

## ARTICLES

## Raman scattering study of acceptor-acceptor-type graphite bi-intercalation compounds

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Stages 4 and 5 FeCl<sub>3</sub>-graphite intercalation compounds (GIC's) were prepared by a two-bulb method, and were used as host materials for the synthesis of graphite bi-intercalation compounds (GBC's), where the bi-intercalated species were ICl, IBr, and SbCl<sub>5</sub>. Various types of GBC's were obtained by changing the reaction temperatures, and the layer sequences were clarified by x-ray diffraction. Lattice dynamics of the resultant GBC's was investigated by Raman spectroscopy. Since the layer sequence of GBC's from a stage 4 FeCl<sub>3</sub>-GIC with one bi-intercalated layer is G(FeCl<sub>3</sub>)G<sub>1</sub>G<sub>2</sub>(I)G<sub>3</sub>G<sub>4</sub>(FeCl<sub>3</sub>)G, where G<sub>n</sub>, (FeCl<sub>3</sub>), and (I) denote the *n*th graphite, FeCl<sub>3</sub>, and bi-intercalated layers, respectively, and all graphene layers are adjacent to an intercalate layer. The GBC's give only one Raman-active  $E_{2g}^{(2)b}$  mode frequency in the Raman spectra although the intercalates are different. GBC's from stage 5 FeCl<sub>3</sub>-GIC with one bi-intercalated layer give the stacking sequence of G(FeCl<sub>3</sub>)G<sub>1</sub>G<sub>2</sub>(I)G<sub>3</sub>G<sub>4</sub>G<sub>5</sub>(FeCl<sub>3</sub>)G. Since two types of graphene layers, interior (G<sub>4</sub>) and bounding (G<sub>1,2,3,5</sub>) layers exist, two peaks identified as Raman-active  $E_{2g}^{(2)i}$  and  $E_{2g}^{(2)b}$  mode frequencies appear in Raman spectra. Both frequencies were affected by the bi-intercalated species. From the  $E_{2g}^{(2)i}$  frequencies, the degree of electron affinities of the bi-intercalated layers was evaluated to be in the order of IBr < ICl < SbCl<sub>5</sub>. For the GBC's with two bi-intercalated layers, their layer sequences were determined to be G(FeCl<sub>3</sub>)GG(I)G(I)GG(FeCl<sub>3</sub>)G or G(FeCl<sub>3</sub>)GG(I)GG(I)G(FeCl<sub>3</sub>)G. In this case, only bounding layers of graphite exist. However, two peaks were observed in the Raman spectra. The difference of the Raman-active  $E_{2g}^{(2)b}$  mode frequencies was due to the intercalate coupling effect.

## I. INTRODUCTION

Lattice dynamics of graphite intercalation compounds (GIC's) has been extensively studied by many researchers and some of the results have been reviewed by Solin, Dresselhaus, and so on.<sup>1-3</sup> Raman scattering of the C-C vibration with  $E_{2g}^{(2)b}$  symmetry in GIC's is known to be affected by the degree of the charge transfer, that is, electron donicity or affinity of the intercalates, and therefore, the lattice dynamics of GIC's has been systematically investigated in terms of their unique stage structures, where stage is defined as the number of graphene layers between the intercalate layers.<sup>4-6</sup> In addition to the experimental reports for the lattice dynamics of GIC's, Chan *et al.*<sup>7</sup> calculated the Raman-active  $E_{2g}^{(2)b}$  and  $E_{2g}^{(2)i}$  mode frequencies of GIC's, and they concluded that the Raman-active  $E_{2g}^{(2)b}$  mode frequencies are affected mainly by three factors; (1) the lattice constant  $d_{c-c}$ , (2) the charge transfer, and (3) the intercalate-coupling effect.

As is mentioned above, the lattice dynamics of GIC's has been well investigated. However, that of graphite bi-intercalation compounds (GBC's) has been only reported by a few groups.<sup>8,9</sup> This is probably because of the difficulty in the preparation of GBC's with good crystallinity. Since GBC's contain two different intercalate species stacked periodically along the *c* axis, physical properties such as magnetic properties, etc.<sup>10-13</sup> have been studied because the multiplier effect of the different intercalates may take place.

