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Structural Properties of Stages 2-3-$EuCl_3$ Graphite Intercalation Compounds

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The structural properties of second and third stage of graphite intercalation compounds graphite-$EuCl_3$ have been studied using x-ray diffraction. The c-axis repeat distances of second and third stage are 13.11 ± 0.07 Å and 16.48 ± 0.06 Å respectively. The $EuCl_3$ intercalate layer forms a three-layer sandwich of Cl-Eu-Cl with the structure to that of YCl_3 type.

Keywords: Graphite, Intercalation, $EuCl_3$

INTRODUCTION

Graphite intercalation compounds (GICs) are typical layered materials, in which intercalate and graphene layers are stacked periodically. Stage of GICs[1] is defined as the number of graphene layers between two nearest-neighbor layers of intercalated material. The structure of GICs depends strongly on stage and/or the kind of intercalated species. Most of the studies until now have dealt with transition-metal dichloride GICs such as $NiCl_2$, $CoCl_2$, and $MnCl_2$ GIC[2,3]. However, there have been very few systematic studies on structural properties of rare-earth metal trichloride GICs. Stumpp et al.[4] have studied the synthesis of GICs with all lanthanide trichlorides as intercalants. The pristine $EuCl_3$ has a hexagonal structure of UCl_3-*type with* three-dimensional arrangements of ions[5,6] with two Eu ions per unit cell

(space group $P6_3/m$)[7,8]. The unit cell parameters are a=7.3746 Å and c= 4.1323 Å[6]. Suzuki et al.[9] have synthesized a well defined stage-2 $EuCl_3$ GIC sample based on single-crystal kish graphite (SCKG). In this work, we use x-ray diffraction to study the structural properties of the stages 2 and 3 $EuCl_3$ GICs.

EXPERIMENTAL

We used a highly oriented pyrolytic graphite, a synthetic polycrystalline material with a crystallite size of about one micron within the graphene layers[10]. GICs containing $EuCl_3$ were prepared by the conventional vapor method in a one-zone sealed quartz ampoule in a chlorine atmosphere at pressures of 1.0 bar and 0.7 bar at ambient temperature. The intercalation was performed in these two ampoules at 500°C for 20 and 14 days, respectively. The GICs samples thus obtained were thoroughly washed with 10% hydrochloric acid solution and again with distilled water to remove excess $EuCl_3$, which remained unreacted on the surface of specimens. The c-axis repeat distances Ic were determined by (00l) reflections data obtained with a Philips x-ray diffractometer, which employed CuKα radiation at 35 KV, 20 mA. The sample compositions have been determined from weight uptake: $C_{23}EuCl_3$ and $C_{34}EuCl_3$ for stage 2 and 3, respectively.

Zero-level precession photographs recorded along [110] of graphene layers for stages 2 and 3, were carried out on a Buerger precession camera (STOE) using Zr-filtered MoKα radiation source to determine the structure of the intercalate layer.

RESULTS AND DISCUSSION

Figure 1 shows the recorded (00l) x-ray diffraction of the well crystallized stages 2 and 3 $EuCl_3$-GICs, which are indexed from (001) to (008) with

increasing 2θ. There is no evidence of diffraction neither from other stages nor from graphite in both compounds. The c-axis repeat distance, Ic, equals 13.11 ± 0.07 Å for the first compound and 16.48 ± 0.06 Å for the second one. From these values the C/$EuCl_3$/C sandwich thickness may be estimated: di=9.77 Å. Our Ic value for the stage 2 compound is a bit smaller than the one previously reported by Suzuki et al.[9] while for the stage 3 compound our value is slightly larger than that found by Stumpp et al. [4].

