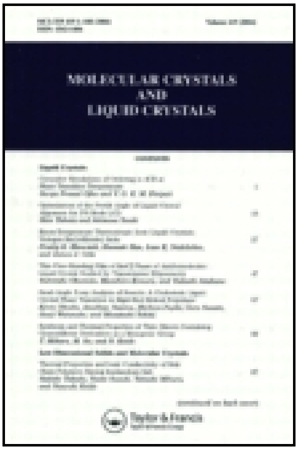

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Preparation and properties of graphite hexafluoroarsenates c x a s f 6 --preparation of stage-2 c 28 a s f 6 by the reaction of stage-1 c 14 a s f 6 with graphite

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PREPARATION AND PROPERTIES OF GRAPHITE HEXAFLUOROARSENATES C_xAsF_6—PREPARATION OF STAGE-2 $C_{28}AsF_6$ BY THE REACTION OF STAGE-1 $C_{14}AsF_6$ WITH GRAPHITE

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Following the reaction of graphite with O_2AsF_6 to produce a stage-1 graphite intercalation compound $C_{14}AsF_6$, a stage-2 $C_{28}AsF_6$ was obtained by the reaction of the stage-1 $C_{14}AsF_6$ with graphite at room temperature. This solid-phase reaction of $C_{14}AsF_6$ with graphite proceeds relatively fast and the reaction is completed within 24 h when an effective mixing is applied to the solid reactants.

Keywords: graphite intercalation compounds; reaction; XRD

INTRODUCTION

Graphite hexafluoroarsenates C_xAsF_6 [1–4] are graphite intercalation compounds (GICs), and are related to but different from C_xAsF_5 GICs [1,5] that are prepared by the reaction of graphite with AsF_5. C_xAsF_5 GICs have drawn much attention particularly because of their high electrical conductivities [6,7]. C_xAsF_6 GICs were found to have unique structures [2,3,8,9] and adsorption properties [10] owing to the nestling of the octahedral AsF_6^- species in the graphite sheets. Nestled compounds have the formula $C_{14n}AsF_6$, where n is the stage number. The in-plane structure of nestled $C_{14n}AsF_6$ is shown in Figure 1 [2]. The XRD patterns of stage-2 nestled $C_{28}AsF_6$ and un-nestled $C_{25}AsF_6$ have shown fine-structured 10 bands arising from two different random stacking sequences [8,9]. In $C_{28}AsF_6$, carbon layers across the intercalate layer are staggered owing to the nestling of AsF_6^-, and the overall stacking sequence is expressed by A|BC|AC|BA|C . . . , where | denotes the intercalate layer. On the other hand,

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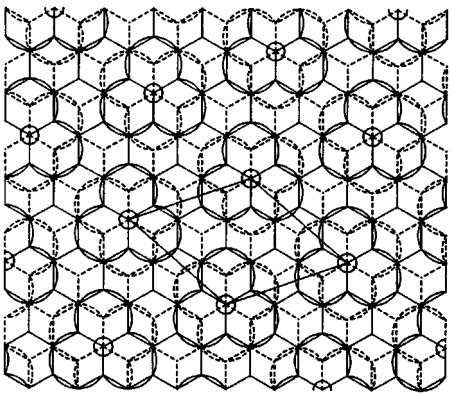

FIGURE 1 In-plane $\sqrt{7} \times \sqrt{7}$ arrangement of AsF_6^- for $C_{14}AsF_6$.

carbon layers across the intercalate layer in $C_{25}AsF_6$ are eclipsed and the stacking sequence is expressed by A|AB|BA|AC|C... In both cases, adjacent carbon layers without interleaved guest species are staggered. Stage-1 $C_{14}AsF_6$ was found to adsorb nitrogen up to the composition $C_{14n}AsF_6 \cdot ½N_2$ at 77 K owing to the low in-plane density of the guest species arising from the nestling of AsF_6^- [10].

$C_{14n}AsF_6$ GICs are readily prepared by the reaction of graphite with O_2AsF_6 at room temperature according to Eq. (1). As this reaction proceeds very quickly [10], it was presumed that higher-stage $C_{14n}AsF_6$ GICs could be obtained by the reaction of lower-stage $C_{14m}AsF_6$ GICs with graphite ($n > m$) according to Eq. (2). In this paper, preparation of stage-2 $C_{28}AsF_6$ by the reaction of stage-1 $C_{14}AsF_6$ with graphite at room temperature is described.

$$14nC + O_2AsF_6 \rightarrow C_{14n}AsF_6 + O_2 \qquad (1)$$

$$14(n - m)C + C_{14m}AsF_6 \rightarrow C_{14n}AsF_6 \qquad (2)$$

EXPERIMENTAL

AsF_5 was prepared by the reaction of fluorine with arsenic at 200°C. O_2AsF_6 was prepared by exposing a mixture of O_2, F_2 and AsF_5 to UV light. A T-shaped reaction cell, shown in Figure 2, with branches of a valve, and FEP and SUS316 tubes (o.d. 10 mm) was used for the preparation of stage-1 $C_{14}AsF_6$ and stage-2 $C_{28}AsF_6$. For the preparation of stage-1 $C_{14}AsF_6$ [10], O_2AsF_6 and SP-1 graphite powder (Union Carbide) were weighed in the SUS316 and FEP tubes, respectively, and after assembling the T-shaped