The present authors<sup>9</sup> have prepared FeCl<sub>3</sub>-SbCl<sub>5</sub>-GBC's from stage 5 FeCl<sub>3</sub>-GIC and the GBC's were studied by Raman spectroscopy. One of the layer sequences of the resultant GBC's was G(FeCl<sub>3</sub>)G<sub>1</sub>G<sub>2</sub>(SbCl<sub>5</sub>)G<sub>3</sub>G<sub>4</sub>(SbCl<sub>5</sub>)G<sub>5</sub>(FeCl<sub>3</sub>)G, where G<sub>n</sub>, (FeCl<sub>3</sub>), and (SbCl<sub>5</sub>) correspond to the *n*th graphite, FeCl<sub>3</sub>, and SbCl<sub>5</sub> layers, respectively, and for this GBC, the peak associated with the  $E_{2g}^{(2)b}$  mode is split to give two frequencies. These results were very interesting, which led us to the further studies of lattice dynamics of GBC's.

In the present work, various acceptor-acceptor-type GBC's have been prepared from stages 4 and 5 FeCl<sub>3</sub>-GIC's and the lattice dynamics of the resultant GBC's has been studied by Raman spectroscopy and, in particular, the effect of the bi-intercalated species on the Raman-active  $E_{2g}^{(2)b}$  and  $E_{2g}^{(2)i}$  frequencies of GBC's has been studied in detail.

## II. EXPERIMENTAL

Natural graphite flakes produced in China and anhydrous FeCl<sub>3</sub> (Nakarai Test) were used as received. Stages 4 and 5 FeCl<sub>3</sub>-GIC's were prepared by a two-bulb method. The detailed experimental procedure was reported elsewhere.<sup>14</sup>

Three types of GBC's were prepared from stage 4 FeCl<sub>3</sub>-GIC. Bi-intercalation of IBr, ICl, and SbCl<sub>5</sub> into the stage 4 FeCl<sub>3</sub>-GIC was also performed by a two-bulb method. The reaction temperatures were ( $T_{\text{GIC}}=343$  K,  $T_{\text{bi}}=338$  K), ( $T_{\text{GIC}}=373$  K,  $T_{\text{bi}}=358$  K), and ( $T_{\text{GIC}}=443$  K,  $T_{\text{bi}}=403$  K) for the synthesis of FeCl<sub>3</sub>-1IBr-GBC, FeCl<sub>3</sub>-1ICl-GBC, and FeCl<sub>3</sub>-1SbCl<sub>5</sub>-GBC, respectively,

where  $T_{\text{GIC}}$  and  $T_{\text{bi}}$  refer to the temperatures of the stage 4  $\text{FeCl}_3$ -GIC and the bi-intercalated species, respectively. The reaction time was 1 day for the preparation of  $\text{FeCl}_3$ -IBr-GBC and  $\text{FeCl}_3$ -ICl-GBC, and 7 days for  $\text{FeCl}_3$ -SbCl<sub>5</sub>-GBC.

Three types of GBC's and one graphite multi-intercalation compound (GMC, defined as the graphite which contains more than three intercalated species) were prepared from stage 5  $\text{FeCl}_3$ -GIC. The reaction temperatures were ( $T_{\text{GIC}}=343$  K,  $T_{\text{bi}}=333$  K), ( $T_{\text{GIC}}=373$  K,  $T_{\text{bi}}=323$  K), and ( $T_{\text{GIC}}=333$  K,  $T_{\text{bi}}=313$  K) for  $\text{FeCl}_3$ -1IBr-GBC,  $\text{FeCl}_3$ -1ICl-GBC, and  $\text{FeCl}_3$ -2ICl-GBC, respectively.  $\text{FeCl}_3$ -1SbCl<sub>5</sub>-1ICl-GMC was prepared from  $\text{FeCl}_3$ -1SbCl<sub>5</sub>-GBC.<sup>9</sup> The reaction temperature was  $T_{\text{GBC}}=333$  K and  $T_{\text{mi}}=313$  K, where  $T_{\text{mi}}$  denotes the temperature of the multi-intercalated species of ICl. The reaction time for the synthesis of GBC's and GMC was set at 1 day.