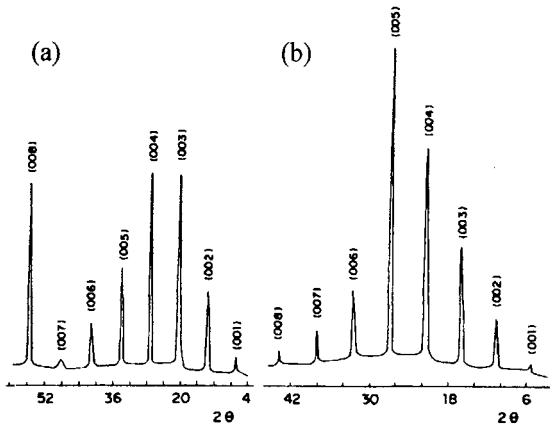

FIGURE 1 The (00l) diffraction patterns of GICs-$EuCl_3$: (a) stage 2, (b) stage 3.

The perfection degree of stage 2 and 3 $EuCl_3$-GICs has been characterized by comparing the full width at half maximun (FWHM) Δθ of the (00l) reflection peaks of the GICs with that of pristine highly-oriented pyrolytic graphite. In Fig. 2, we have plotted the FWHM for highly-oriented pyrolytic graphite, and for the stages 2 and 3 $EuCl_3$-GICs in units of Δ(Sin θ/λ) versus Sin θ/λ. This Fig. 2 reveals that the FWHM of the reflections for the intercalation compounds is not significantly different from those for the parent material, highly-oriented pyrolytic graphite. By comparing the results of the GICs 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.

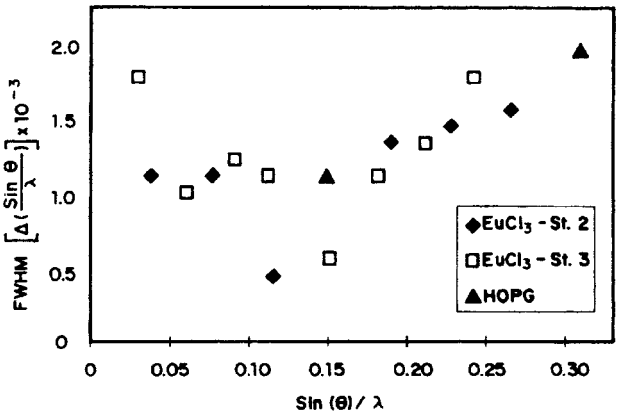

FIGURE 2 Plot of the full width at half maximum (FWHM) of the (00l) diffraction lines in units of $\Delta(\text{Sin } \theta/\lambda)$ versus Sin θ/λ for stages 2 and 3 $EuCl_3$-GICs and pristine graphite.

Precession photographs recorded about the common [110] axis of the graphene layers and the primitive intercalate cell give direct information on the intercalate's stacking sequence. In the case of the stage 2 compound, shown in Fig.3(a), the row 00l shows sharp reflections along $\bar{c}^*$ indicating high fidelity of staging. The same characteristic is observed for the stage 3 compound as shown in Fig.3 (b). Fig.3(c) and 3(d) present a schematic interpretation of the a-axis precession photographs shown respectively in Fig. 3(a) and 3(b). The average c-axis repeat distances are Ic = 13.10 ± 0.33 Å for stage 2 and 16.48 ± 0.06 Å for stage 3 compounds. Thus, we have determined the Ic values by two different methods and the results are practically the same.

