into the stage-5 $FeCl_3$ graphite intercalation compound (GIC). The stage-5 $FeCl_3$ GIC is obtained when the temperature of graphite is set at 788 K, and the temperature of $FeCl_3$ at 573 K in the two-zone system. Since the stage-5 $FeCl_3$ GIC has four consecutive vacant galleries in the *c*-axis direction, the $FeCl_3$-ICl graphite bi-intercalation compounds (GBC's) with one and two ICl layers are studied. When the temperature of the stage-5 $FeCl_3$ GIC is held at 373 K and the temperature of ICl at 323 K, the $FeCl_3$-ICl GBC with one ICl layer is obtained. The layer sequence of the GBC is found to be an admixture of $G(FeCl_3)GG(ICl)GGG(FeCl_3)G$ and $G(FeCl_3)GGG(ICl)GG(FeCl_3)G$ by XRD, where G, $(FeCl_3)$, and (ICl) refer to graphite, $FeCl_3$, and ICl layers, respectively. The $FeCl_3$-ICl GBC with two ICl layers is prepared with the temperatures of the stage-5 $FeCl_3$ GIC and ICl at 333 and 313 K, respectively. Its layer sequence is determined to be $G(FeCl_3)GG(ICl)G(ICl)GG(FeCl_3)G$. From the result of the layer sequence of the $FeCl_3$-ICl GBC with two ICl layers, the order of the degree of the charge transfer is shown to be $FeCl_3$ GIC > ICl GIC.

I. INTRODUCTION

Graphite intercalation compounds (GIC's) are attractive materials because of their unique layered structures.[1-3] Since the GIC's with stage numbers above 2 have more than one vacant gallery, other substances can enter into the GIC's to form graphite bi-intercalation compounds (GBC's). Many studies have been done concerning the preparations,[4-7] structures,[8] chemical properties,[9] and formation mechanisms[10,11] of GBC's.

Recently, the present authors have studied the bi-intercalation processes of H_2SO_4 into the stages 4–6 $FeCl_3$ GIC's (Ref. 12) and also the preparation of $FeCl_3$-IBr-H_2SO_4 graphite multi-intercalation compounds[13] (GMC's) from the $FeCl_3$-IBr GBC's. The results were very interesting, particularly when the stage-5 $FeCl_3$ GIC was used as a starting material to prepare the GBC's and GMC's. The stage-5 $FeCl_3$ GIC has four consecutive vacant galleries in the *c*-axis direction, and the first bi-intercalation of H_2SO_4 or IBr takes place at either of two equivalent middle vacant galleries. The layer sequence was shown to be $G(FeCl_3)G_1G_2(I)G_3G_4G_5(FeCl_3)G$, where G_n, $(FeCl_3)$, and (I) refer to the *n*th graphite, $FeCl_3$, and H_2SO_4 or IBr layers, respectively.[12,13] The layer sequence of the GBC prepared from the stage-5 $FeCl_3$ GIC is asymmetric. Therefore, the charge densities of the five graphite layers in the *c*-axis direction of the GBC are not identical, and resultant layers with different charge densities have an important effect on the second bi-intercalation or multi-intercalation processes into the GBC.

The stage-5 $FeCl_3$ GIC may give the various $FeCl_3$-ICl GBC's with one to four ICl layers. In particular, the $FeCl_3$-ICl GBC's with one and two ICl layers are interesting because of the reasons mentioned above. In the present paper, the $FeCl_3$-ICl GBC's with one and two ICl layers are prepared from the stage-5 $FeCl_3$ GIC and the layer sequences of the GBC's are studied by x-ray diffraction (XRD). From these studies, the degree of the charge transfer between the intercalate and graphite layers is discussed.

II. EXPERIMENT

The stage-5 $FeCl_3$ GIC was prepared from natural graphite flakes produced in China and reagent grade anhydrous $FeCl_3$ by an ordinary two-bulb method. The GIC was obtained when the temperature of graphite flakes was set at 788 K and the temperature of $FeCl_3$ at 573 K in the two-zone system.[12]

The preparation of $FeCl_3$-ICl GBC with one ICl layer was made by keeping the temperatures of the stage-5 $FeCl_3$ GIC and ICl at 373 and 323 K, respectively, for 24 h. The $FeCl_3$-ICl GBC with two ICl layers was obtained when the temperature of the stage-5 $FeCl_3$ GIC was held at 333 K and the temperature of ICl at 313 K for 24 h.

The XRD data were collected with Cu $K\alpha$ radiation monochromatized by highly oriented pyrolytic graphite using a scintillation detector. Typical working conditions were set at 35 kV and 20 mA, and a scanning speed was set at 2°/min with a time constant of 0.5 s. All data were recorded in a computer.

