

STRUCTURAL STUDY OF STAGE 4-TbCl₃ GRAPHITE INTERCALATION COMPOUND

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Introduction

Graphite intercalation compounds (GIC's) are quasi-2D materials, which offer an extraordinary abundance of interesting phenomena. This abundance comes about through the interplay between intercalant-intercalant forces and graphite-intercalant forces, which ultimately are responsible for the intercalation process. Stage of GIC's is defined as the number of graphene layers between two nearest neighbor layers of intercalated species. The structure of GIC's depends strongly on stage and/or the kind of intercalated species [1]. Previous reports [2-7] of synthesis and structural studies on GIC's based on rare-earth metal trichlorides have been extended to others. The pristine TbCl₃ has an orthorhombic structure of PuBr₃ type (space group D_{2h}¹⁷-Cmcm) which is not *a priori* a layer structure. The layer character depends on the atomic-site parameters. Each cation is located at the center of a trigonal prism formed by the anions. These prisms are stacked on each other to infinity. Neighboring prism columns are shifted by $c/2$ so that each cation obtains another (2+1) neighbors in the equatorial plane. One of the equatorial neighbors is roughly 1 Å farther away and this gives rise to the layer character of this structure. The lattice parameters are $a=3.86$ Å, $b=11.71$ Å, and $c=8.48$ Å [8]. In this paper we reported for the first time, as far as we know, the structural study of the TbCl₃-GIC by measurements of X-ray and electron diffraction.

Experimental

Natural graphite flakes from Madagascar was used as host material. TbCl₃-GIC was synthesized by the one-zone vapor transport method in sealed quartz ampoules under a 0.6 bar chlorine high purity gas at ambient temperature. The intercalation was carried out at $T = 508$ °C reaction temperature and with 9 days reaction time. The GIC samples thus obtained were thoroughly washed with 25% hydrochloric acid solution and again with distilled water to remove excess TbCl₃, which remained unreacted on the surface of samples. The c-axis repeat distance of this compound I_c was determined by (001) reflection pattern data obtained with a powder Philips-PW 3710 x-ray diffractometer, using CuK α ($\lambda = 1.5418$ Å) radiation at 40 kV and 20 mA. Zero level precession photographs recorded along (110) of graphene layers for stage 4, were performed on a Buerger precession camera (Charles Supper) using Zr-filtered Mo K α ($\lambda = 0.7107$ Å) in order to determine the structure of the intercalate layer. Electron diffraction was also carried out to determine the in-plane structure of the TbCl₃ intercalate layer by using a Hitachi H-600 transmission electron microscopy operated at 100 kV ($\lambda = 0.037$ Å). The TEM samples for the room temperature measurements were supported on Cu-grids and were transferred into the vacuum chamber of the microscopy. The electron diffraction pattern was taken when the beam was normal, or nearly normal, to the layers planes by exploring several parts of a sample with a selected area diffraction aperture of 2 μ m.

Results and Discussion

The x-ray diffraction pattern obtained of the sample prepared in this study (Figure 1), indicated that the stage 4 TbCl₃-GIC was formed. Indexing of the x-ray diffraction pattern was accomplished from (001) to (008) with increasing 2θ . There was no evidence of diffraction neither from other stages nor from graphite in this compound, which suggests a well defined stage. Stage 4 TbCl₃-GIC sample gave identity period $I_c = (19.73 \pm 0.17)$ Å in good agreement with of the theoretical value $I_c = 19.71$ Å. The perfection degree of stage 4 TbCl₃-GIC was characterized by comparing the full width at half maximum (FWHM) $\Delta\theta$ of the (001) reflection peaks of the GIC, with that of pristine natural graphite flakes. In Figure 2, was plotted the FWHM for natural graphite flakes, and for the stage 4 TbCl₃-GIC in units of $(\sin\Delta\theta/\lambda)$ versus $\sin\theta/\lambda$. Figure 2 revealed that the FWHM of the reflections for the intercalation compound are not significantly different from those for the parent material, natural graphite flakes. By comparing the results of the GIC to that of pristine graphite, we can conclude that the samples, not only are single staged, but also that there is no appreciable statistical disorder of the graphene layers after intercalation. Precession photographs about the common (110) axis of the graphene layers and the primitive intercalate cell provide direct information on the intercalate's stacking sequence. Figure 3a shows the row (001) sharp reflections along c^* confirming high fidelity of staging. Figure 3b shows a schematic interpretation of the a-axis precession photograph. The average c-axis repeat distance is $I_c = 19.714$ Å which agrees well with that obtained by diffractometry. The analysis of (hk0) reflections on electron diffraction pattern, Figure 4a, shows the a-axis of the intercalated layer rotated with respect to the graphene a-axis $\theta_{TbCl_3} = 22^\circ$. The parameters for the TbCl₃, $b = 11.75$ Å and $c = 8.68$ Å, as in case of the CuCl₂ layers, were obtained using as a model the twinning of the TbCl₃ layers [9-10]. These unit cell parameters are almost the same as those of the pristine TbCl₃[8].

