Se atoms and Se$_6$ molecules as guests in Se-carbons - prepared by reduction of a SeCl$_4$-graphite precursor

Se atoms and Se_6 molecules as guests in Se–carbons—prepared by reduction of a $SeCl_4$–graphite precursor

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Abstract. A $SeCl_4$–graphite intercalation compound precursor was reduced by a solution of lithium diphenylide in tetrahydrofuran at room temperature. X-ray diffraction measurements gave two distinguishable stages. One stage represented a Se-atom intercalation the other represented an intercalation of Se_6 molecules. The in-plane diffraction patterns were estimated by selected-area electron diffraction, the existence of two different guest species (atoms and molecules) could be proved. The Se_6-molecule phase shows an incommensurate lattice with regard to the host lattice, but they are in the same orientation. The lattice parameter of intercalated Se_6 is $a_{Se6-guest} = 1158 \pm 36$ pm, $c_{Se6-guest} = 483 \pm 38$ pm, which fits with the lattice parameter of non-intercalated Se_6 molecules. Se atom domains show a $2 \times a_{graphite}$ superlattice with respect to the host lattice, which is a commensurate superstructure. Raman scattering data showed the occurrence of an acceptor-type graphite intercalation compound. Three different types of spectra could be obtained, two kinds of spectra consists of doublets at 1588 cm^{-1} and 1608 cm^{-1}, with different intensity ratios. These two kinds of spectra are certainly attributed to Se-atom domains, with different stages. A third type of spectrum show bands at higher wavenumbers (1646 cm^{-1} and 1653 cm^{-1}). These bands are probably correlated to Se_6-molecule domains. They represent maybe very early stages of nanoparticle formation.

1. Introduction

Graphite intercalation compounds with elemental selenium or selenium compounds as guests have not achieved high attention until now [1–5]. The Sharp Corporation in Japan has synthesized Se–carbon films by a chemical vapour deposition (CVD) process [2, 3]. According to these patents, the Se–carbons show an anomalous, high c-axis thermoelectric power, $S = 150$–900 μV K^{-1} [2]. Also, the thermoelectric figure of merit is unique [2]:

$$Z = S^2 \sigma / \kappa \tag{1}$$

where σ and κ are, respectively, the c-axis electrical and thermal conductivities. Selenium–graphite intercalation compounds (GICs) show experimental values of $ZT > 30$, that is more than an order of magnitude larger than that of any previously known thermoelectrical material [2].

An ordered, stage-3, Se–GIC showed the composition $C_{24}Se$, identity period in the c-direction (I_c) of 1218 pm [4]. Raman scattering showed a homogeneous sample, with peaks

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at 1357.78 cm^{-1}, 1590.04 cm^{-1} and 1616.75 cm^{-1} [4]. The electrical conductivity was two orders of magnitude greater than pristine carbon film [4]. Their largest *c*-axis thermoelectric power was 45 μV K^{-1} [4]. This is a high value, but still much lower than the values reported by the Sharp Corporation [2].

In the present work we discuss a second possibility for the preparation of Se–carbon materials. Pre-existing layered carbon materials can be intercalated by a wide variety of metal chlorides (e.g. $NiCl_2$ [6], $NbCl_5$ [7], $TaCl_5$ [8], $HgCl_2$ [9], $BiCl_3$ [10] and $PdCl_2$ [11]) or by alkali metals [12]. Host materials can be either thin films, graphite flakes or carbon fibre. Unfortunately, from thermodynamical reasons the direct incorporation of metals into a pre-existing carbon lattice is not possible, with the exception of alkali metals.

The intercalation of $SeCl_4$ into graphite was successful and details of the characterization of the $SeCl_4$–GIC were published elsewhere [5]. Metal chloride GICs can be reduced by hydrogen gas at higher temperatures [13–17]. X-ray diffraction (XRD) [14] and electron diffraction [15] investigations on such reduced $TaCl_5$–GICs show that due to the high reductive atmosphere the metallic tantalum particles can be built, although tantalum is an excellent carbide former.

To avoid damaging the host lattice by partial exfoliation, the reduction was performed by a solution of lithium diphenylide in tetrahydrofuran (THF) at room temperature [18, 19]. The samples were investigated by XRD and by selected-area electron diffraction (SAED) to determine the intercalated species and the stages. Raman scattering was used to discuss the interaction between the host and the guest.