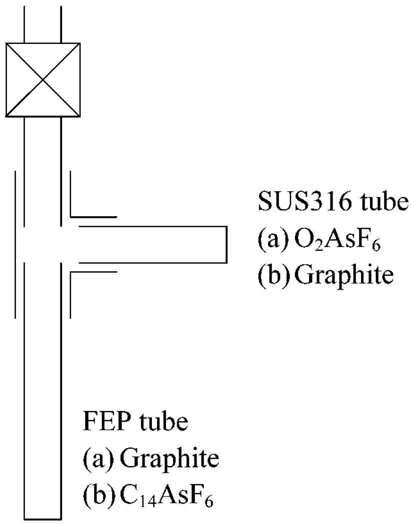

FIGURE 2 Schematic diagram of the T-shaped cell. (a) for the reaction of $14C + O_2AsF_6 \rightarrow C_{14}AsF_6 + O_2$. (b) for the reaction of $14C + C_{14}AsF_6 \rightarrow C_{28}AsF_6$.

cell, O_2AsF_6 was transferred onto the graphite, and the mixture was shaken by hitting the end of the elastic FEP tube by the blades of a small electric fan. For the preparation of stage-2 $C_{28}AsF_6$, the SUS316 tube was filled with graphite and the FEP tube with $C_{14}AsF_6$. Sample compositions were determined by gravimetry. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku Rint 2200 using CuKα radiation in the Debye-Scherrer geometry. Pyrolytic graphite was used as the counter monochromator. Powder samples were loaded into a 0.7 mm diameter thin-walled quartz capillary in a dry box under an Ar atmosphere.

RESULTS AND DISCUSSION

The reactions for the preparation of stage-1 (Eq. (3)) and stage-2 (Eq. (4)) were run for 10 min and 24 h, respectively.

$$14C + O_2AsF_6 \rightarrow C_{14}AsF_6 + O_2 \tag{3}$$

$$14C + C_{14}AsF_6 \rightarrow C_{28}AsF_6 \tag{4}$$

The compositions of the prepared stage-1 and stage-2 GICs were $C_{13.7}AsF_6$ and $C_{27.4}AsF_6$, respectively. Their XRD patterns are given in Figure 3. The c-axis repeat-distances, I_c, are 0.76 and 1.09 nm for $C_{13.7}AsF_6$ and

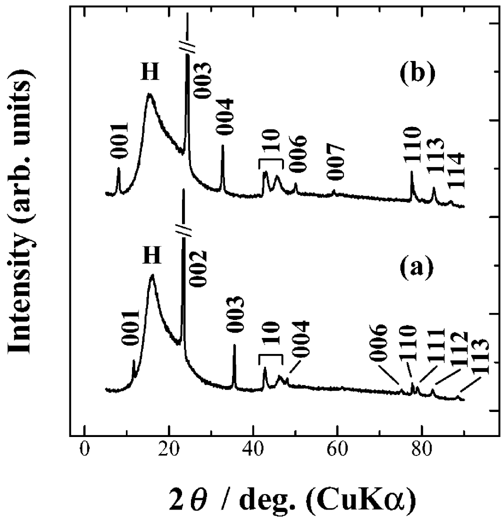

FIGURE 3 XRD-patterns for (a) nestled stage-1 $C_{13.7}AsF_6$ made by the reaction of graphite with O_2AsF_6, and (b) nestled stage-2 $C_{27.4}AsF_6$ made by the reaction of $C_{13.7}AsF_6$ with graphite.

$C_{27.4}AsF_6$, respectively. The XRD patterns show the typical features of those for nestled stage-1 and stage-2 $C_{14n}AsF_6$ [2,8,9]: (i) The small I_c values of 0.76 and 1.09 nm, which corresponds to the sandwich thickness of *ca.* 0.42 nm, (ii) the low-angle halo designated by H arising from the 100 reflection of the $\sqrt{7} \times \sqrt{7}$ in-plane superlattice shown in Figure 1, and (iii) the fine-structured 10 bands, arising from random stacking sequences A|B|C|A|C|B|A... for the stage-1 $C_{13.7}AsF_6$ and A|BC|AC|BA|C... for the stage-2 $C_{27.4}AsF_6$. The XRD pattern of the stage-2 $C_{27.4}AsF_6$ made by the reaction of $C_{13.7}AsF_6$ with graphite is essentially the same as that of the stage-2 $C_{28}AsF_6$ obtained by the reaction of graphite with O_2AsF_6 according to Eq. (5) [8,9].

$$28C + O_2AsF_6 \rightarrow C_{28}AsF_6 + O_2 \tag{5}$$

The results clearly indicate that a stage-2 $C_{28}AsF_6$ GIC was formed by the reaction of a stage-1 $C_{14}AsF_6$ GIC with graphite at room temperature according to Eq. (4). Although reaction (4) is a solid-phase reaction, it proceeds very easily at room temperature indicating a high mobility of AsF_6^- anions within the graphite gallery and across the crystallite interfaces.

The present reaction of $C_{14}AsF_6$ with graphite was run for 24 h to insure the completion of the reaction. Our preliminary results on the rate of the reactions via Eq. (2) indicate that this solid-phase reaction can be completed within an hour when an effective mixing is applied to the solid reactants. The results also indicated that higher-stage C_xAsF_6 GICs, with nestled or un-nestled AsF_6^-, can be obtained by the reaction of lower-stage C_yAsF_6 GICs with graphite.

CONCLUSIONS

A stage-2 $C_{28}AsF_6$ GIC was formed by the reaction of a stage-1 $C_{14}AsF_6$ GIC with graphite at room temperature. This solid-solid reaction of $C_{14}AsF_6$ with graphite proceeds relatively fast; the reaction is completed within 24 h. In general, higher-stage C_xAsF_6 GICs, with nestled or un-nestled AsF_6^-, can be obtained by the reaction of lower-stage C_yAsF_6 GICs with graphite.

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