The layer sequences of the $FeCl_3$-ICl GBC's were determined by comparing the observed XRD patterns with the calculated ones. The calculation of the $(00l)$ XRD intensities was carried out from the following equation:[14]

$$I_{00l}=K|F_{00l}|^2LPA \ , \tag{1}$$

where I_{00l} is the integrated intensity of the $(00l)$ line, K is the scale factor, F_{00l} is the structure factor, and L, P, and A are the Lorenz factor, polarization factor, and absorp-

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tion factor, respectively.

The structure factor in Eq. (1), which depends on the atomic position (z_j), density (N_j), Debye-Waller factor (B_j) of the jth atomic layer, and atomic scattering factor (f_j) of the jth atom[15] in the galleries, is expressed as follows:[14]

$$|F_{00l}| = |\Sigma_j N_j f_j \exp(-B_j \sin^2\theta/\lambda^2)\exp(2\pi i l z_j)| \ . \quad (2)$$

The atomic position, the density, and the Debye-Waller factor of the intercalate in the galleries will be published elsewhere.[16]

To evaluate the reliability of the layer sequences, the crystallographic R factor is obtained.[17]

III. RESULTS

Figure 1 shows the XRD pattern of the stage-5 $FeCl_3$ GIC prepared by the two-bulb method. From the sharp lines in the XRD pattern and a crystallographic R factor of 8.9%, the sample has a well-defined stage. The $G(FeCl_3)G$ sandwich thickness is determined to be $d_i = 0.943$ nm, which is in good agreement with those in the literature.[18–20]

Figure 2(a) shows the observed XRD pattern of the $FeCl_3$-ICl GBC with one ICl layer. The c-axis repeat distance is calculated to be $I_c = 2.657$ nm, which is almost equal to the sum of 0.943 nm [$G(FeCl_3)G$ thickness[16]]+0.710 nm [G(ICl)G thickness[16]]+3×0.3354 nm (interlayer spacing of graphite), where (ICl) refers to the ICl layer. Figure 2(b) shows the calculated XRD pattern on the basis of the layer sequence in the inset. Here, the solid lines, open circles, and solid squares refer to graphite, $FeCl_3$, and ICl layers, respectively. The observed and calculated XRD patterns are in good agreement, leading to the conclusion that the layer sequence of the $FeCl_3$-ICl GBC with one ICl layer and the layer parameters[16] used in this calculation are valid. In addition, a crystallographic R factor is obtained to be 11.6%. The value is acceptable considering that the x-ray measurement was performed at a relatively fast scanning rate of 2°/min. The layer sequence is again verified by this small R factor. In the case of this layer sequence, there may be an admixture of $G(FeCl_3)GG(ICl)GGG(FeCl_3)G$ and $G(FeCl_3)GGG(ICl)GG(FeCl_3)G$. A crystallographic R factor for the two layer sequences with the same ratio is determined to be 9.3%, which is, to some extent, smaller than a value of 11.6% obtained without considering the admixture. From this result, it is very likely that the layer sequence of the $FeCl_3$-ICl GBC with one ICl layer is the above admixture.

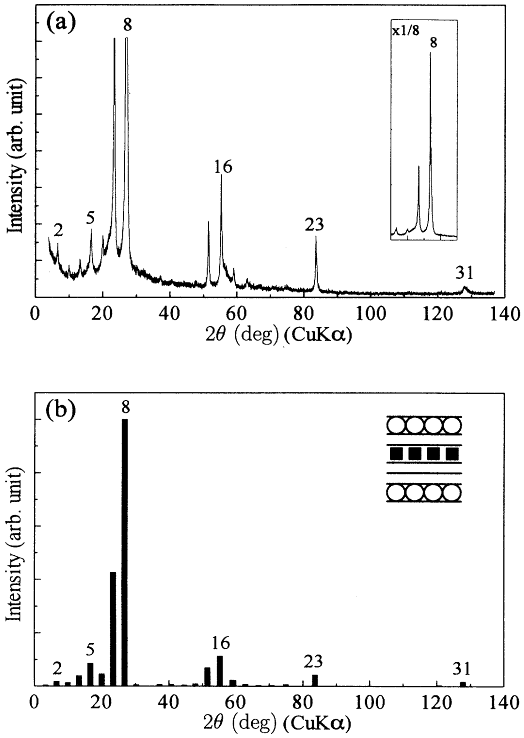

FIG. 2. XRD patterns of $FeCl_3$-ICl GBC with one ICl layer. (a) is the observed pattern and (b) is the calculated one on the basis of the stacking sequence in the inset. The solid lines, open circles, and solid squares refer to graphite, $FeCl_3$, and ICl layers, respectively.

