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Structural Study of a Novel Graphite Bi-Intercalation Compound

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Novel graphite biintercalation compound with layers of $SmCl_3$ and $ErCl_3$ is synthetized by the one-zone vapour method. A well defined stage-3 $SmCl_3$ graphite intercalation compound with the c-axis repeat distance $I_c = 16.60 \pm 0.07$ Å is used as the host matrix.The X-ray diffraction shows a creation of a new compound with $I_c = 19.70 \pm 0.05$Å. Based on these data a ...G-$SmCl_3$ -G-$ErCl_3$... stacking sequence is proposed. The electron diffraction shows a-axis of the intercalated layer is rotated with respect to the graphene a-axis by 42°, and 19°, 42° for $SmCl_3$ and $ErCl_3$ layers, respectively. The parameters of the lattices obtained are a_{SmCl3} =7.37 Å, .a_{ErCl3} = 6.75 Å, and b_{ErCl3} = 11.73 Å.

Keywords: Graphite; Biintercalation; $SmCl_3$; $ErCl_3$

INTRODUCTION

Graphite biintercalation compounds (GBCs) consist of two different intercalated layer types arranged in alternating stacking sequence[1] . These compounds form a very important class of materials because of their physical and chemical properties offering a wider area of research compared to binary graphite intercalation compounds (GICs). Most of the works until now have been realized with transition metal trichlorides[1-2], transition metal dichloride-trichloride[3-5], and transition metal rare earth metal trichlorides GBCs[4], respectively. From the particular reaction conditions known for synthetizing

pure stages $SmCl_3$ - GIC and $ErCl_3$ - GIC from HOPG and flakes graphite[6-10], it has been possible to prepare pure GBCs. It is very important that the second intercalation reaction proceeds smoothly.The pristine $SmCl_3$ has a structure of UCl_3 type[11-12] with three dimensional (3D) bonding , while the pristine $ErCl_3$ has a structure of YCl_3 type with two dimensional (2D) bonding[13]. The pristine $SmCl_3$ is hexagonal with two Sm ions per unit cell (space group P 6_3 / m)[12]. The unit cell parameter are a = 7.378Å and c = 4.171 Å[12]. The Sm ions are located on symmetry sites at (1/ 3,2/ 3,1/ 4) and the chloride ions on mirrors (x, y, 1/ 4 ; -y, x-y, 1/ 4 ; y-x , -x , 1/ 4)[14]. The pristine $ErCl_3$ is monoclinic with two Er ions per unit cell (space group C 2 m)[13]. The lattice parameters are a = 6.80 Å, b = 11.79 Å, c = 6.39 Å , and β = 110.7°. In this paper we reported for the first time, as far as we know, the structural study of the $SmCl_3$ - $ErCl_3$ -GBC by measurements of x-ray and electron diffraction.

EXPERIMENTAL

$SmCl_3$-GICs were prepared by the one-zone vapour transport method using a highly oriented pyrolytic graphite (HOPG) with a mosaic spread of less than 1° as starting host material. The samples were in the form of thin rectangular plates of dimensions 4.0 x 3.0 x 0.026 mm^3. Reaction silica tube was sealed under 0.8 bar Cl_2 high purity gas and placed in a furnace at T= 600° C during 8 days. The GICs samples thus obtained were thoroughly washed with 25% hydrochloric acid solution to remove excess $SmCl_3$, which remained unreacted on the surface of samples. The c-axis repeat distance of this compound was confirmed by (00l) X-ray diffraction using CuK_α radiation to be well defined stage-3. Samples of $SmCl_3$ -$ErCl_3$ -GBCs were prepared by a sequential intercalation method: the intercalant $ErCl_3$ was intercalated into the empty graphene galleries of stage-3 $SmCl_3$ -GIC inside a sealed two zone

Pyrex glass tube under 0.5 bar Cl_2 , and was kept at 400-350 ° C (ΔT= 50° C) for 10 days. The $SmCl_3$-$ErCl_3$-GBCs samples were equally washed with a hydrochloric acid solution of the same concentration in order to remove unreacted excess $ErCl_3$ .Stage purity and c-axis repeat distance were confirmed by x-ray diffraction analyses using CuK_α radiation and determined from the (00l) reflections. Electron diffraction was also performed to determine the in-plane structure of the $SmCl_3$ and $ErCl_3$ intercalate layers by means a HITACHI H-600 transmission electron microscopy operated at 100 Kv (λ = 0.037Å) The electron diffraction pattern was obtained when the beam was normal, or nearly normal, to the layer planes by exploring several parts of a sample with a selected area diffraction aperture of 2 μ m.