X-ray diffraction (XRD) was used for the elucidation of the crystallinity and the layer sequences of the  $\text{FeCl}_3$ -based GBC's and GMC. Layer sequences of the GBC's with  $\text{FeCl}_3$ -1ICl,  $\text{FeCl}_3$ -2ICl and  $\text{FeCl}_3$ -1IBr were already reported elsewhere.<sup>15,16</sup>

The Raman spectra were excited by using a 514.5 nm line of an argon-ion laser (NEC, GLG3260). In order to prevent the decomposition of GBC's, the laser power was not allowed to exceed 10 mW. The scattered light was collected in a backscattering geometry. All spectra were recorded using a spectrometer (Jobin-Yvon, T64000) equipped with a multi-channel charge-coupled device detector. Each measurement was carried out at room temperature with an integration time of 600 s.

### III. RESULTS AND DISCUSSION

Figures 1(a)–1(c) show XRD patterns of the  $\text{FeCl}_3$ -based GBC's from a stage 4  $\text{FeCl}_3$ -GIC. As is obvious from these patterns, the degree of crystallinity of the GBC's is high. Well crystallized GBC's and GMC from stage 5  $\text{FeCl}_3$ -GIC

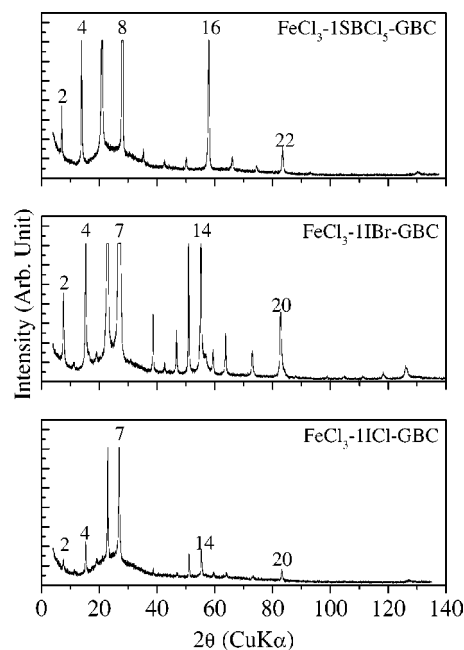
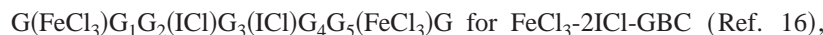
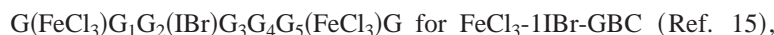


FIG. 1. XRD patterns of GBC's with one bi-intercalated layer prepared from stage 4  $\text{FeCl}_3$ -GIC. Number on peaks denote the index ( $00l$ ).

have been also obtained. By calculating the structure factor, the layer sequences of GBC's were determined: For all GBC's from stage 4  $\text{FeCl}_3$ -GIC, the layer sequence is found to be  $\text{G}(\text{FeCl}_3)\text{G}_1\text{G}_2(\text{I})\text{G}_3\text{G}_4(\text{FeCl}_3)\text{G}$ , where (I) denotes the bi-intercalated layer. Crystallographic  $R$  factors of the GBC's from stage 4  $\text{FeCl}_3$ -GIC were 15.4, 6.0, and 12.8% for  $\text{FeCl}_3$ -1IBr-GBC,  $\text{FeCl}_3$ -1ICl-GBC, and  $\text{FeCl}_3$ -1SbCl<sub>5</sub>-GBC respectively. In addition, another probable sequence of  $\text{G}(\text{FeCl}_3)\text{G}(\text{I})\text{GGG}(\text{FeCl}_3)\text{G}$  gives too large a crystallographic  $R$  factor to be likely. From the above reasons, the layer sequence of  $\text{G}(\text{FeCl}_3)\text{G}_1\text{G}_2(\text{I})\text{G}_3\text{G}_4(\text{FeCl}_3)\text{G}$  is very probable. From stage 5  $\text{FeCl}_3$ -GIC, layer sequences of the GBC's are as follows:



