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Gold-potassium sheets intercalated into graphite: Chemistry and structure of a first stage ternary compound

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ABSTRACT

A ternary graphite-potassium-gold compound $K_{1.3}Au_{1.5}C_4$ was synthesized by immersing a pyrographite platelet in various potassium metal-based molten alloys. Numerous reaction parameters were investigated (duration, temperature, composition of the alloy) in order to determine the stability conditions of the ternary compound. Using complementary X-ray diffraction and ion beam analysis experiments, the optimal conditions of preparation of this compound have been pointed out. The composition and homogeneity were evidenced by ion beam analysis and X-ray diffraction allowed to determine its repeat distance (1311 pm) and its c-axis stacking sequence (K-Au-Au-Au-K). The 2D unit cell observed thanks to Transmission Electron Microscopy (TEM) is square with a = 1192 pm, no-commensurate with that of graphite.

1. Introduction

The anisotropic 2D feature of graphite is so considerable that it is henceforth quite easy to prepare some isolated graphene planes. This opportunity is one cause of the large current development of the chemistry and physics of graphene [1–5]. This anisotropy confers also on graphite the ability to be an excellent host material for intercalation reactions.

The intercalation of the metallic elements is simple in the case of the most electropositive ones as the alkali metals (Li, K, Rb, Cs) [6,7] and several other metals as Ca, Sr, Ba, Eu, Yb [8–10] leading to a single-layered intercalated sheet.

In order to intercalate other metals, it is particularly recommended to use an alkali metal as an intercalation vector [11–13]. The reaction is carried out between bulk graphite and a binary liquid alkali metal-based alloy. The alkali element firstly generates a pre-opening of the van der Waals's nanospaces and also plays the role of a flux, which allows the decreasing of the reaction temperature, thanks to the precocious liquefaction of the alloy. The lowering of this temperature is indeed essential because a low reaction temperature allows avoiding the destruction of the graphene planes (therefore the carbon atoms have to remain sp^2 hybridized throughout the reaction).

Numerous binary and ternary graphite intercalation compounds (GIC) have been synthesized using this effective way. For instance, Hg, Tl, Bi, Sb, As [11,14], that are weakly electropositive elements, have been intercalated using alloys prepared from a heavy alkali metal. In these cases, both elements intercalate simultaneously leading to ternary phases for which the intercalated sheets are poly-layered; it is interesting to underline that a lot of them can exhibit superconducting properties [15,16].

Gold is an odd metal, because it possesses the highest electronegativity (Pauling's scale) among the whole of the metals. On the other hand, it precedes exactly mercury and thallium (elements able to be intercalated) in the sixth period of the periodic table. Because of these specific features, we have tried to intercalate gold into graphite using potassium as an intercalation vector. The results of the numerous experiments carried out in this aim have been largely fruitful, since a stable novel ternary graphite-potassium-gold compound has been discovered then isolated [17]. An extensive study of this ternary phase constitutes the topic of this paper.

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2. Experiment

2.1. Synthesis

Synthesis details have been published in a previous paper [17] and is not detailed here. In summary, the preparation of the reactive alloy and the sample recovery must be performed in a glove box under very pure argon atmosphere. Gold and potassium are precisely weighed and introduced in a stainless steel reactor which is heated in order to obtain a homogeneous liquid. Next the highly oriented pyrographite platelet of $8 \times 2 \times 0.5\ mm^3$ is introduced in this molten potassium-gold alloy. In order to facilitate the recovery of the sample after reaction, the platelets are maintained in alloys thanks to a tungsten sample-holder. The reactor is then tightly closed and the intercalation reaction is carried out outside the glove box at a given temperature for a precise reaction time. At the end of the reaction, the reactor is opened and heated in the glove box and the sample is extracted from the liquid alloy. The excess of alloy is eliminated using a coupled furnace-centrifuge device and the sample is placed under argon into a glass capillary for its first characterization by X-ray measurements.

2.2. Sample characterization

The samples are characterized by X-ray diffraction, electron microscopy and ion beam analysis. As the reactions have been performed using highly oriented pyrographite samples, it is possible to observe 00*l* and *hk*0 reflections separately. In this aim, X-ray diffraction experiments were realized with a Bruker D8 diffractometer using molybdenum Kα1 radiation ($\lambda K_{\alpha 1} = 70.926$ pm) with a Lynxeye detector, and the sample is placed so that the incident beam is parallel to the *ab* planes. The quantitative analysis of the 00*l* reflections allows the determination of the *c*-axis experimental electronic density profile. The rotating crystal method was performed with a Bruker Apex II Duo diffractometer provided with a four circles goniometer (KAPPA) equipped with a molybdenum high power source (beam size 100 μm), a graphite monochromator and a CCD detector. This measurement needs a very small and very thin micrometric sample, precisely oriented.