2. Experimental details

The starting material was a stage-3 $SeCl_4$–GIC [5]. Highly oriented pyrolytic graphite (HOPG), type ZYA from Advanced Ceramics, Cleveland, OH was used as the host material. The intercalation compound was stored for one week at room temperature in a solution of lithium diphenylide in THF. After this period of time the sample was filtered and washed with THF in an ultrasonic bath, to remove the LiCl formed. Before the measurements were taken the sample was cleaved along the basal plane. An Hitachi H-9000 transmission electron microscope with a LaB_6 cathode was used, the microscope was operated at 300 kV. The in-plane diffraction patterns were observed by SAED, which gave (*hk*0) reflections.

A Rigaku Rotaflex diffractometer with θ–2θ scan, equipped with a Cu anode ($\lambda = 154.178$ pm) was used and operated at a 40 kV accelerating voltage and a 150 mA anode current. The step size was 0.02° and the measured range $2\theta = 3$–80° (printed out in the range $2\theta = 5$–80°). The samples were fixed with their basal planes parallel to the sample holder. Due to this orientation and the measurement geometry is it only possible to observe (00*l*) reflections.

The Raman measurements were performed by a T64000 Raman microscope from Jobin Yvon. The measurement conditions were: laser power 20 mW ($\lambda = 514.5$ nm), and sample collection time 30 s (every spectra is the average of 10 scans at 30 s collection time). All investigations were performed at room temperature in air, with a lateral resolution of 1 μm. The reference material was pristine HOPG.
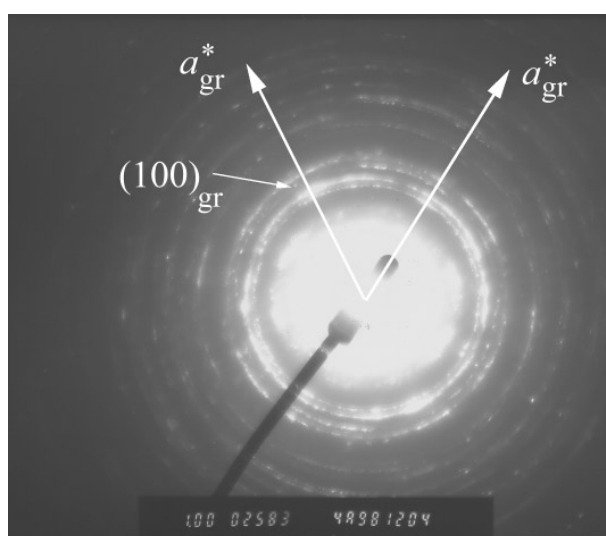
3. Results and discussion

3.1. Transmission electron microscopy and SAED

A transmission electron microscopy (TEM) study showed no occurrence of nanometre-sized particles intercalated into the carbon host lattice, which were formed by treatment with
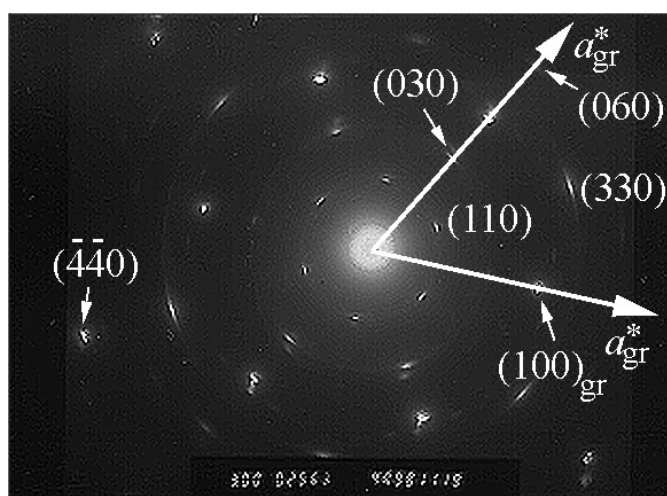
(*a*)

(*b*)

Figure 1. (*a*) A SAED image of a single domain, camera length 3 m, magnification 300.000×. This image shows a hexagonal guest lattice additional to the hexagonal host lattice. The pattern shows a single Se$_6$-molecule domain ($a_{guest} = 1158 \pm 36$ pm), see text. (*b*) SAED image, camera length 1 m, magnification 300.000×. This image represents an area with Se-atom domains ($a_{guest} = 2 \times a_{graphite} = 491 \pm 15$ pm). The reciprocal axes (a_{gr}^*) of graphite are shown, the subscript 'gr' denotes graphite reflections.

hydrogen gas at higher temperatures [14]. Domains could not be observed by TEM. However, SAED patterns give evidence that the host is still intercalated. Randomly two distinguishable in-plane patterns (figures 1(*a*) and (*b*)) can be observed. One pattern consists of well resolved diffraction spots, a second hexagonal pattern that is additional to the hexagonal carbon host lattice can be detected (figure 1(*a*)).