The  $R$  factor of the GMC was 12.6%. This value is acceptable considering that the XRD measurement was performed at a relatively fast scanning rate of  $2^\circ/\text{min}$ .

Figure 2 shows the Raman spectra of all the GBC's prepared from stage 4  $\text{FeCl}_3$ -GIC. Only one peak appeared in each Raman spectrum of GBC's. As is clear from the stacking sequence of GBC, no interior layer of graphite exists. Hence, the peaks in Fig. 2 can be assigned as Raman-active  $E_{2g}^{(2)b}$  mode frequencies. The frequencies in Fig. 2 are affected by the bi-intercalated species, and are in the order of

$\text{FeCl}_3\text{-SbCl}_5\text{-GBC} > \text{FeCl}_3\text{-ICl-GBC} > \text{FeCl}_3\text{-IBr-GBC}$ . The difference should be derived from the difference of the electron affinities of bi-intercalated species, that is, the degree of charge transfer. The details will be discussed later.

In Fig. 3, Raman spectra of GBC's with one bi-intercalation layer prepared from stage 5  $\text{FeCl}_3$ -GIC are shown. The spectrum of  $\text{FeCl}_3$ -1SbCl<sub>5</sub>-GBC is also shown as comparison.<sup>9</sup> Two peaks around 1587 and 1605  $\text{cm}^{-1}$  are observed in Fig. 3. These GBC's give the layer sequence of  $\text{G}(\text{FeCl}_3)\text{G}_1\text{G}_2(\text{I})\text{G}_3\text{G}_4\text{G}_5(\text{FeCl}_3)\text{G}$ , and therefore four

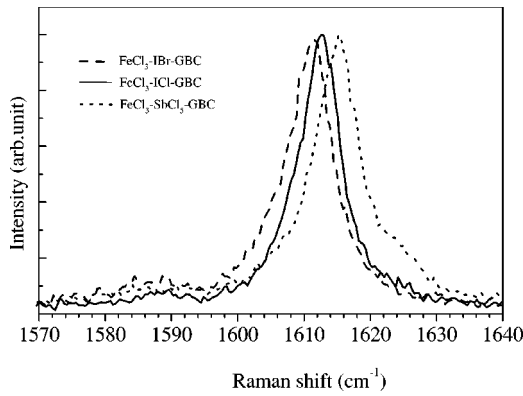


FIG. 2. Raman spectra of GBC's with one bi-intercalated layer prepared from stage 4  $\text{FeCl}_3$ -GIC.

graphene layers of  $G_1$ ,  $G_2$ ,  $G_3$ , and  $G_5$  are adjacent with one intercalated layer (bounding layer) and the fourth graphene layer of  $G_4$  is not adjacent with any intercalated layers. Hence, the lower frequency around  $1587 \text{ cm}^{-1}$  is assigned as an  $E_{2g}^{(2)i}$  mode ( $G_4$ ) and the higher frequency around  $1605 \text{ cm}^{-1}$  is assigned as an  $E_{2g}^{(2)b}$  mode ( $G_1$ ,  $G_2$ ,  $G_3$ , and  $G_5$ ). In addition, the peak intensity ratio of  $I(1605 \text{ cm}^{-1})/I(1587 \text{ cm}^{-1})$  is determined to be 4, indicating that the above assignment is quite valid.

