STRUCTURAL STUDY OF STAGE 3-$HoCl_3$ GRAPHITE INTERCALATION COMPOUNDS

V. González[(1)], O. González[(1,2)], and C. Millán[(3)]
1. Dpto. de Ciencia de los Materiales IIBCA-UDO, 2. Dpto. de Física UDO-Sucre
3. Dpto. Cursos Básicos UDO-Anzoátegui, Venezuela.

Introduction

Graphite intercalation compounds (CIG´s) are quasi-two-dimensional metals characterized by a large anisotropy in chemical bonding, which, for both graphite and intercalate, is strong in the basal plane (a, b) directions and very much weaker in the perpendicular stacking (c) direction [1]. By choosing of the intercalant species and concentration, it has been possible to prepare a larger number of compounds [2]. Previous reports [3,9] of synthesis and structural studies on GIC´s based on rare-earth metal trichlorides have been extended to others. The pristine $HoCl_3$ has a monoclinic structure of YCl_3 type with two Ho ions per unit cell (space group C2/m) and two-dimensional (2D) bonding [10]. The lattice parameters are a = 6,85 Å, b = 11,85 Å, c = 6,39Å, and β = 110,8º. In this paper we report the structural study of the $HoCl_3$-GIC´s by measurements of x-ray and electron diffraction.

Experimental

Natural graphite flakes from Madagascar and highly oriented pyrolytic graphite (HOPG) were used as host materials. $HoCl_3$-GIC´s were synthesized by the one-zone vapor transport method in sealed quartz ampoules under a chlorine pressure of 0,85 bar at ambient temperature. The intercalation was carried out at a T=750ºC reaction temperature and with 15 days reaction time, both with natural graphite (130 – 35) μm and HOPG (3 x 5 x 0,06) mm^3. The GIC´s samples thus obtained were thoroughly washed with 25% hydrochloric acid solution and again with distilled water to remove excess $HoCl_3$, which remained unreacted on the surface of samples. The c-axis repeat distances of these compounds Ic were determined by (00l) reflection patterns data obtained with a powder Siemens - D5000 x-ray diffractometer, which employed CuK_α(λ=1,5418 Å) radiation at 35 kV and 20 mA. From weight uptake measurements it was possible to determine the chemical formula: $C_{20,5}HoCl_3$ and $C_{23,8}HoCl_3$ of the natural graphite and HOPG GIC´s, respectively. Zero-level precession photographs recorded along [110] of graphene layers for stage 3, were performed on a Buerger precession camera (S.T.O.E) using Z r - filtered MoK_α(λ = 0,7107 Å) radiation source in order to determine the structure of the intercalate layer. Electron diffraction was also carried out to determine the in - plane structure of the $HoCl_3$ intercalate layer by using a HITACHI H - 600 transmission electron microscopy operated at 100kV (λ= 0,037 Å). The TEM samples for the room-temperature measurements were supported on Cu-grids and were rapidly transferred into the vacuum chamber of the microscope. This was made to prevent some deintercalation process. 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 2μm.

Results and Discussion

The obtained x-ray diffraction patterns Figure 1(a) and 1(b) of the samples prepared in this study indicated that the stage 3 $HoCl_3$-GIC´s were formed in (a) natural graphite and (b) highly oriented pyrolytic graphite (HOPG), respectively. Indexing of the x-ray diffraction patterns obtained was accomplished from (001) to (009) with increasing 2θ. There was no evidence of diffraction neither from other stages nor from graphite in both compounds, which suggests well defined stages. Stage-3 $HoCl_3$-GIC´s samples gave identity periods Ic = (16,28 ± 0,03) Å (natural graphite) and Ic = (16,29 ± 0,04) Å (HOPG) are in good agreement with that reported by Stumpp[11].

Precession photographs recorded about the common [110] axis of the graphene layers and the primitive intercalate cell provide direct information on the intercalate´s stacking sequence. Figures 2(a) and 3(a) shows the row (00l) sharp reflections along **c*** confirming high fidelity of staging belonging (2) natural graphite and (3) HOPG. Figures 2(b) and 3(b) show a schematic interpretation of the a-axis precession photographs. The average c-axis repeat distances are Ic = (16,24 ± 0,21) Å (natural graphite) and Ic =(16,30 ± 0,13) Å (HOPG) which agree well with that obtained by diffractometry. The analysis of (hk0) reflections on electron diffraction patterns, Figures 4(a), 4(b), 5(a) and 5 (b), showed the a-axis of

the intercalated layer rotated with respect to the graphene a-axis θ_{HoCl3} = 21º, 44º (natural graphite) and θ_{HoCl3} = 21º, 30º, 44º (HOPG). The parameters for the $HoCl_3$, a_{HoCl3} = 6,82 Å, b_{HoCl3} = 11,82 Å (natural graphite), a_{HoCl3} = 6,83 Å, b_{HoCl3} = 11,84 Å (HOPG). As in case of the $CuCl_2$ layers, the parameters were obtained using as a model the twining of the $HoCl_3$ layers [12, 13], which agree with those parameters of pristine substances, a_{HoCl3} = 6,85 Å and b_{HoCl3} =11,85 Å.

