LETTER TO THE EDITOR

SeCl$_4$ graphite intercalation compound: a precursor material for encapsulated selenium nanoparticles

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Abstract.   Selenium tetrachloride (SeCl$_4$) has been intercalated from the gas phase in the presence of chlorine gas into highly orientated pyrolytic graphite. A mixture of second- and third-stage SeCl$_4$ graphite intercalation compounds was obtained. X-ray diffraction measurements presented evidence that the b-axis of SeCl$_4$ is orientated perpendicular to the basal plane of the graphite. X-ray diffraction data gave evidence that SeCl$_4$ forms monolayers inside the host lattice. A selected-area electron diffraction study of the in-plane lattice showed ($h0l$) reflections of SeCl$_4$. The axis of the guest is commensurate with the a-axis of graphite. The lattice parameters for the intercalated species are nearly identical to those of pristine SeCl$_4$.

Incorporation of nanoparticles or nanorods into a carbon host lattice is of great interest as regards the basic science. A common route for preparing such materials is that of evaporating carbon and metals with an arc discharge in an inert atmosphere [1]. This technique leads mainly to nanometre-sized carbide particles inside the host material [1–3]. The intercalation of alkali metals can be directly performed from the gas phase [4]. A more unusual way is to use metal chloride graphite intercalation compounds (GICs) [5, 6] as precursor materials and to reduce these compounds by means of hydrogen gas [7]. This method has three advantages compared to the more common arc discharge technique:

(a) Due to the highly reductive atmosphere, it is possible to form metallic nanoparticles and nanorods of tantalum [7]. The conventional synthesis via the arc discharge method produces TaC nanoparticles and nanorods inside the host lattice [3].

(b) The precursor material has alternating graphene (IUPAC nomenclature for a single carbon layer with graphite structure) and metal chloride layers. Due the formation of monolayers of guests between two sheets of graphene, the reduced compounds contain real two-dimensional particles. EXAFS measurements on Ni GICs gave evidence of monolayers of Ni between the graphene sheets [8].

(c) The host material for intercalation reactions of metal chlorides can be either graphite flakes or carbon fibres [9]. Larger amounts of materials can be synthesized through reduction of metal chloride GICs.

The direct incorporation of selenium into carbon by a CVD process failed [10]. However, a wide variety of metal chlorides (e.g. NbCl$_5$ [11], TaCl$_5$ [12], CuCl$_2$ [13], NiCl$_2$ [14],

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BiCl$_3$ [15]) can be intercalated into a carbon host. Such metal chloride GICs are classical two-dimensional electrical conductors. The lattice parameters of intercalated and pristine metal chlorides are not necessarily identical [16]. Selenium chloride GICs were not described in the literature. They could act as precursors for preparing selenium nanoparticles inside a carbon host lattice. In the present work we characterize a SeCl$_4$ GIC.

Selenium tetrachloride (SeCl$_4$) was mixed with highly oriented pyrolytic graphite (HOPG) from Advanced Ceramics Corporation, USA, in a glass ampoule. After evacuation, chlorine gas was condensed in it (under 450 mbar at room temperature) and the ampoule was sealed. The mixture was heated for four days at 190 °C. The success of the intercalation was demonstrated by x-ray diffraction (XRD) and the in-plane superlattice was estimated by selected-area electron diffraction (SAED).
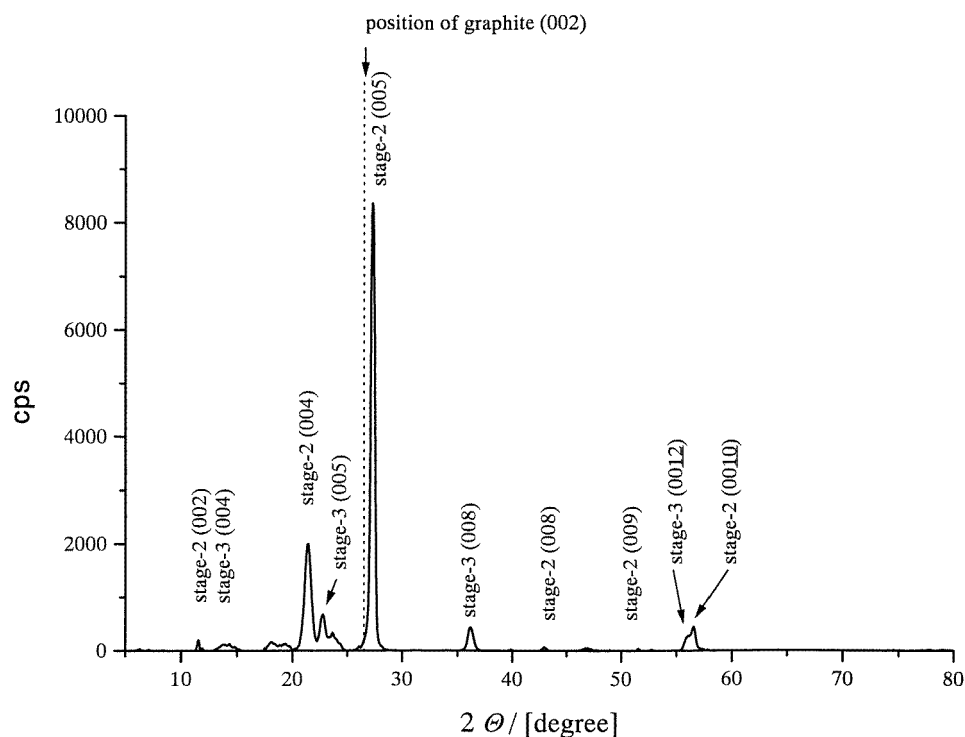