In general, two possibilities exist for the intercalated selenium: (i) the intercalation of selenium atoms, similar to intercalated Fe atoms [19] or (ii) one of the numerous selenium

allotropes is formed [20–25]. The observed (figure 1(a)) hexagonal in-plane lattice fits only with the a-axis of the rhombohedral Se_6 allotrope (experimentally observed is: 1158 ± 36 pm; and pristine Se_6 [21] is 1136 pm). This is an incommensurate superlattice (1158 pm $=$ $4.72 \times a_{graphite}$) but an oriental relationship to the host lattice exist. From $a_{guest} = 1158$ pm and $a_{graphite} = 245.4$ pm the stoichiometry of a third stage can be calculated. The unit cell of a third stage Se_6–GIC contains 144 C atoms and 4 Se atoms, it can be described as $C_{36}Se$.

The second type of SAED pattern could be most frequently collected, it consists of diffraction rings that are additional to the hexagonal carbon lattice (figure 1(b)). These diffraction data do not fit with any reported selenium allotrope, also these reflections are not attributed to pristine $SeCl_4$ or LiCl. The SAED pattern (figure 1(b)) can be hexagonal indexed. A ($2 \times a_{graphite}$) superlattice in respect to the carbon host lattice ($a_{graphite} = 245.4$ pm) was observed. The same superlattice exists in KC_{24} [12]. An earlier work gave the composition SeC_{24} of Se–carbon with Se-atoms as the guest [4].

3.2. XRD

Figure 2 shows the XRD pattern. Some fringes are broad whilst others are narrow, one part of the (00l) reflections is unsymmetrical. Most of the observed reflections can be indexed into two different series, but reflections for LiCl could be not observed. One of the reflection series shows $I_c = 1433 \pm 38$ pm, the second shows $I_c = 1214 \pm 22$ pm. The last identity period is in good agreement with a stage-3 Se–GIC described earlier by another group [4], they found $I_c = 1218$ pm. In general, the identity period in the c-direction of a GIC can be described by the formula

$$c_{(n)} = (n - 1)c_{(1/2)} + c_{(1)} = (n - 1)c_{(1/2)} + c_{(1/2)} + c_{guest} \qquad (2)$$

where n is the stage index, $c_{(1)}$ is the identity period of a stage-1 intercalation compound $=$ $c_{(1/2)} + c_{guest}$ and $c_{(1/2)}$ is the distance between two adjacent graphene (IUPAC nomenclature of a single carbon layer with graphitic character) sheets it is half of the identity period in the c-direction of pristine graphite $= 335$ pm. From this easy relation is it now evident that the second observed identity period ($I_c = 1433$ pm) can not be attributed to a Se-atom GIC.

It should be proven whether $I_c = 1433$ pm fits with an intercalated selenium allotrope. The SAED pattern (figure 1(a)) makes it probable that Se_6 is the guest in some domains. According to the literature $c_{Se6} = 443$ pm [19]. Equation (3) shows that the second observed phase ($I_c = 1433$ pm) fits with a stage-3 Se_6–GIC:

$$c_{stage\text{-}3\ Se6-GIC, theor.} = 2 * 335 \text{ pm} + 335 \text{ pm} + 443 \text{ pm} = 1488 \text{ pm}. \qquad (3)$$

The XRD pattern (figure 2) shows a phase with an identity period in the c-direction of 1433 ± 38 pm. The slight misfit to the theoretical value (1488 pm) can be explained by a one-dimensional disordered sample.

The following are some general remarks on the XRD pattern (figure 2). It is well known that GICs are organized in domains, their existence is experimentally proven [26]. Such domains are generally randomly distributed in the host lattice. Due to the random distribution of two or more different domains with distinguishable identity periods, the sample can be described as one-dimensional disordered. Such systems show the observed features in their XRD pattern [27, 28].