Conclusions

Graphite intercalation compounds of $HoCl_3$ have been prepared via vapor phase method. The structural study was performed from (001) and (hk0) reflections by x-ray diffractometry, zero-level precession camera, and electron diffraction techniques respectively. The results of c-axis repeat distances Ic found from (001) in the zero-level photographs are in good agreement with those obtained by x-ray diffractometry. The twining model allowed to determine the $HoCl_3$ parameters.

References

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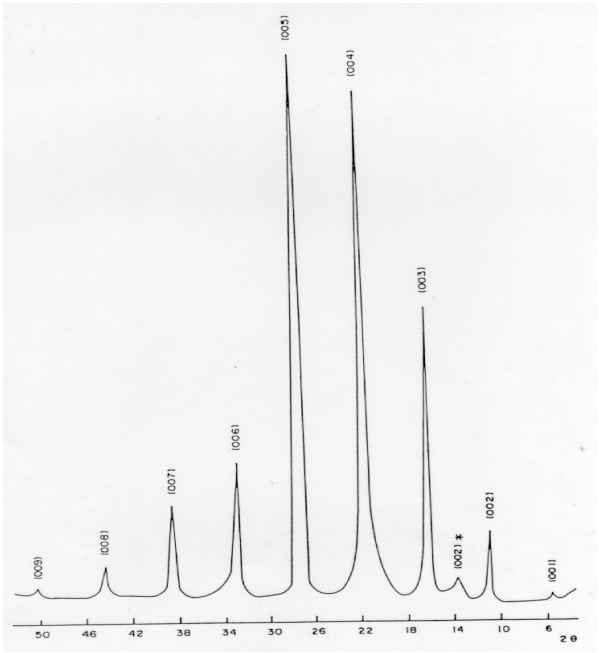
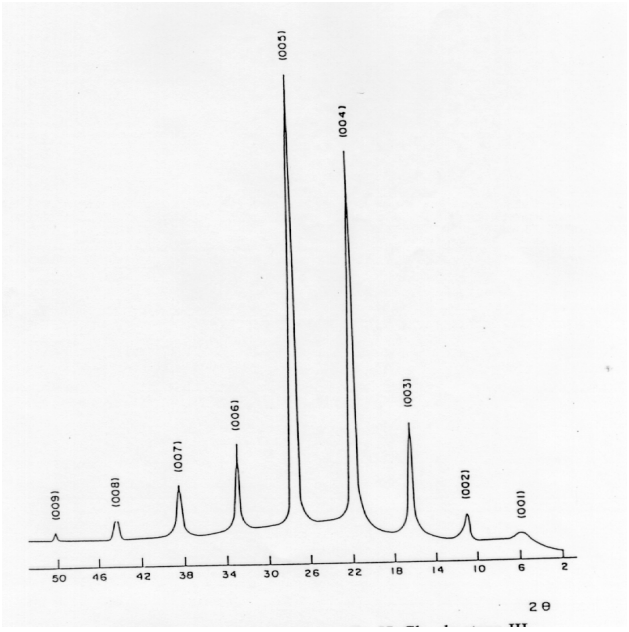
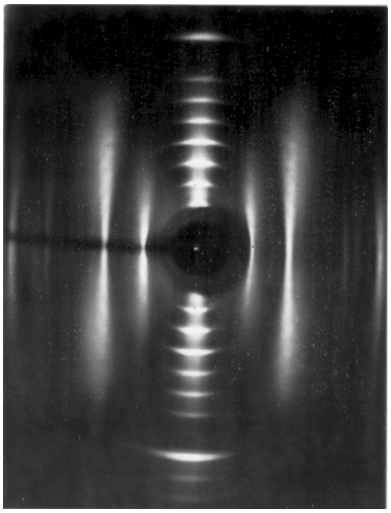


(a)

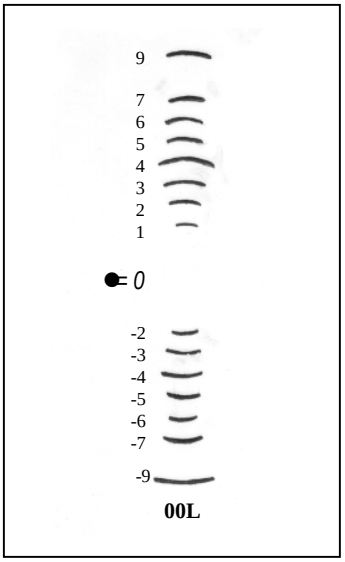


(b)

Figure 1. The (00l) diffraction patterns of stage 3 $HoCl_3$ – GIC´s: (a) natural graphite, (b) highly oriented pyrolytic graphite (HOPG).