Scanning Electron Microscopy (SEM) observations were performed using a HITACHI S4800 FEG equipped with an Energy Dispersive X-ray (EDX) spectrometer. A platelet of sample is sticked on the sample-holder using a carbon scotch. After a very brief air exposure, the sample is transferred into the SEM apparatus. Then, several areas of different samples have been studied and Energy Dispersive X-ray Spectroscopy (EDXS) measurements were mainly used to determine the K/Au atomic ratio of the intercalated species.

The Transmission Electron Microscopy experiments (TEM) were carried out with a FEI Tecnai G2 F20 S-Twin microscope equipped with an air-tight sample-holder cooled with liquid nitrogen. The interest of this sample-holder is twofold. Firstly, the sample does not undergo any exposure to air since its preparation is realized in a glove box until its introduction into the TEM column. On the other hand, it can be cooled down to the temperature of liquid nitrogen, avoiding the migration of the intercalated species under the electron beam.

For nuclear microprobe analyses (NMA), we used a proton beam of 3050 keV and a particle detector at 170° from incident beam axis. In this study, elastic scattering (denoted RBS for Rutherford Back Scattering) between the target and the ion beam is the only interaction needed for elementary titration of carbon, potassium and gold. A single spectrum includes the whole information for the whole elements. For carbon and potassium, the choice of $^1H^+$ beam instead of the often used ^4He beam enables to benefit from enhanced scattering on carbon and potassium with so-called non-Rutherford cross-sections [18,19]. For gold, there is no deviation from Rutherford scattering. So, scattering cross-sections used for spectra simulation do not need to rely on experimental cross-sections. The beam was scanned on a sample surface of $200 \times 200\ \mu m^2$, with lateral resolution at a few micrometers level (beam size $3.5 \times 4\ \mu m^2$). Such an analysis is a good indicator for probing the homogeneity of the GIC [20].

Sample compositions are determined by adjustment between experimental and simulated spectra. The core of the simulation code SimNRA [21] is based on the main features of the interaction of the ions with matter such as nuclear interaction kinematics and related cross-sections data, electronic stopping power, and so on … It assumes a layered target composed of a stacking of several slices, each slice having a given composition and a given thickness. A former simulation considering a single thick layer enables a rough adjustment of the bulk composition. Then, thin layers are added at the top of the target definition and, thanks to the depth resolution of RBS, their composition and thickness adjusted to reflect surface composition modifications. The simulated spectrum is so made up of the superimposed contributions of all the interactions, with each isotope of each element in each sublayer of the defined solid.

3. Results and discussion

3.1. Synthesis optimization

It is well known that for the synthesis of GIC using an alkali metal-based molten alloy, the latter composition and the reaction time and temperature are the main parameters. Indeed, a small variation of each of them is able to significantly modify the composition and structure of the obtained sample. Numerous experiments were carried out varying the composition range of the potassium-gold alloy (from 5 to 50 gold at.%), the reaction temperature and the reaction time in order to determine the best synthesis conditions to obtain graphite intercalation compounds containing gold. The nature of the reaction products depending on the temperature and the composition of the reactive alloy is summarized Fig. 1.

In all cases, intercalation into graphite occurs, leading to either a pure compound or a mixture of phases. The pure potassium-gold GIC denoted γ-phase [22] belonging to the first stage is observed over a wide range of temperature and composition of the reactive alloy. We have successfully isolated this compound in an alloy containing 34 to 40 gold at.% for a temperature included between 420 at 650 °C and the optimized synthesis parameters correspond to a 34 gold at.% alloy heated at 440 °C for 8 days (as detailed in Ref. [17]).

3.2. Determination of the elementary composition of the γ-GIC

In the case of the intercalation of heavy elements (i.e. potassium and gold) into graphite, the first step for the determination of the chemical composition consists in carrying out experiments with a scanning electron microscope coupled to an EDX spectrometer. By this way, the K/Au atomic ratio has been evaluated close to 0.87. By combination of this data with the quantitative analysis of the 00*l* X-ray diffraction pattern, a first formula corresponding to $K_{1.3}Au_{1.5}C_4$ has been proposed for the γ-compound [17]. However, the exact determination of the formula of the compound by an appropriate technique remains a hard task to undertake.

Elementary chemical analyses, thermogravimetric techniques or electron microprobe instrument cannot lead to a reliable determination of the chemical composition. In order to avoid this difficulty, ion beam analyses were performed, regarding that the used nuclear microprobe instrument constitutes a powerful tool for the analysis of such GIC [20,23].