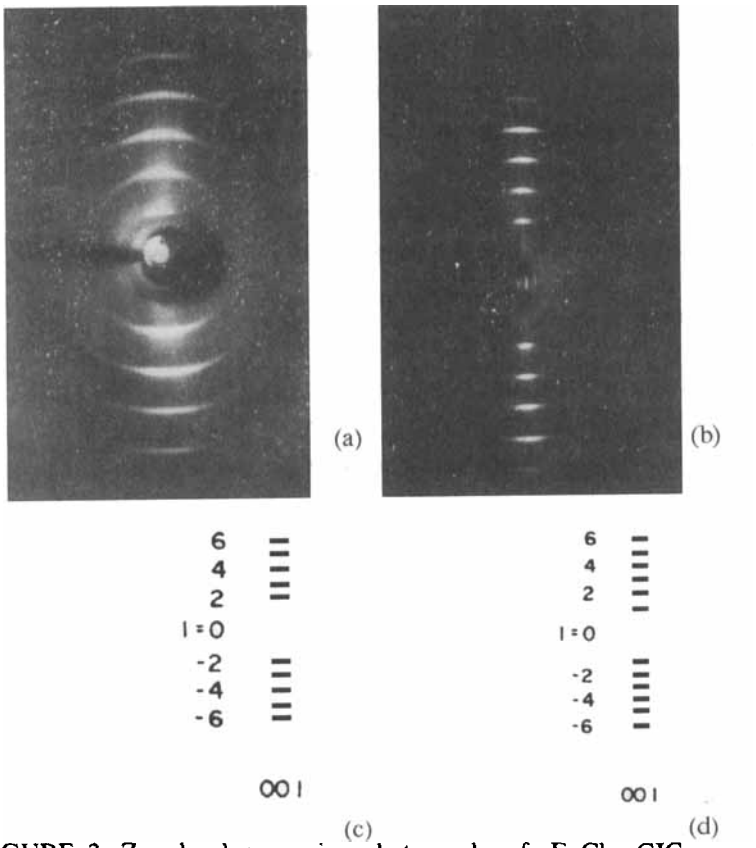

FIGURE 3. Zero-level precession photographs of $EuCl_3$- GIC recorded along [110] of carbon: (a) stage 2, (b) stage 3, (c) and (d) schematic interpretation of the stage 2 and 3 precession photographs.

CONCLUSIONS

Stage 2 and stage 3 $EuCl_3$-Graphite compounds have been prepared at 500°C via vapor phase. This synthesis technique allows formation of stage compounds, rich with metal trichlorides. We have obtained information about the c-axis repeat distance Ic between two intercalated layers, and determined the stage n, also the homogeneity of $EuCl_3$-GICs have been investigated via FWHM analysis. The structural properties have been

analysed from angular positions, linewidths, (00l) reflections determined by x-ray diffractometry and zero-level precession photographs techniques. The results concerning c-axis repeat distances Ic obtained from (00l) reflections in the zero-level photographs are in good agreement in both cases of stage 2 and stage 3 compounds. Further, these c-axis repeat distances indicate that the $EuCl_3$ intercalate layer structure changes from UCl_3-type with 3-dimensional ordering to that of YCl_3 type with 2-dimensional one.

References

[1.] M.S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).

[2.] G. Dresselhaus, J.T. Nicholls, and M.S. Dresselhaus, in Graphite Intercalation Compounds II, edited by H. Zabel and S.A. Solin (Springer-Verlag, Berlin, 1990).

[3.] M. Suzuki, CRC Crit. Rev. Solid State Mater. Sci. **16**, 237 (1990).

[4.] E. Stumpp, Mater. Sci. Eng. **31**, 53 (1977).

[5.] A.F. Wells, *Structural Inorganic Chemistry*, 3rd ed. (Oxford University Press, New York, 1962).

[6.] *Structural Chemistry of Layer-Type Phases*, edited by F. Levy (Reidel Dordrecht, 1976).

[7.] D.H. Templeton, C.H. Dauben, J. Am. Chem. Soc. **76**, 5237 (1954).

[8.] B. Morosin, J. Chem. Phys. **49**, 3007 (1968).

[9.] I.S. Suzuki, M. Suzuki, Ch.R. Burr, D.M. Hwang, E. Stumpp, Phys. Rev. B, **43**, 4295 (1991).

[10.] A.W. Moore, in Chemistry and Physic of Carbon, edited by P. L. Walker and P.A. Thrower Dekker, New York, 1973), vol. **11**, p. 69.