Figure 1. The XRD pattern of SeCl$_4$ GIC; Cu K$\langle\alpha\rangle$ radiation, 40 kV accelerating voltage, 100 mA anode current. A mixture of a second-stage SeCl$_4$ GIC ($I_c = 1623$ pm $\pm$ 55 pm) and a third-stage SeCl$_4$ GIC ($I_c = 1962$ pm $\pm$ 18 pm) was obtained; unreacted graphite was not observed. The shape of the reflections, the shifts, the intensity ratios and the few missing reflections indicate a highly disordered sample [18].

Pristine SeCl$_4$ crystallizes in a monoclinic crystal system with the following lattice parameters [17]: $a = 1649$ pm, $b = 975$ pm, $c = 1490$ pm, $\beta = 117.0°$. Figure 1 shows the XRD pattern of a SeCl$_4$ GIC; the pattern shows a disordered sample, a common result for layered materials such as GICs [18], clays and micas. Disordered GICs can show broad and sharp (00l) reflections for one identity period; weaker reflections can be totally absent; some reflections of one identity period can be shifted [18]. A mixture of a second-stage SeCl$_4$ GIC ($I_c = 1623$ pm $\pm$ 55 pm) and a third-stage SeCl$_4$ GIC ($I_c = 1962$ pm $\pm$ 18 pm) was formed. Through the knowledge of the lattice parameters of pristine SeCl$_4$, it can be determined that
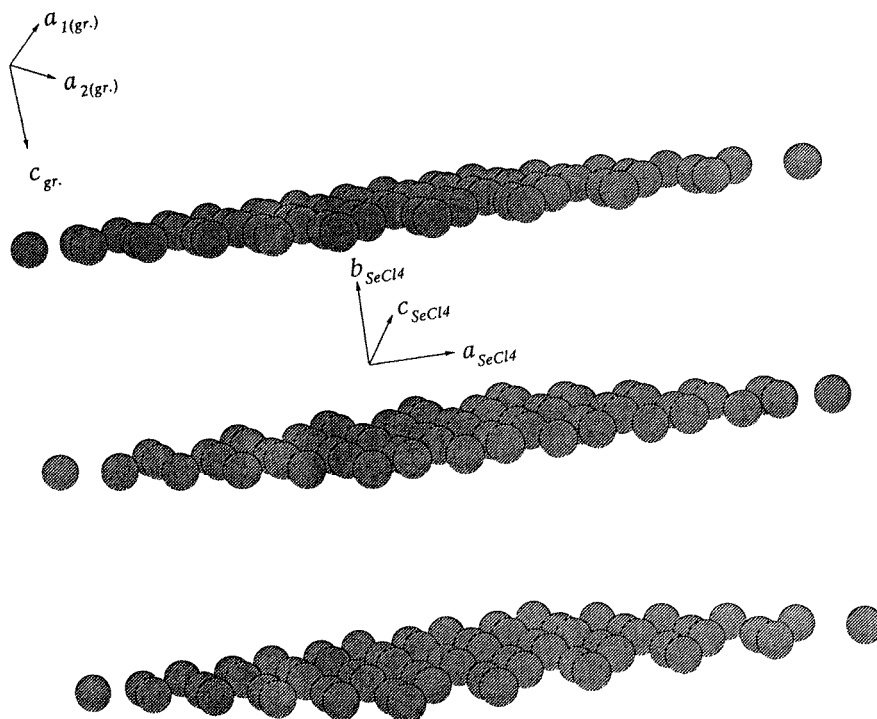
Figure 2. A schematic sketch of a graphite host lattice with the axes at the top and the relative orientation of the guest lattice between the sheets of graphene. The b-axis of the guest lattice acts as a spacer for the host lattice (c_{gr} is parallel to b_{SeCl_4}).

the guests are orientated with their b-axes perpendicular to the basal plane of the graphite (figure 2). Due to this orientation of the guests, the small axis of the guest crystal acts as a spacer for the host lattice:

$$I_{\text{guest}} = I_{c(\text{second-stage GIC})} - I_{c(\text{graphite})} = 1623 \text{ pm} - 670 \text{ pm} = 953 \text{ pm} \approx I_{b(\text{SeCl}_4)}.$$

The standard deviation of the identity period is large due the high degree of disordering in the sample, ± 55 pm. Taking this standard deviation into consideration, the estimated value of 953 pm $\pm$ 55 pm fits very well with the b-axis of SeCl$_4$ ($b = 975$ pm). The interlayer spacing provides evidence that a monolayer of SeCl$_4$ is incorporated between two graphene sheets.

