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Heavy alkali metal-arsenic alloy-based graphite intercalation compounds: Investigation of their synthesis and of their physical properties

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ABSTRACT

Heavy alkali metal-arsenic alloys intercalate easily into graphite, leading to the formation of a new family of ternary graphite intercalation compounds (GICs). Pure phases formulated as MAsxC4s (M = K, Rb or Cs; s = stage; $x \leq 1$) have been synthesized at the laboratory. This article aims to expose all physical measurements performed on these intercalation compounds to get an idea about their electronic properties.

Electrical conductivity measurements have been performed both parallel and perpendicular to the basal planes, between 4.2 and 295 K. Room temperature resistivity values lie between 16 and 35 μΩ cm and the anisotropic resistivity takes a value of an order of magnitude of 10^4. Dynamic magnetic susceptibility measurements, carried out at low temperature on some phases, showed that they do not exhibit superconducting transition up to 1.3 K. Raman spectroscopy investigation, which is a useful tool to study the electronic and the chemical stability of GICs, highlighted a significant up-shift of the G-band of the carbon intra-layer vibration frequency, compared to the pure graphite vibration mode. Undoubtedly, this is related to the electronic charge transfer established between graphite layers and intercalated species.

1. Introduction

Graphite contains layers of carbon atoms. Each layer is arranged in hexagons, with an atom at each nexus. The network of carbon atoms, connected by the shortest bonds, looks like a honeycomb. This two-dimensional single plane is called “graphene”. The layers slide over each other easily because there are only weak forces between them, making graphite a slippery and a lubricant material. Therefore, many substances called intercalates, can enter into the gallery of the graphite to form graphite intercalation compounds (GICs).

This study is a continuation of previous similar studies regarding the intercalation of metallic alloys into graphite, for which some conditions seem absolutely necessary in order to allow the intercalation; This study is a continuance of previous similar research work concerning the intercalation of metallic alloys in graphite, for which some conditions seem absolutely necessary to allow such processes to occur.

One of the components of the alloy must be a heavy alkali metal (strongly electropositive), and the other one should be an element whose electronegativity is close to 2

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(in the Pauling's scale). The components of the alloy have to be miscible in the liquid phase for all the compositions. By this way, numerous metallic alloys have been successfully intercalated into graphite leading to new ternary graphite intercalation compounds; K–Hg, Rb–Hg [1–3], K–Tl, Rb–Tl [4–6], K–Bi, Rb–Bi, Cs–Bi [7,8], Cs–Sb [9] and K–As, Rb–As, Cs–As [10–14]. In general, these compounds share a common chemical formula that can be written as MM'_xC_{4s}, where M = alkali metal, M′ = second element, s = stage and $x \leq 1$. Thereafter, other binary alloys have been successfully invested such as alkali metal-hydrides [15,16], alkali metal sulfides [17,18] or newly discovered compounds resulting from the action on graphite of Li alloyed with alkaline-earth or with rare earth elements [19–21], or simply from the action of the heavy alkali-metal-gold alloys on a graphite sample [22,23].

2. Chemical description of the alkali-arsenic-based intercalation compounds

As in the case of bismuth or antimony-alkali systems, novel GIC compounds are obtained when a heavy alkali metal-arsenic alloy is made using a platelet sample of HOPG pyrographite, in a sealed glass tube under vacuum. The reaction mixture is heated to the melting temperature of the reactant alloy. The procedure of the intercalation reaction into graphite of species associating an alkali metal and a second weakly electro-negative one is described in detail in the following references [10–13]. Several phases were obtained by varying the stoichiometry of the reactant alloy, temperature and reaction time. They are different in color and thickness. Some of them have a spectacular metallic luster. They have been named α, β, γ and δ according to their respective inter-planar distance (di), which is the thickness of the intercalated graphite interval. Numerous phases have been observed during the experiment and a good number of them have been successfully isolated. They are tabulated in Table 1 with the corresponding chemical operating conditions allowing their formation and the data related to their chemical identity. The latter are shown schematically in Fig. 2a. The stage (s) indicates the number of carbon layers between two successive intercalated intervals of graphite. To control the nature of the phase (or phases) present within the sample after reaction, systematic recording of the (00*l*) X-ray reflections by means of a classical θ/2θ diffractometer equipped with a K_α molybdenum source is routinely used. During this operation, the sample must be suitably oriented with respect to the incident X-ray beam.A set of the typical X-ray (00*l*) patterns recorded during this work demonstrating the high homogeneity and purity of the synthesized phases are shown in Fig. 1. This preliminary chemical characterization of the sample is subsequently followed by an examination by means of a scanning electron microscope. Fig. 3 reproduces some examples of the X-ray EDS (Energy dispersive spectroscopy) analysis performed showing the clearly simultaneous insertion within graphic intervals of the two alloying constituents.

The major feature of these ternary GICs is the significant amount of the alloy intercalated into the host material. Structural analysis showed that the intercalated species are arranged as a multi-layer stacking model along the *c*-axis of graphite. An example of this configuration is illustrated in Fig. 2b. This three-layer stacking mode is the most common structure of this family of ternary compounds [[24,25]]. Otherwise, the in-plane structural studies based on the analysis of the (*hk*0) reflection family have evidenced that the metallic sheets intercalated into these lamellar materials are perfectly ordered in parallel to the grapheme layers, by adopting various two-dimensional structures, with geometries that can commensurate or not, with respect to the graphite unit cell [26].

3. Physical properties

This paper focuses primarily on the most important results obtained from all the physical investigations, carried out on these ternary compounds. Electrical resistivity, dynamic magnetic susceptibility and Raman spectroscopy experiments have been performed on samples prepared as single phases. It is important to note that similar previous studies performed on related donor-graphite systems have shown that they are metallic parallel to the direction of graphene layers and highly anisotropic. It was also reported that some of them become superconducting at a low temperature [27,28].

Table 1
The heavy alkali metal-arsenic–graphite intercalation compounds of stage 1 and 2 (isolated and synthesized in a reproducible way). The synthesis conditions are indicated for each ternary compound.

System	Stage and type	Reactant alloy at. As%	Temperature reaction (°C)	Duration reaction	Repeat distance *Ic* (pm)	Interplanar distance di (pm)	Chemical formula
G–K–AS phases	1 α	20	630	30 min	950	950	$KA_{s0,60}C_4$
	2 α	32	630	6 h	1285	950	$KA_{s0,60}C_8$
	1 β	38	570	1 h	988	988	$K_{1,38}AsC_4$
	2 δ	38	570	5 h	1380	1045	$KAsC_8$
G–Rb–AS phases	1 α	32	640	10 min	987	987	$RbAs_{0,6}C_4$
	2 β	40	610	72 h	1375	1040	$Rb_{0,8}AsC_8$
	2 γ	32	640	17 h	1400	1065	$RbAsC_8$
G–Cs–AS phases	1 α	32	650	20 min	1050	1050	$CsAs_{0,6}C_4$
	2 β	38	640	120 h	1415	1080	$Cs_{0,8}AsC_8$
	1 γ	55	610	24 h	1110	1110	$CsAsC_4$
	2 γ	50	620–630	48 h	1445	1110	$CsAsC_8$

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