3.3. Raman microscopic investigations

The same sample was transferred to a Raman microscope and investigated in air. More than 70 point analyses were collected. Raman spectroscopy showed an inhomogeneous sample.
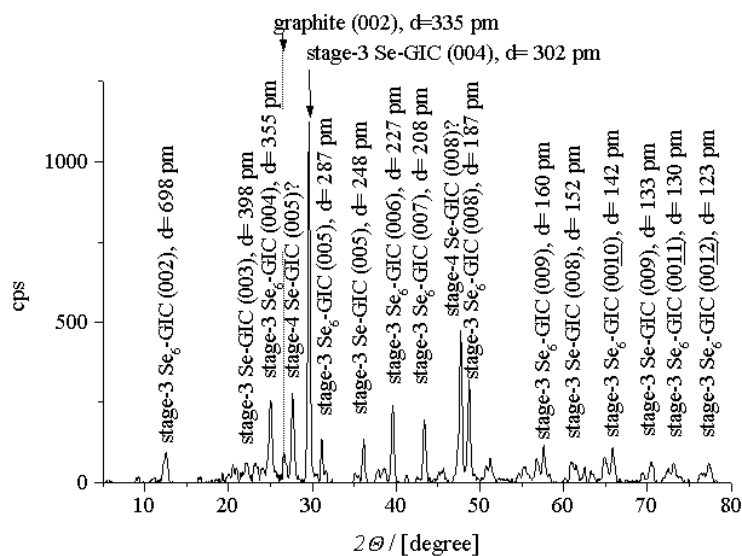
Figure 2. The XRD pattern with a Cu anode ($\lambda = 154.178$ pm) (cps on the ordinate denotes counts s^{-1}). At least two distinguishable identity periods can be found. One period represents a stage-3 Se-atom GIC ($I_c = 1214 \pm 22$ pm), as previously described [4]. The second phase consists of Se$_6$-molecule domains, such stage-3 Se$_6$–GICs shows an identity period $I_c = 1433 \pm 38$ pm, see text for details.

Three different spectra could be observed to be randomly distributed across the basal plane. Spectra with a doublet at 1588 cm^{-1} and 1608 cm^{-1} (figure 3(*a*)) were most frequently observed; all spectra of this type are dominated by the upper band. Such domains are always larger than 1 μm, this was also the lateral resolution by Raman microscopy. Such spectra are certainly attributed to Se-atom domains, because the SAED patterns for this phase were most frequently collected. Spectra, as shown in figure 3(*b*), are not so frequently measured. These spectra are characterized by different pronounced high-shifts for the upper bands (the maximum position was 1653 cm^{-1}). Most of these spectra consist of three or four Raman peaks. According to the literature [29], this is not possible for a common GIC. It can be explained by the random distribution of the different domains. If the lateral domain size is smaller than 1 μm, two or more neighboured domains will be collected at the same time. Distinguishable domains with different shifted Raman modes could generate spectra with three or more bands. Highly upshifted bands, which may represent Se$_6$ intercalation compounds, were not observed in Se-carbon films prepared by CVD. A third, but very rarely observed, spectrum is shown in figure 3(*c*). It is basically identical to the spectra shown in figure 3(*a*), but the doublet shows a different intensity ratio. The spectra in figure 3(*c*) are dominated by lower bands. According to the literature [29], such spectra (figures 3(*a*) and 3(*c*)) belong to different stages of intercalation. In fact, the XRD pattern shows a stage-4 Se–GIC as a minor phase, which correlates with the measured frequency by Raman spectroscopy.