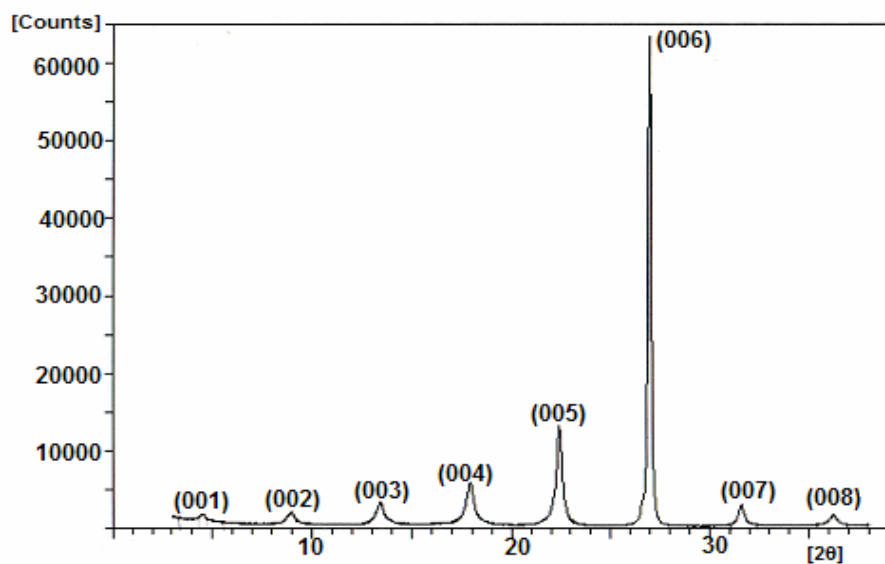


Figure 1. The (001) diffraction pattern of the stage TbCl_3 -GIC in natural graphite from Madagascar.

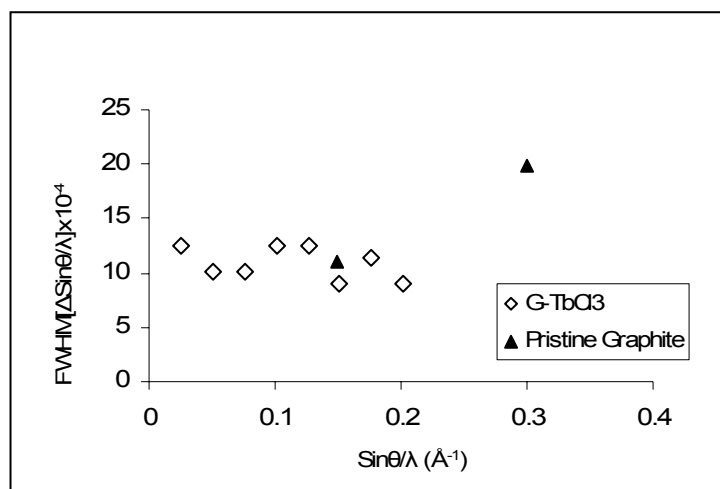
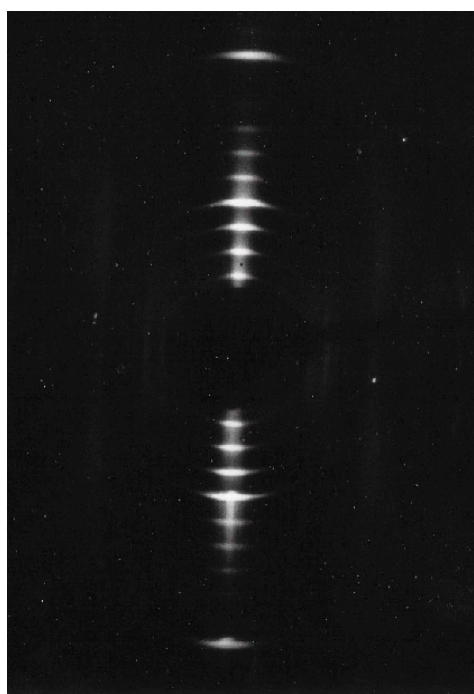
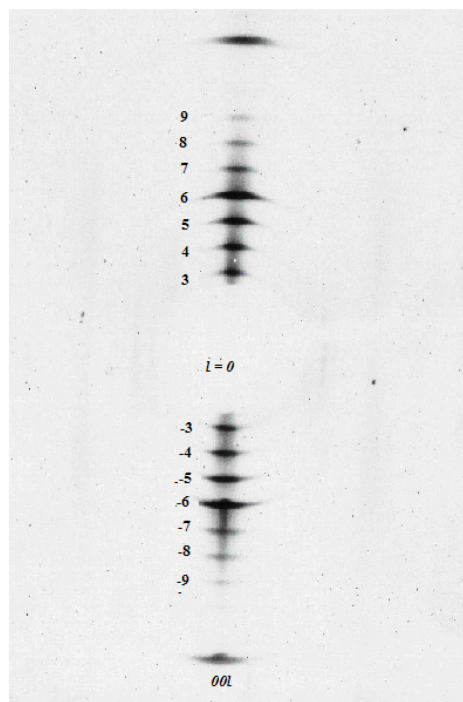