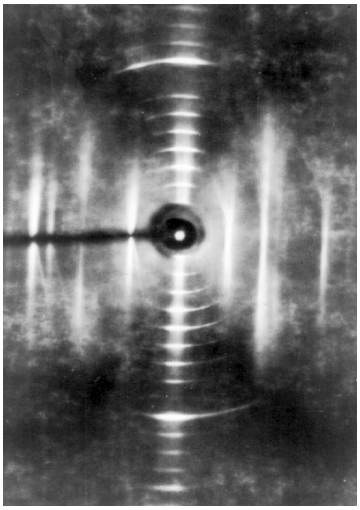


(a)

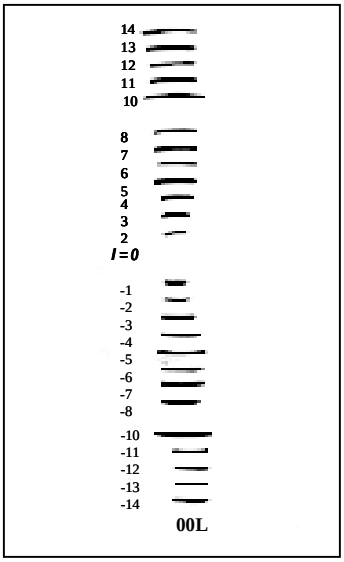


(b)

Figure 2. (a) Zero-level x-ray precession photograph from stage 3 $HoCl_3$ – GIC (natural graphite), (b) schematic interpretation of the stage 3 precession photograph.

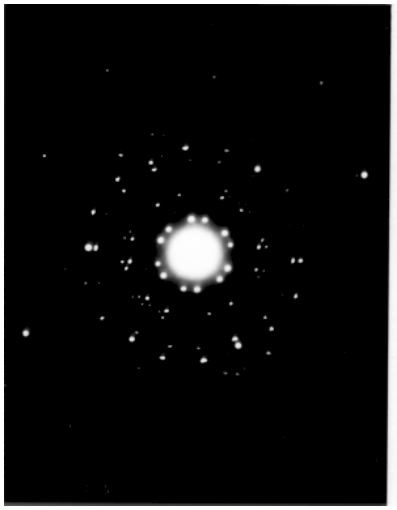


(a)

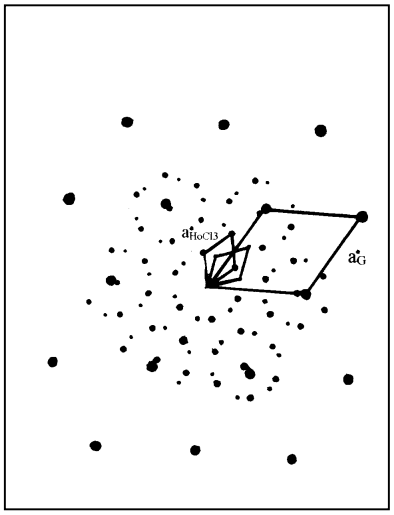


(b)

Figure 3. (a) Zero-level x-ray precession photograph from stage 3 $HoCl_3$ – GIC (HOPG), (b) schematic interpretation of the stage 3 precession photograph.

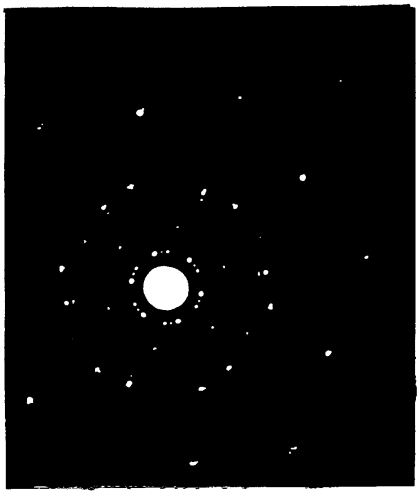


(a)

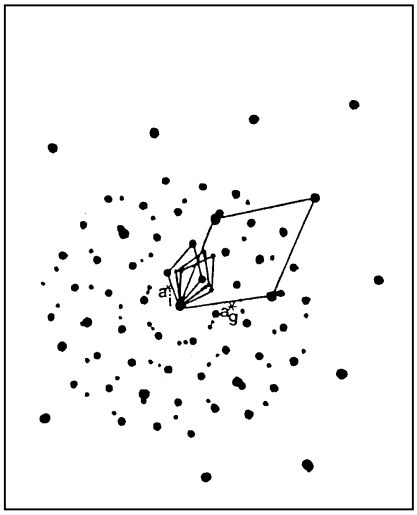


(b)

Figure 4. (a) Electro diffraction pattern of stage 3 $HoCl_3$ – GIC (natural graphite), (b) Orientation of $HoCl_3$ layers with respect to graphene layer.



(a)



(b)

Figure 5. (a) Electro diffraction pattern of stage 3 $HoCl_3$ – GIC (HOPG), (b) Orientation of $HoCl_3$ layers with respect to graphene layer.