RESULTS AND DISCUSSION

Figure 1 shows (00l) X-ray diffractograms of a stage-3 $SmCl_3$ -GIC before (a) and after (b) biintercalation with $ErCl_3$ taken a room temperature, which are indexed from (001) to (008) with increasing 2Θ. It is worth noting that there is no evidence of diffraction neither from other stages nor from graphite in both compounds, which confirms well defined stages. Stage-3 $SmCl_3$-GIC sample gives a c-axis repeat distance I_c = 16.60 ± 0.07 Å in accord to the value reported early [11]. On the other hand, an identity period in c-direction I_c = 19.70 ± 0.05 Å is obtained for the new GBC.

In order to model the structural sequence of $SmCl_3$ -$ErCl_3$ -GBC, one can observe that I_c = 19.70 Å is practically equal to the sum of $d_{i\,(1)}$ = 9.90 Å and $d_{i\,(2)}$ = 9.77 Å.The latter values are the interlayer van der Waals spacings filled with $SmCl_3$ and $ErCl_3$, respectively. So, the ... G- $SmCl_3$ -G- $ErCl_3$-G ... stacking sequence may be proposed on the basis of our XRD data.

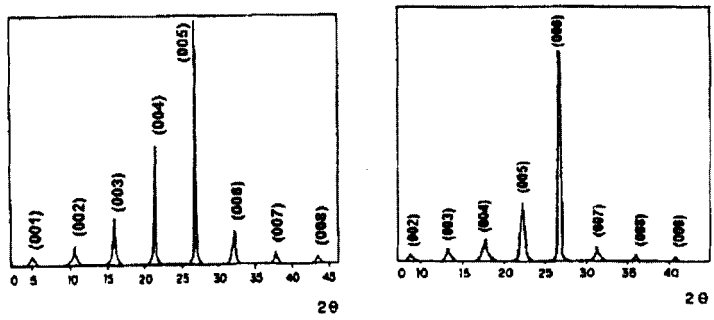

Figure 1. (a) The (00l) x-ray diffraction of a stage-3 $SmCl_3$ - GIC which is the precursor compound for the formation of (b) $SmCl_3$ -$ErCl_3$ -GBC.

Figure 2a shows electron diffraction pattern obtained from GBC sample at room temperature. As can be seen from Figure 2 b, $SmCl_3$ layers form a hexagonal structure with the (hk0) pattern of which is rotated by 42° with respect to the C layer pattern, while $ErCl_3$ yields a pattern that is rotated by 19°

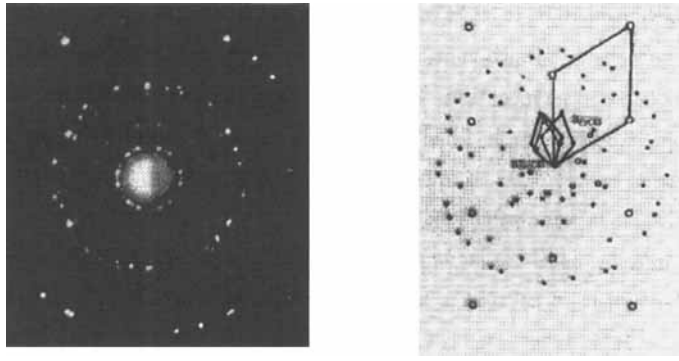

Figure 2. Electron diffraction pattern of (a) $SmCl_3$ - $ErCl_3$ -GBC, (b) orientation of $SmCl_3$ and $ErCl_3$ layers with respect to graphene layer.

and 42° with respect to the graphite pattern. Moreover, the parameter a_{SmCl3}=7.373 Å obtained is three times larger than the graphite parameter a_G =2.456 Å, forming a (3X3) commensurate structure. This unit cell parameter, a_{SmCl3} , is almost the same as that of the pristine $SmCl_3$, a_{SmCl3} =7.378 Å[11] . The parameters for the $ErCl_3$, a_{ErCl3} = 6.75 Å and b_{ErCl3} = 11.73 Å, as in case of the $CuCl_2$ layers,were obtained using as a model the twinning of the $ErCl_3$ layers.[15]

CONCLUSIONS

Graphite biintercalation compounds of $SmCl_3$ - $ErCl_3$ have been prepared via vapor phase method using a sequential intercalation taking in account that this reaction proceeds smoothly. The structural study has been realized from (00l) and (hk0) reflections by x-ray and electron diffractometries obtaining parameters of the host matrix and final compounds which provides a key to understanding of the structure with well defined stages.

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