Figure 3 shows the observed XRD pattern of the $FeCl_3$-ICl GBC with two ICl layers. The c-axis repeat distance is $I_c = 3.038$ nm. The value is almost equal to

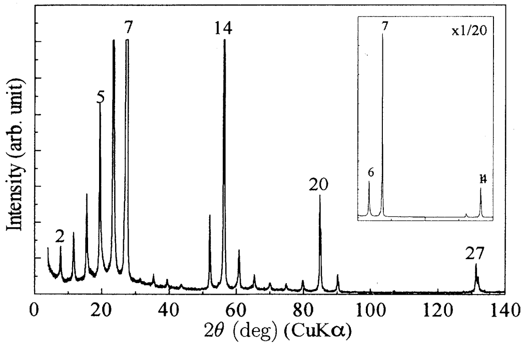

FIG. 1. Observed XRD pattern of stage-5 $FeCl_3$ GIC. The number on the diffraction peaks indicates the index (00l).

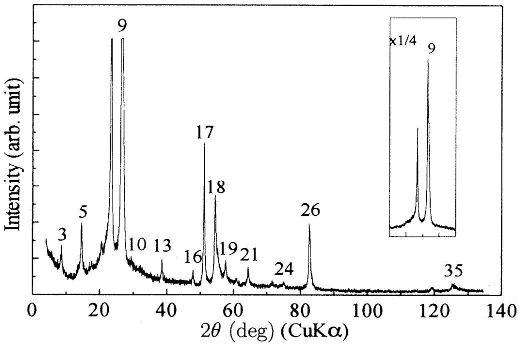

FIG. 3. Observed XRD pattern of $FeCl_3$-ICl GBC with two ICl layers.

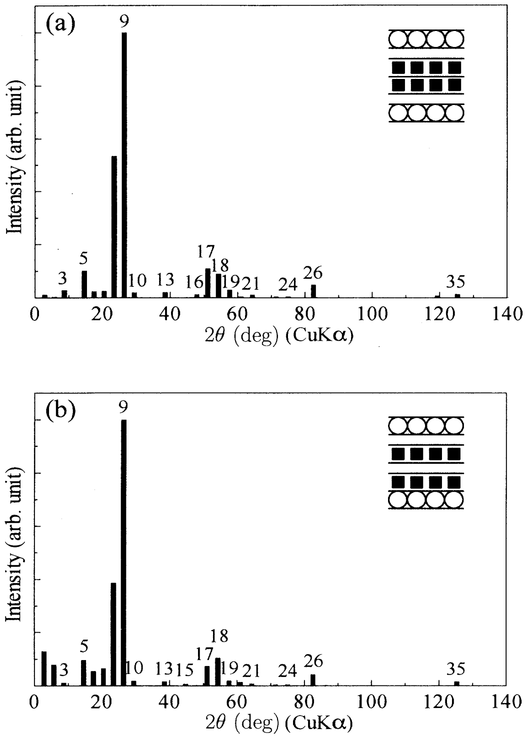

FIG. 4. Calculated XRD patterns of $FeCl_3$-ICl GBC with two ICl layers on the basis of the stacking sequences in the insets.

the sum of 0.943 nm + 2×0.710 nm + 2×0.3354 nm, that is, the number of bi-intercalated ICl layers is identified to be two. For the GBC with two ICl layers, two layer sequences may be proposed as shown in the insets in Figs. 4(a) and 4(b) with the calculated XRD patterns on the basis of the sequences. For these calculated patterns, the prominent differences lie in the angular range 35°–60° in 2θ. In Fig. 4(a) weak peaks indexed with $l = 13$ and 16 appear and the intensity of the peak with $l = 17$ is stronger than that of the peak with $l = 18$. On the other hand, in Fig. 4(b) weak peaks indexed with $l = 13$ and 15 are seen and the intensity of the peak with $l = 17$ is weaker than that of the peak with $l = 18$. For the observed XRD pattern in Fig. 3, the weak peak indexed with $l = 16$ can be seen, but the peak with $l = 15$ cannot be observed. In addition, the intensity of the peak indexed with $l = 17$ is stronger than that of the peak indexed with $l = 18$. From these comparisons, it is concluded that the layer sequence of the $FeCl_3$-ICl GBC with two ICl layers is determined to be the inset in Fig. 4(a). This conclusion is also led by a crystallographic R factor of 15.5% for the layer sequence in Fig. 4(a), which is much smaller than a factor 24.9% for the sequence in Fig. 4(b).

