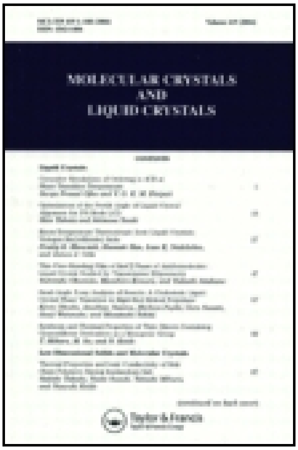

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Takeshi Abe [a], Yasuo Mizutani [b], Yasukazu Yokota [b], Minoru Inaba [a] & Zempachi Ogumi [a]

[a] Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto, 606-8501, Japan

[b] Institute of Advanced Energy, Kyoto University, Uji, Kyoto, 611-0011, Japan

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Raman Scattering Study of $FeCl_3$ Based Graphite Bi-Intercalation Compounds

TAKESHI ABE[a], YASUO MIZUTANI[b], YASUKAZU YOKOTA[b], MINORU INABA[a] and ZEMPACHI OGUMI[a]

[a]*Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606–8501, Japan and* [b]*Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611–0011, Japan*

$FeCl_3$-IBr, -ICl, and -$SbCl_5$ – graphite bi-intercalation compounds (GBC's) have been synthesized from a stage 4 $FeCl_3$ – graphite intercalation compound (GIC), and their lattice dynamics has been investigated by Raman spectroscopy. First, layer sequences of these GBC's were determined by x-ray diffraction, and the sequence was determined to be $G(FeCl_3)G_1G_2(I)G_3G_4(FeCl_3)G$, where G_n, $(FeCl_3)$, and (I) refer to the *n*th graphite, $FeCl_3$, and bi-intercalate layers, respectively. The sequences were the same irrespective of bi-intercalated species. These GBC's give only one peak identified as Raman active mode frequency in the Raman spectra. The peak frequencies were found to be affected by bi-intercalated species, and the frequencies were in the order of IBr <ICl <$SbCl_5$. From this result, the degree of charge transfer was determined to be in the order of IBr < ICl < $SbCl_5$.

Keywords: graphite; bi-intercalation; $FeCl_3$

INTRODUCTION

Graphite intercalation compounds (GIC's) have been extensively studied by many researchers. In particular, physical properties such as electrical conductivity, magnetic properties, lattice dynamics etc, have been studied because of the unique stage structures of GIC's [1, 2]. These properties are known to be systematically affected by the stage, defined as the number of graphene layers between intercalates' layers.

High stage GIC's have more than one vacant gallery and therefore another substance can intercalate into the gallery in a limited condition to form graphite bi-intercalation compounds (GBC's). Many studies have been made in terms of preparations [3-6], structures [7], physical properties [8-11] and formation mechanisms [12, 13] of the GBC's, however, there are few studies on the lattice dynamics of the GBC's [14, 15]. In the present work, three kinds of GBC's have been prepared from stage 4 $FeCl_3$-GIC and then the lattice dynamics of the resultant GBC's was investigated by Raman spectroscopy, in particular, Raman active $E_{2g}^{(2)b}$ mode frequencies have been focused.

Experimental

Stage 4 $FeCl_3$-GIC was prepared from natural graphite flakes and anhydrous $FeCl_3$ (Nakarai Tesk) by two-bulb method. The detail preparation procedure was reported elsewhere [13]. Bi-intercalation of IBr, ICl, and $SbCl_5$ was also performed by a two-bulb method. The reaction temperatures were (T_{GIC} = 343 K, T_{bi} = 338 K) , (T_{GIC} = 373 K, T_{bi} = 358 K) , and (T_{GIC} = 443 K, T_{bi} = 403 K) for $FeCl_3$-IBr-GBC, $FeCl_3$-ICl-GBC, and $FeCl_3$-$SbCl_5$-GBC, respectively, where T_{GIC} and T_{bi} refer to the temperatures of stage 4 $FeCl_3$-GIC and bi-intercalated species, respectively. The reaction time was one day for the preparation of $FeCl_3$-IBr-GBC and $FeCl_3$-ICl-GBC, and seven days for $FeCl_3$-$SbCl_5$-GBC.

Resultant GBC's were studied by x-ray diffraction (XRD) and the stacking sequences were determined by calculating structure factor. 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 at 1/8°/min with a time constant of 5 s.

Raman spectra were excited by using a 514.5 nm line (10 mW) of an argon ion laser. 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.

