STRUCTURAL STUDY OF STAGE 2-$SmCl_3$ GRAPHITE INTERCALATION COMPOUNDS

O. González[1, 3], F. Mago[2], V. González[3], I Cedeño[2] and L. Marcano[2]
1. Dpto. de Física UDO-Sucre, 2. Dpto. de Química UDO-Sucre,
3. Dpto. de Ciencia de los Materiales IIBCA-UDO, Venezuela.

Introduction

Graphite intercalation compounds (CIG´s) provide an interesting field of research into of layered materials, in which intercalate and graphene layers are stacked periodically. Stage of GIC´s is defined as the number of graphene layers between two nearest neighbor layers of intercalated material. The structure of GIC´s depends strongly on stage and/or the kind of intercalated specimens [1].

The pristine $SmCl_3$ has a structure of UCl_3 type [2] with three dimensional (3D) bonding. The pristine $SmCl_3$ is hexagonal with two Sm ions per unit cell (space group P63/m). The unit cell parameters are a = 7,378 Å and c = 4,171 Å [3,4]. The Sm ions are located on symmetry sites at (1/3, 2/3, 1/4) and the chloride ions on mirror (x, y, ¼; -y, x-y, ¼; y-x, -x, ¼) [5]. In this paper we describe the results concerning to the structural study of $SmCl_3$-GIC´s by measurements of x-ray and electron diffraction.

Experimental

GIC´s were prepared using pristine natural graphite flakes size (130 – 35) μm and highly oriented pyrolytic graphite (HOPG) of dimensions (2 x 7 x 0,05) mm^3 and commercial anhydrous $SmCl_3$ by the one-zone vapor transport method in sealed quartz ampoules under ~ 0,85 bar chlorine high purity gas and placed in a tube-shaped furnace at T=610ºC during a reaction time of 6 days. The GIC´s samples thus obtained were thoroughly washed with 25% hydrochloric acid solution and again with distilled water to remove excess $SmCl_3$, which remained unreacted on the surface of samples. The c-axis repeat distances Ic were calculated from (00l) reflection patterns obtained with a powder Siemens-D5000 x-ray diffractometer, which employed CuK_α(λ= 1,5418 Å) radiation at 35 kV, 20 mA. From weight uptake measurements (53,62 % 52,27 %), it is possible to determine the chemical formula: $C_{18,5}SmCl_3$ and $C_{12,3}SmCl_3$ of the natural graphite and HOPG GIC´s, respectively. Zero-level precession photographs recorded along [110] of graphene layers for stage 2, were performed on a Buerger precession camera (Charles Supper) using Zr-filtered MoK_α(λ= 0,719 Å) radiation source to determine the structure of the intercalate layer. Electron diffraction was also carried out in order to determine the in - plane structure of the $SmCl_3$ intercalate layer by using a HITACHI H - 600 transmission electron microscopy operated at 100 kV (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

Figure 1 shows (00l) x-ray diffraction patterns of stage 2 $SmCl_3$-GIC´s belonging to (a) natural graphite and (b) highly oriented pyrolytic graphite taken at room temperature, which were indexed from (001) to (007) with increasing 2θ. As it can be observed there is no presence of diffraction neither from other stages nor from graphite in both compounds, which suggests well defined stages. Stage-2 $SmCl_3$-GIC´s specimens gave c-axis repeat distances Ic = (13,16 ± 0,11) Å (natural graphite) and Ic =(13,28 ± 0,08) Å (HOPG) in agreement to the values reported early [6].

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. Figure 2 reveals the row (00l) sharp reflections along **c*** indicating high fidelity of staging for (a) natural graphite and (b) HOPG. Figures 2(c) and 2(d) show a schematic interpretation of the a-axis precession photographs corresponding to Figures 2(a) and 2(b), respectively. The average c-axis repeat distances are Ic = (13,20 ± 0,30) Å (natural graphite) and Ic =(13,29 ± 0,40) Å (HOPG) for stage 2 GIC´s.These values are in good agreement with the previous values obtained by x-ray diffractometry for natural graphite and HOPG samples and those reported by Cedeño [6].

Figures 3(a) show electron diffraction patterns obtained on both GIC´s samples at room temperature. As it can

be seen from Figures 3(c) and 3(d), $SmCl_3$ layers form a hexagonal structure with the (hk0) pattern of which is rotated by $\pm 22^o$ with respect to the graphene layer pattern. Further, the obtained parameter $a_{SmCl3} = 7,43Å$ is three times larger than the graphite parameter $a_G = 2,456Å$, forming a (3X3) commensurate structure. This unit cell parameter, a_{SmCl3}, is almost the same as that of the pristine $SmCl_3$, $a_{SmCl3} = 7,378Å$ [2].

