Novel Ternary Donor-Acceptor Heterostructure: Stage 1 $CoCl_2$-K-GIC

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Introduction

While ternary heterostructures of graphite intercalation compounds (GIC's) with a c-axis sequence CACBCAC (C = graphite basal plane; A,B = intercalate layers) have been synthesized with both A and B either of the donor type[1], or acceptor type[2-4], we report here the first successful preparation of a donor-acceptor-type heterostructure with a repeat sequence C-$CoCl_2$-C-K-C.

Experimental

The heterostructure GIC sample was prepared from a single crystal of Kish graphite (SCKG) by a sequential intercalation procedure. First a stage 2 $CoCl_2$-GIC was prepared in the usual manner[5]. The sample was then transferred under He atmosphere into a pyrex tube containing pure potassium. After evacuating, the glass tube was sealed off and placed in a vertical two-stage x-ray furnace. During the intercalation procedure the sample and alkali temperatures were kept constant at T_c=230°C and T_K=130°C. The formation of the heterostructure was monitored by x-ray scattering with MoK_α radiation, monochromated by a graphite (002) reflection.

Results and Discussion

Figure 1 shows a sequence of (00ℓ) reflections taken during the intercalation of K in stage 2 $CoCl_2$-GIC. The patterns of Fig. 1 are indexed with the notation nI(00ℓ), where n is the stage number, ℓ is the order of the c-axis reflection and I denotes the intercalate species: I = Co for $CoCl_2$-GIC, H for the $CoCl_2$-K-GIC heterostructure, and K for K-GIC. For 3 hours, we find two reflections corresponding to 2Co(003) and 2Co(004), which appear at 2θ=9.67° and 12.90° (Fig. 1a), yielding a repeat distance of 12.65Å. These Bragg peak intensities decrease with time, and a new reflection at 2θ=8.34° appears after 3 hours. This reflection corresponds to 1H(003) of the stage 1 C-$CoCl_2$-C-K-C heterostructure, and exhibits a repeat distance of $d_H=d_1+d_2$=14.65Å, where d_1=9.30Å is the C-$CoCl_2$-C package thickness and d_2=5.35Å is the C-K-C package thickness. After 6 hours, the 1H(005) reflection appears at 2θ=13.93°, and the heterostructure peaks grow gradually at the expense of the stage 2 $CoCl_2$-GIC peaks. After 4 more hours the intensity of the 1H(003) peak becomes larger than the 2 Co(004) peak, and finally after 45 hours we find reflections at 1H(003), 1H(005), 1H(006) and 2Co(004), which remain stable. The final product is therefore a mixture of a stage 1 C-$CoCl_2$-C-K-C heterstructure and a stage 2 $CoCl_2$-GIC with a ratio of roughly 1:1.

The coexistence of two different compounds may be understood within the framework of Dumas-Hérold domains. The potassium can only intercalate into the open galleries of the stage 2 $CoCl_2$-GIC, thereby forming a heterostructure, but can not proceed if $CoCl_2$ domains within the same gallery block further alkali migration. However, at higher K-vapor pressure, the $CoCl_2$ domains can be pushed together by the surrounding K-atoms, resulting in a two-component system of stage 1 K-GIC and stage 1 $CoCl_2$-GIC.

To confirm the stacking sequence of the stage 1 heterostructure, we calculated the x-ray structure factor for a C-K-C-$CoCl_2$-C sequence[6], which is in excellent agreement with the observed intensities.

A more detailed discussion of our results will be published in a forthcoming paper.

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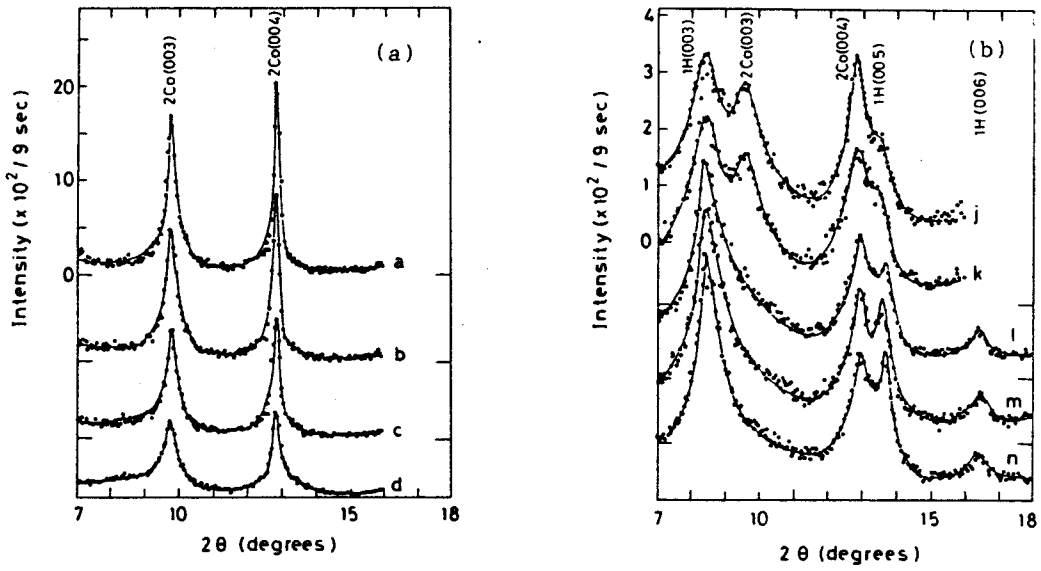

Fig. 1 Variation of (00ℓ) x-ray diffraction pattern with time during the sequential intercalation of potassium atoms into stage 2 $CoCl_2$-GIC. The reflections labeled 1H(00ℓ) and 2Co(00ℓ) correspond to stage 1 heterostructure $CoCl_2$-K-GIC and stage 2 $CoCl_2$-GIC respectively. Solid lines are a guide to the eye.
(a) a: 0.4 hours, b: 1.3, c: 2.2, d: 4.0
(b) j: 11.2, k: 12.2, l : 23.4, m: 29.3, n: 34.1

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