Third stage SeCl$_4$–GICs show Raman spectra with doublets at 1586 cm^{-1} and 1606 cm^{-1}, in which the lower band is always the strongest band in the spectrum [30]. So all of the Raman spectra collected from the Se–carbon samples are distinguishable from the SeCl$_4$–GIC precursor. However, some of the recorded spectra (figure 3(*b*)) are extremely upshifted, such shifts were not observed in other GICs [29–31]. Their occurrence may be attributed to Se$_6$ domains.
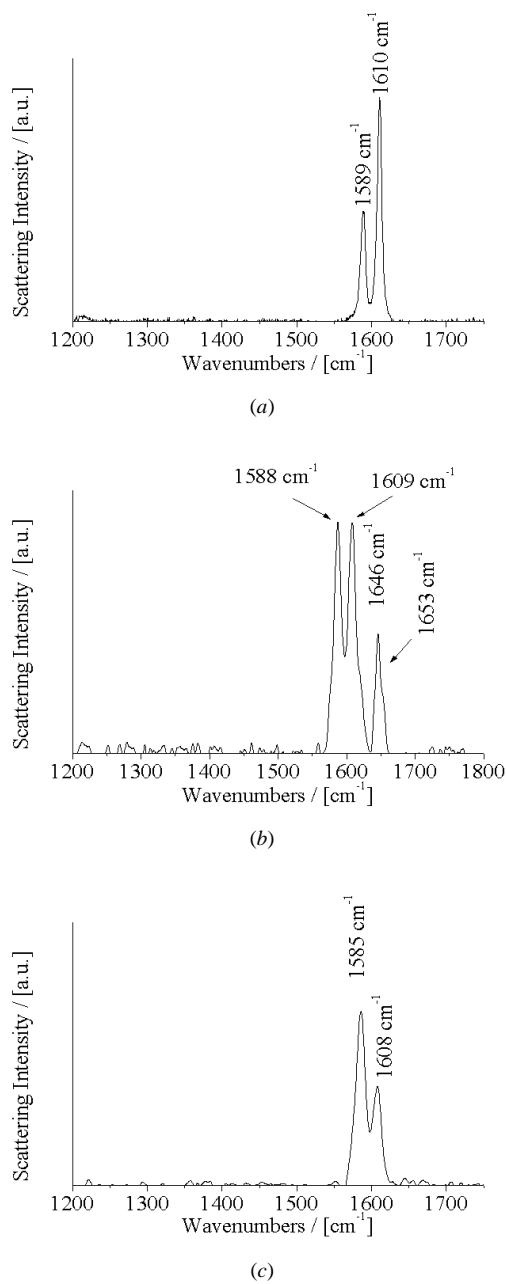
Figure 3. (*a*) Raman spectra, stage-3 Se-atom GIC, (*b*) some Raman spectra show very upshifted bands: such spectra could be attributed to Se_6-molecule GICs and (*c*) Raman spectra very similar to the spectrum shown in figure 3(*a*), but with a different intensity ratio, most probably a stage-4 Se-atom GIC, see text.

No reason for the high upshift (unusual charge transfer interaction) can be given until now.

Se_6–GICs may represent the early stages of nanoparticle formation. Shuvage *et al* [19] found that Ni monolayers can appear as ordinary GICs. Large Pd nanoparticles prepared from a $PdCl_2$–GIC precursor by hydrogen reduction can only be described as Pd–graphite (no Raman

shift comparable to graphite). However, Pd nanoparticles with an average size of 7 nm and retaining a host–guest interaction can be prepared by the reduction of a PdCl$_2$–GIC precursor by lithium diphenylide in THF at room temperature, to give a Pd–GIC [32].

4. Conclusion

Se–carbon can, for the first time, be prepared by the reduction of a SeCl$_4$–GIC precursor by lithium diphenylide in THF at room temperature. The sample was an inhomogeneous product. Bulk XRD data showed a one-dimensional disordered sample. Randomly spaced Se-atom and Se$_6$-molecule domains were observed by SAED and Raman microscopy. Se-atom domains occurred most frequently, their domain sizes were several micrometres in the lateral direction. Se$_6$-domains were observed less frequently. Some of these domains are smaller than 1 μm in the lateral dimension.

Se-atom GICs show a commensurate ($2 \times a_{graphite}$) superstructure, the identity period (third stage) in the c-direction was 1211 ± 18 pm. Such domains showed Raman spectra with a doublet at 1588 ± 1 cm^{-1} and 1608 ± 2 cm^{-1}.

Se$_6$-molecule GICs show an incommensurate superlattice, but with an orientation relationship to the guest lattice. The lattice parameters for the intercalated Se$_6$ is $a_{guest} = 1158 \pm 36$ pm and $c_{guest} = 483 \pm 38$ pm, which fits with the lattice parameters of pristine Se$_6$ ($a = 1136$ pm, $c = 443$ pm [21]). The identity period in the c-direction of a third stage Se$_6$–GIC was estimated to be 1433 ± 38 pm. High-shifted Raman bands (up to 1653 cm^{-1}) are probably due to such domains. The reasons for the very pronounced upshift can not be given until now. They may represent very early stages of nanoparticle formation.

We have no opportunity to perform transport measurements to compare our sample, with those described in the literature, which show quite different Seebeck coefficients [2, 4]. However, this paper shows that different phases exist in one sample and the Raman shift is distinguishable between the domains. Such differences in the charge transfer of the Se–carbon could possibly explain the different observed Seebeck coefficients in CVD-grown Se–carbon films between the different films reported in the literature [2, 4]. Until now, it was not possible to prepare with, high-fidelity, a single phase.

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