Conclusions

Graphite intercalation compounds of $SmCl_3$ 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 intercalated layers form a commensurate structure.

References

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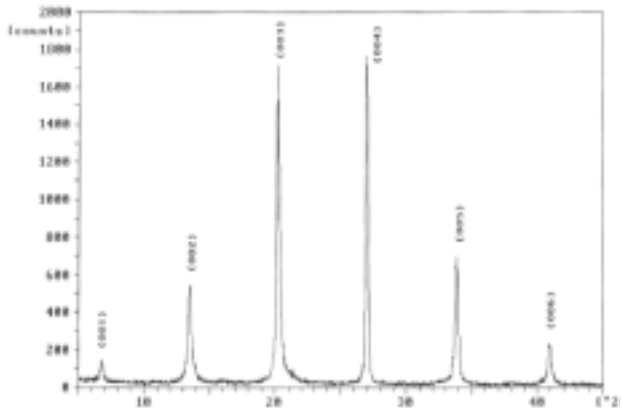
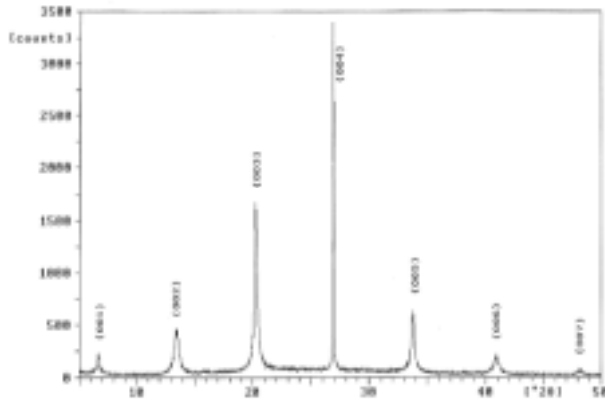
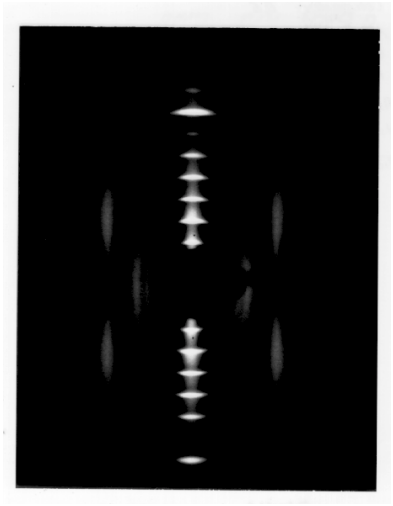


(a)

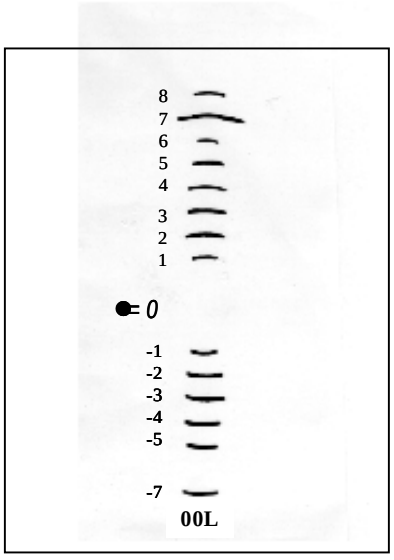


(b)

Figure 1. The (00l) diffraction patterns of stage 2 $SmCl_3$ – GIC´s: (a) natural graphite, (b) highly oriented pyrolytic graphite.

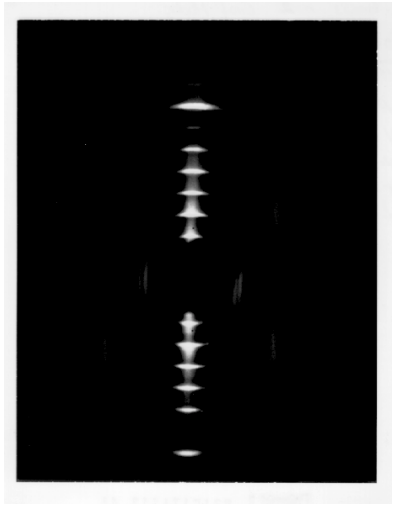


(a)

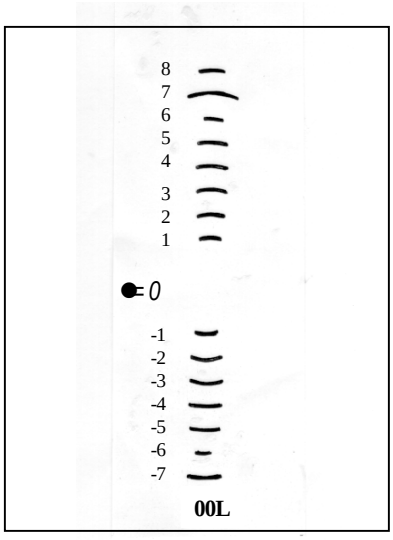


(b)

Figure 2. (a) Zero-level x-ray precession photograph from stage 2 $SmCl_3$ – GIC (natural graphite), (b) schematic interpretation of the stage 2 precession photograph.