As is mentioned above, Chan *et al.*<sup>7</sup> reported the effect of charge transfer and change of in-plane lattice constant on the  $E_{2g}^{(2)b}$  mode frequencies, and concluded that the Raman-active  $E_{2g}^{(2)b}$  mode frequencies are affected by three factors: (1) lattice constant  $d_{c-c}$ , (2) charge transfer, and (3) intercalate-coupling effect. In their theory,<sup>7</sup> the lattice constant is assumed to be the same for each graphene layer. By applying their theory, the lower frequency around  $1587 \text{ cm}^{-1}$  assigned as  $E_{2g}^{(2)i}$  mode is almost entirely affected by the lattice constant  $d_{c-c}$ . The lattice constant has been known to correlate with the degree of charge transfer from the intercalate layer. In Fig. 3, the frequencies of the  $E_{2g}^{(2)i}$  mode are on the order of  $\text{FeCl}_3\text{-1IBr-GBC} < \text{FeCl}_3\text{-1ICl-GBC} < \text{FeCl}_3\text{-1SbCl}_5\text{-GBC}$ . Hence, the degree of electron affinities of the bi-intercalated layer is on the order of  $\text{IBr} < \text{ICl} < \text{SbCl}_5$ . The Raman-active  $E_{2g}^{(2)b}$  mode frequencies in Figs. 2 and 3 are also affected by the bi-intercalated layers. When the intercalate-coupling effect is assumed to strongly influence the Raman frequencies, then the graphite

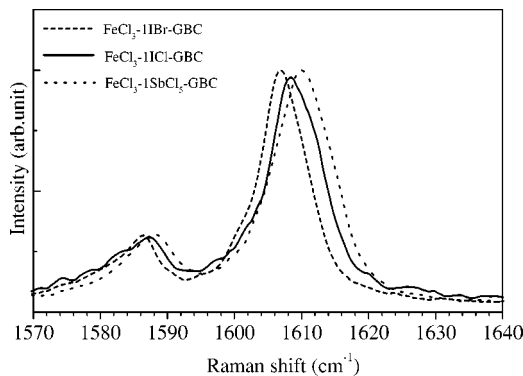


FIG. 3. Raman spectra of GBC's with one bi-intercalated layer prepared from stage 5  $\text{FeCl}_3$ -GIC.

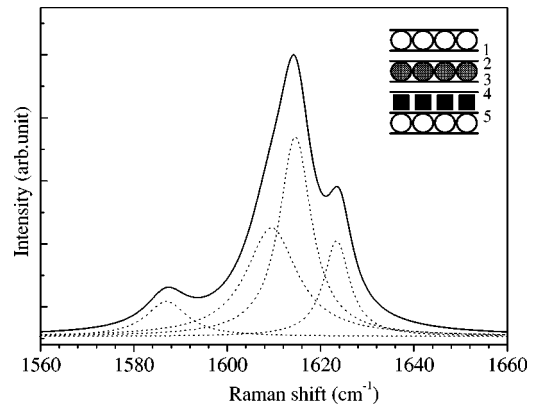


FIG. 4. Raman spectrum of  $\text{FeCl}_3\text{-1SbCl}_5\text{-1ICl-GMC}$  prepared from stage 5  $\text{FeCl}_3$ -GIC. Inset denotes the layer sequence of the GMC. Open circles, solid circles, and solid squares correspond to the  $\text{FeCl}_3$ ,  $\text{SbCl}_5$ , and  $\text{ICl}$  layers, respectively.

layers of  $G_1$  ( $G_4$ ) and  $G_2$  ( $G_3$ ) in Fig. 2 should give different frequencies. Therefore, the different frequencies of  $E_{2g}^{(2)b}$  mode are also due to the charge transfer.