Figure 2. Plot of the full width at half maximum (FWHM) of the (001) diffraction lines in units of $\sin(\Delta\theta)/\lambda$ versus $\sin\theta/\lambda$ for stage 4 TbCl_3 -GIC and pristine graphite.

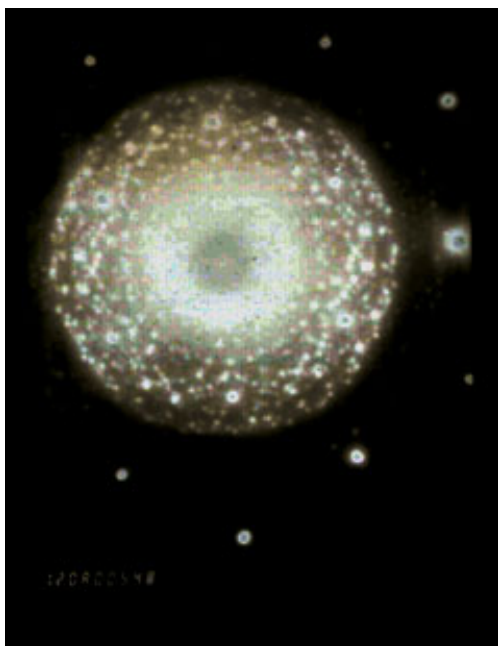


(a)

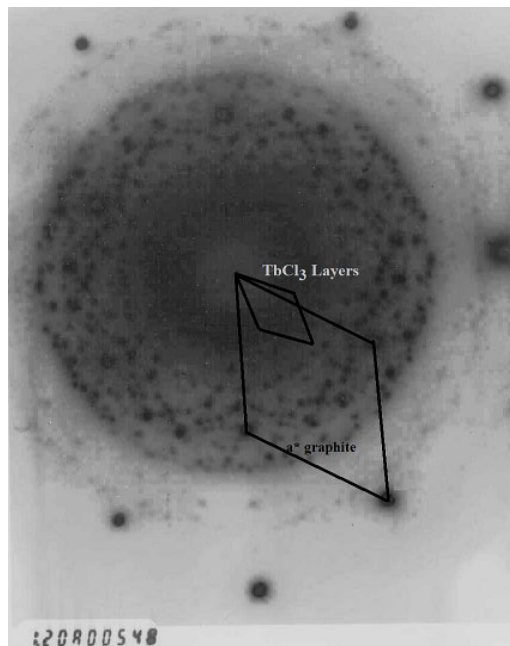


(b)

Figure 3. (a) Zero-level x-ray precession photograph from stage 4 TbCl_3 -GIC recorded along $[110]$ of graphite layers and (b) schematic interpretation of the stage 4 precession photograph.



(a)



(b)

Figure 4. (a) Electron diffraction pattern of stage 4 TbCl_3 -GIC., (b) Orientation of TbCl_3 layers with respect to graphene layer.

Conclusions

Graphite intercalation compound of $TbCl_3$ was prepared via vapor phase method. The structural study was performed from (00l) and (hk0) reflections by x-ray diffractometry, zero-level precession camera, and electron diffraction techniques respectively. The results of c-axis repeat distances I_c found from (00l) reflections in the zero-level photographs are in good agreement with those obtained by x-ray diffractometry.

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