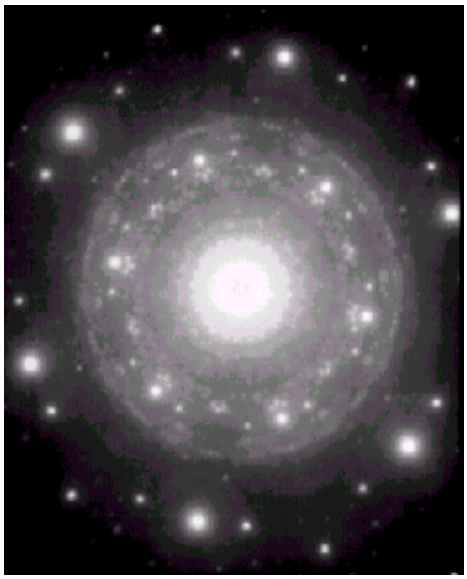


(a)

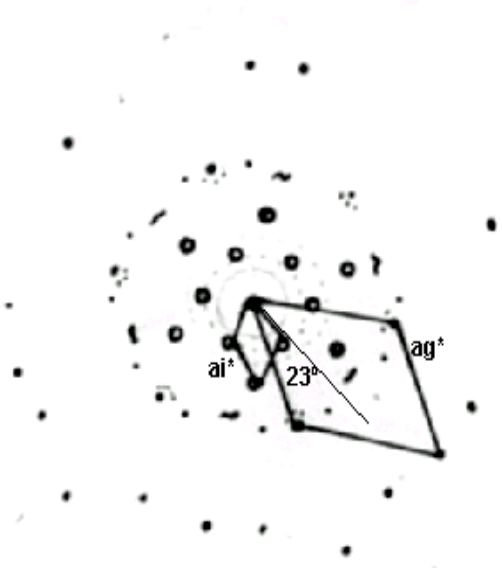


(b)

Figure 3. (a) Zero-level x-ray precession photograph from stage 2 $SmCl_3$ – GIC (HOPG), (b) schematic interpretation of the stage 2 precession photograph.

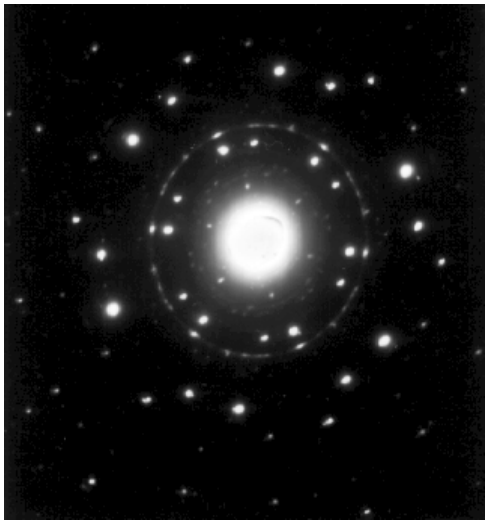


(a)

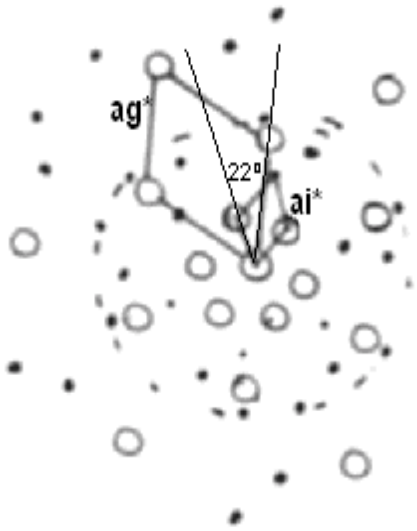


(b)

Figure 4. (a) Electro diffraction pattern of stage 2 $SmCl_3$ – GIC (natural graphite), (b) Orientation of $SmCl_3$ layers with respect to graphene layer.



(a)



(b)

Figure 5. (a) Electro diffraction pattern of stage 2 $SmCl_3$ – GIC (HOPG), (b) Orientation of $SmCl_3$ layers with respect to graphene layer.