Figure 4 shows the Raman spectra of  $\text{FeCl}_3\text{-1SbCl}_5\text{-1ICl-GMC}$ . Since the GMC is not sufficiently stable, peaks due to the decomposition are observed. Dotted lines in Fig. 4 are obtained by the Lorentzian line-shape analysis. Four peaks are observed after deconvolution of the spectrum. Higher frequencies around  $1614$  and  $1623 \text{ cm}^{-1}$  correspond to the above GMC by considering the spectrum of  $\text{FeCl}_3\text{-2SbCl}_5\text{-GBC}$ ,<sup>9</sup> and peaks of lower frequencies should be derived from the decomposed GMC as mentioned above. In the previous studies,<sup>9</sup> we observed the peak split in the Raman spectrum of  $\text{FeCl}_3\text{-2SbCl}_5\text{-GBC}$ . The peaks associated with the  $E_{2g}^{(2)b}$  mode in this work are also split to give two frequencies as observed in Fig. 4. This is probably due to the intercalate-coupling effect. Since the layer sequence of  $\text{FeCl}_3\text{-1SbCl}_5\text{-1ICl-GMC}$  is  $G(\text{FeCl}_3)G_1G_2(\text{SbCl}_5)G_3G_4(\text{ICl})G_5(\text{FeCl}_3)G$ , the GMC contains a graphene layer adjacent to two intercalated layers, as shown by  $G_5$ . This graphene layer should be affected by a double intercalate-coupling effect and hence the Raman-active  $E_{2g}^{(2)b}$  mode fre-

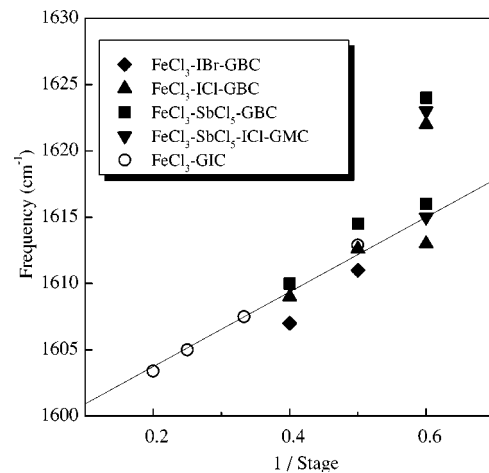


FIG. 5. Plot of Raman-active  $E_{2g}^{(2)b}$  mode frequencies against reciprocal stage number.

quencies of this graphene layer should shift to higher frequencies.

Figure 5 shows plots of the Raman-active  $E_{2g}^{(2)b}$  mode frequencies of the GBC's and GMC in this work against reciprocal stage number together with the results for FeCl<sub>3</sub>-GIC's and FeCl<sub>3</sub>-SbCl<sub>5</sub>-GBC's (Ref. 9) as comparison. A line in Fig. 5 is drawn by a least-squares fitting to the data of FeCl<sub>3</sub>-GIC's. The stage of the GBC with one bi-intercalated layer prepared from stage 4 FeCl<sub>3</sub>-GIC is regarded as 2, and those of GBC with one and two bi-intercalated layers from stage 5 FeCl<sub>3</sub>-GIC are as 5/2 and 5/3, respectively. The stage of FeCl<sub>3</sub>-1SbCl<sub>5</sub>-1ICl-GMC is regarded as 5/3. As is clear from Fig. 5, the frequencies become higher on the order of IBr<ICl<SbCl<sub>5</sub>. In addition all data are not far from the line for FeCl<sub>3</sub>-GIC's except for those affected by a double intercalate-coupling effect, indicating that the multiplier effects caused by bi-intercalated or multi-intercalated species do not appear for the lattice dynamics of GBC's. The double intercalate coupling layers can be regarded as those of a quasi-stage-1 compound. The difference between the Raman-active frequency of the double intercalate coupling layers and that of an acceptor-type stage

1 compound is caused only by the difference of the degree of charge transfer and is hence small.

#### IV. CONCLUSION

Various GBC's and a GMC have been prepared from stage 4 and 5 FeCl<sub>3</sub>-GIC's, and the lattice dynamics of the resultant GBC's and GMC have been investigated by Raman spectroscopy. The peak frequencies are found to be affected by the bi-intercalated or multi-intercalated species. From this result, the degree of charge transfer was determined to be in the order of IBr<ICl<SbCl<sub>5</sub>. Multiplier effects on the Raman-active frequencies caused by the bi-intercalated or multi-intercalated species were not observed.

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