Figure 3 shows the in-plane diffraction pattern estimated from SAED. From the XRD results it is now evident that this pattern shows ($h0l$) reflections. The SAED image was obtained at a magnification of 300.000. It is complex, and shows domain twinning of two mirrored lattices (represented by domains A and B). Domain twinning is a common feature and was observed in other GICs by means of SAED [19, 20].

The orientations of the $a^*_{\text{SeCl}_4}$- and $c^*_{\text{SeCl}_4}$-axes for both domains are indicated in figure 3. The angle between $a^*_{\text{SeCl}_4}$ and $c^*_{\text{SeCl}_4}$ is $\beta^* = 180° - \beta = 63° \pm 0.5°$, which is the same as that in the pristine compound. Although the a^*_{gr}- and $c^*_{\text{SeCl}_4}$-axes coincide, due to the different crystal systems (hexagonal: $a_{\text{gr}} = h \times d_{(h00)\text{gr}}$; monoclinic: $c_{\text{SeCl}_4} = (l \times d_{(00l)\text{SeCl}_4})/\sin\beta$), the reflections do not superimpose. The two different sets of reflections can be clearly distinguished. The c_{SeCl_4}-axis shows a close relationship with the underlying graphene lattice ($a_{\text{gr}} = 245.4$ pm): $c_{\text{SeCl}_4} = 6 \times a_{\text{gr}} = 1533$ pm $\pm$ 48 pm (pristine SeCl$_4$: $c = 1490$ pm); this axis coincides with the graphite axis. A slight misfit between the host lattice and the a_{SeCl_4}-axis
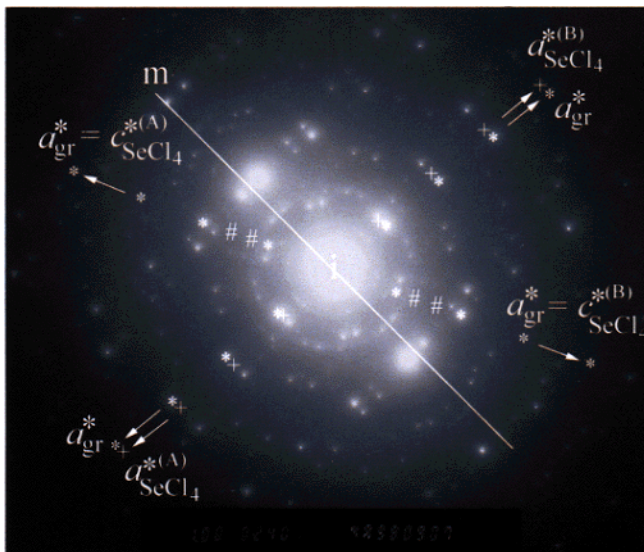
Figure 3. The SAED pattern of the in-plane lattice; 300 kV accelerating voltage, 1 m camera length. The pattern can be interpreted as a superposition of two reciprocal lattices, due to the twinning of domain A and domain B. The SAED image shows $(h0l)_{SeCl_4}$ reflections; the $a^*_{SeCl_4}$- and $c^*_{SeCl_4}$-axes of the guest lattice are indicated, as well as the axis of the graphite lattice (a^*_{gr}). The reciprocal angle between the two axes of the SeCl$_4$ lattice is $\beta^* = 180° - \beta = 63° \pm 0.5°$, identical to that in pristine SeCl$_4$. A mirror plane (m) exists between the two lattices; the centre acts as an inversion point (i). The following symbols are used: $*$ indicates $(h00)_{gr}$ reflections; # indicates $(00l)_{SeCl_4}$ reflections; + indicates $(h00)_{SeCl_4}$ reflections.

was detected, as regards their lattice constants: $a_{SeCl_4} = 1633$ pm ± 32 pm $\approx 7 \times a_{gr}$ (pristine SeCl$_4$: 1652 pm), and as regards their slightly different angles ($\beta^*_{SeCl_4} = 63° \pm 0.5°$, $\beta^*_{gr} = 60°$).

Selenium tetrachloride was successful intercalated into graphite. The lattice parameters of the guest particles show close relationships with the lattice parameters of the pristine metal chloride. Monolayers of SeCl$_4$ are incorporated between sheets of graphene. Because these monolayers are present between the graphene sheets, SeCl$_4$ GIC can act as a precursor material for preparation of two-dimensional selenium nanoparticles inside the carbon host lattice. Nanoparticles in the quantum-size regime can show uncommon magnetization due a quantum-size effect [21]. Two-dimensional selenium nanoparticles will be prepared from this SeCl$_4$ GIC precursor.

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