IV. DISCUSSION

Figure 5 summarizes the bi-intercalation process of H_2SO_4,[12] the multi-intercalation process of IBr and H_2SO_4,[13] and the bi-intercalation process of ICl into the stage-5 $FeCl_3$ GIC. From Fig. 5 the first bi-intercalation into the stage-5 $FeCl_3$ GIC takes place at either of two equivalent middle vacant galleries irrespective of the intercalates. The reason is very simply explained by considering the charge transfer. The layer sequence of the stage-5 $FeCl_3$ GIC is shown as $G(FeCl_3)G_1G_2G_3G_4G_5(FeCl_3)G$. Since the stage-5 $FeCl_3$ GIC is an acceptor type GIC, some amounts of charge in G_1 and G_5 transfer to the $FeCl_3$ layer. Hence, H_2SO_4 IBr, and ICl bi-intercalate more easily into gallery between G_2 and G_3 (or G_3 and G_4) because G_2, G_3, and G_4 have more charge than G_1 and G_5. The layer sequence of these GBC's is shown to be an asymmetric structure of $G(FeCl_3)G_1G_2(I)G_3G_4G_5(FeCl_3)G$. Here, I corresponds to respective H_2SO_4, IBr, and ICl layers. The charge density of the nth graphite layer is a function of n, and hence the difference of the charge density influences the second bi-intercalation and multi-intercalation processes.

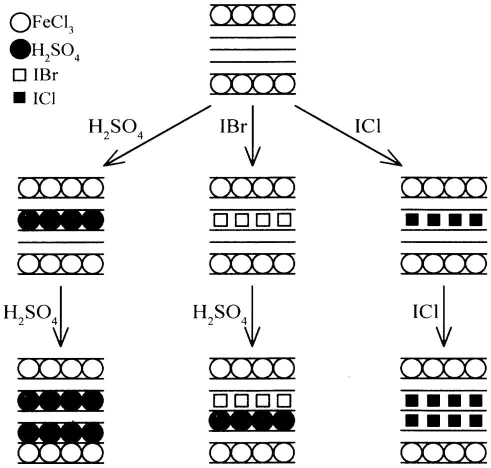

FIG. 5. Bi-intercalation and multi-intercalation processes for stage-5 $FeCl_3$ GIC.

The second bi-intercalation of H_2SO_4 occurs between G_4 and G_5 as shown in Fig. 5. The result shows that the charge of G_4 and G_5 transfers to the second bi-intercalated H_2SO_4 layer more easily than that of G_3 and G_4 does; in other words, the degree of the charge transfer between G_3 and the "first" bi-intercalated H_2SO_4 is larger than that between G_5 and $FeCl_3$. Consequently, the electron affinity of the H_2SO_4 layer is considered to be larger than that of the $FeCl_3$ layer, that is, the degree of the charge transfer is on the order of H_2SO_4 GIC > $FeCl_3$ GIC.

Similarly, from the layer sequences of $FeCl_3$-IBr-H_2SO_4 GMC and $FeCl_3$-ICl GBC with two ICl layers, the degree of the charge transfer between $FeCl_3$ and graphite layers is larger than that between IBr and graphite layers, and the degree of the charge transfer between $FeCl_3$ and graphite layers is larger than that between ICl and graphite layers, respectively. Hence, it is concluded that the orders of the electron affinities of the intercalate layers are as follows: $FeCl_3$ layer > IBr layer and $FeCl_3$ layer > ICl layer. In addition, it is known that the stage number of the IBr GIC is always larger than 2 (Ref. 21) and that ICl GIC can have stage-1 structure.[22] The facts indicate that the electron affinity of the ICl layer is larger than the IBr layer. This result can be understood from the analogy for the order of the electron affinities of silver halides; AgCl > AgBr > AgI.[23] Therefore, the degree of the charge transfer is determined to be H_2SO_4 GIC > $FeCl_3$ GIC > ICl GIC > IBr GIC. These results are quite useful for intercalation chemistry.

V. CONCLUSIONS

The stage-5 $FeCl_3$ graphite intercalation compound (GIC) was prepared by an ordinary two-bulb method, and $FeCl_3$-ICl graphite bi-intercalation compounds (GBC's) were synthesized from the $FeCl_3$ GIC. The layer sequences of the $FeCl_3$-ICl GBC's with one and two ICl layers were studied by x-ray diffraction. The results are summarized as follows.

(1) $FeCl_3$-ICl GBC with one ICl layer is obtained from the stage-5 $FeCl_3$ GIC when the temperature of the GIC is kept at 373 K and the temperature of ICl at 323 K. The layer sequence is an admixture of G($FeCl_3$)GG(ICl)GGG($FeCl_3$)G and G($FeCl_3$)GGG(ICl)GG($FeCl_3$)G, where G, ($FeCl_3$), and (ICl) refer to graphite, $FeCl_3$, and ICl layers, respectively.

(2) $FeCl_3$-ICl GBC with two ICl layers is synthesized when the temperature of the stage-5 $FeCl_3$ GIC is held at 333 K and the temperature of ICl at 313 K. The layer sequence is G($FeCl_3$)GG(ICl)G(ICL)GG($FeCl_3$)G.

(3) From the layer sequence of the $FeCl_3$-ICl GBC with two ICl layers, the degree of the charge transfer is on the order of $FeCl_3$ GIC > ICl GIC.

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