RESULTS AND DISCUSSION

XRD results

FIGURE 1 shows the typical XRD pattern of $FeCl_3$-$SbCl_5$-GBC. As is shown in FIG. 1, well crystallized GBC was found to be obtained. From the XRD pattern, the *c*-axis repeat distance of the GBC is 2.547 nm, which is almost equal to the sum of 0.943 nm (sandwich thickness of $G(FeCl_3)G$, where G and ($FeCl_3$) denote graphite and $FeCl_3$ layers, respectively) + 0.936 nm (sandwich thickness of $G(SbCl_5)G$) + 2 x 0.3354 nm (interlayer spacing of graphite). Hence, only one layer of $SbCl_5$ bi-intercalated into the stage 4 $FeCl_3$-GIC. By calculating structure factors, the stacking sequence of the $FeCl_3$-$SbCl_5$-GBC is determined to be $G(FeCl_3)GG(SbCl_5)GG(FeCl_3)G$. Another probable sequence of $G(FeCl_3)G(SbCl_5)GGG(FeCl_3)G$ gives too large crystallographic *R* factor, and therefore $SbCl_5$ bi-intercalates into the middle of vacant galleries. Other

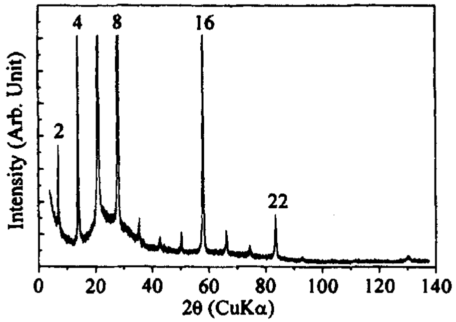

FIGURE 1 XRD pattern of $FeCl_3$-$SbCl_5$-GBC with one $SbCl_5$ layer. Number on peaks denotes the index (00*l*).

GBC's are also characterized by XRD. The *c*-axis repeat distances are 2.330 and 2.325 nm for $FeCl_3$-IBr-GBC and $FeCl_3$-ICl-GBC, respectively, and the stacking sequences are the same as $G(FeCl_3)G_1G_2(I)G_3G_4(FeCl_3)G$, where G_n and (I) corresponds to the *n*th graphite and bi-intercalated layer, respectively

Raman spectra

FIGURE 2 shows the Raman spectra of all the GBC's. 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 peak in FIG. 2 should be assigned as Raman active $E_{2g}^{(2)b}$ mode frequency. Chan et al. [16] reported the effect of charge transfer and change of in-plane lattice constant on $E_{2g}^{(2)b}$ mode frequencies, and concluded that the Raman active $E_{2g}^{(2)b}$ mode frequencies are affected by three factors of 1) lattice constant $d_{c\text{-}c}$, 2) charge transfer and 3) intercalate-coupling effect. In addition, they reported that the effect of charge transfer on Raman frequencies of acceptor type GIC's is not strongly dependent on the degree of charge transfer. For this reason, the GBC's in this work, in which the charge densities of graphite layers is not equivalent, give only one peak associated with the $E_{2g}^{(2)b}$ mode. In FIG. 2, the Raman active

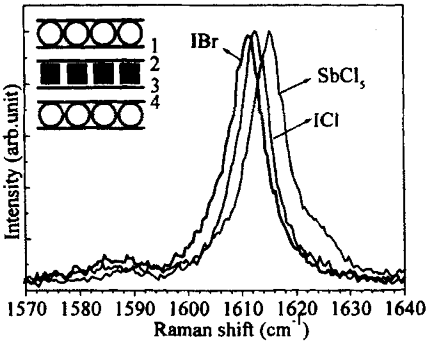

FIGURE 2 Raman spectra of $FeCl_3$-based GBC's with one bi-intercalated layer. Inlet denotes the stacking sequence of the GBC.

$E_{2g}^{(2)b}$ mode frequencies are affected by the bi-intercalated species. When the intercalate-coupling effect is assumed to affect strongly the Raman frequencies, then the graphite layers of G_1 (G_4) and G_2 (G_3) should give different frequencies. Hence, the different frequencies in FIG. 2 are due to the lattice constant and charge transfer. Lattice constant is greatly affected by charge transfer, and therefore the difference of Raman active $E_{2g}^{(2)b}$ mode frequencies are concluded to be the difference of charge transfer of bi-intercalated layers. Table 1 shows the Raman active $E_{2g}^{(2)b}$ mode frequencies of GBC's in this work together with that of stage 2 $FeCl_3$. It is clear from Table 1 that the degree of charge transfer of bi-intercalated species is in the order of IBr < ICl < $FeCl_3$ < $SbCl_5$, which is in good agreement with our previous results [14, 17].

TABLE 1 Raman active $E_{2g}^{(2)b}$ mode frequencies

bi-intercalated species	IBr	ICl	$SbCl_5$	cf) $FeCl_3$
$E_{2g}^{(2)b}$ mode frequencies (cm^{-1})	1611	1612	1615	1613

CONCLUSION

$FeCl_3$-IBr, -ICl, and $SbCl_5$-graphite bi-intercalation compounds (GBC's) have been prepared from stage 4 $FeCl_3$-GIC, and the lattice dynamics of the resultant GBC's has been investigated. All the GBC's give only one peak identified as Raman active $E_{2g}^{(2)b}$ mode frequency. The peak frequencies were affected by bi-intercalated species. From this result, the degree of charge transfer was determined to be in the order of IBr < ICl < $SbCl_5$.

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