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Synthesis, structure and electrical behavior of the heavy alkali metal-arsenic alloys based graphite intercalation compounds

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ABSTRACT

Intercalation reaction occurs when an excess of a liquid heavy alkali metal-arsenic alloy is contacted with a graphite sample under vacuum. This leads to the formation of several novel ternary phases. X-ray structural analysis was conducted to determine how intercalated metallic alloy is arranged between the graphitic layers. The results have shown that these phases are composed of poly6layered sheets alternately stacked with carbon layers along the c-axis. In addition, these layers are perfectly ordered with respect to the adjacent carbon planes. Two-dimensional super-lattices have been recorded and analyzed. The electrical conductivity has been studied both parallel and perpendicular to the basal planes, between 4.2 and 295 K. The basal-plane behavior is metallic, but the c-axis resistivity displays very high resistivity. The room temperature anisotropy is of the order of 10^4, which increases for some phases, by more than one order of magnitude at 4.2 K.

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1. Introduction

Over the past few years, graphite intercalation compounds (GIC) have become the subject of intense study in many laboratories worldwide for numerous reasons. These materials have stimulated the interest of physicists and chemists. The most exhaustive comprehensive review of this field is found in Ref. [1]. The compounds of the present work are the result of continued development in the field of ternary GICs. The beginning was with mercury and thallium in the form of binary alloys with potassium and rubidium [2–6] and with alkali-metal hydrides [7–9]. After having successfully intercalated into graphite both bismuth [10,11] and antimony [12,13], when alloyed with a heavy alkali metal, it seemed of interest to continue along these lines with the elements which follow in the periodic classification; arsenic that is miscible in any proportion with potassium, rubidium and cesium. We found that a number of these alloys could be successfully intercalated into graphite, giving birth to a considerable range of new ternary GICs [14–16]. In what follows, we first present a brief summary of the preparation conditions and compositional and X-ray parameters of the resulting compounds. This is followed by the results of an electrical conductivity study both parallel and perpendicular to the basal planes.

2. Experimental

The reaction is carried out as follows: the pristine graphite (HOPG sample or single crystal) and the alloy are put together in a glass tube and sealed under vacuum. The tube is subsequently heated until the alloy melts, and the reaction occurs between graphite and the liquid alloy. It is necessary to use a large excess of alloy in order to avoid any variation of its composition during the intercalation. After the reaction, the sample is carefully cleaned in order to remove any excess alloy that adheres to its surface. Afterword, it is subjected to X-ray examination for (001) reflections. The intercalation reaction is clearly expressed by a spectacular change of the sample graphite color. As the reaction is performed on pyrographite samples, it is possible to study separately (00l) and (hk0) reflections. For this, X-ray diffraction experiments were realized using a classical Bruker diffractometer using Molybdenum $K\alpha_1$ radiation ($\lambda K_{\alpha 1} = 70.926$ pm) with a Lynxeye detector in its θ-2θ configuration. For the c-axis investigation, the sample is placed so that the incident beam is parallel to the a-b planes. After acquisition, a quantitative analysis of the 00l reflections can be used to determine the stacking sequence of the intercalated atomic species. For the in-plane structure investigation, hk0 reflections were recorded and analyzed. The sample is now placed so that the X-ray incident beam is perpendicular to the a-b plane direction of sample. For more details and more resolution of the reciprocal lattice, X-ray

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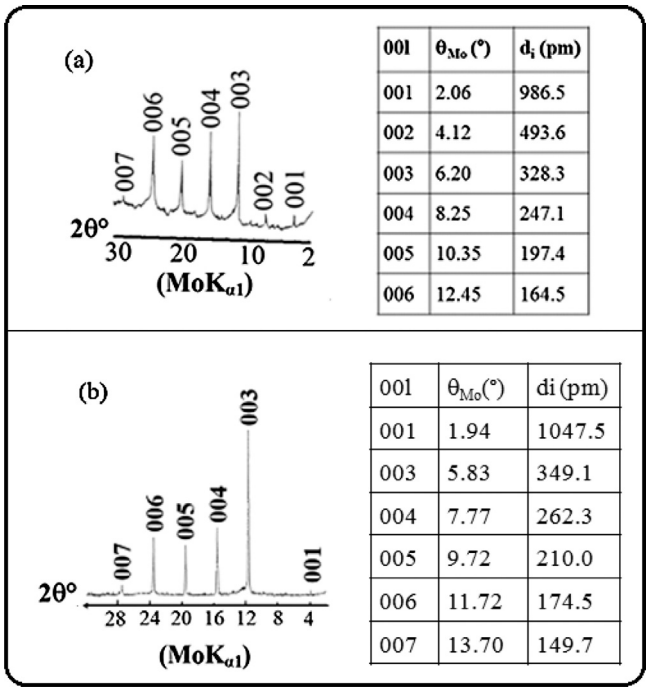
photographic techniques have been invested, namely; the monochromatic Laue method equipped with a powerful X-ray synchrotron radiation (L.U.R.E), precession camera fitted with a Molybdenum $K\alpha_1$ X-ray source and micro-diffraction technique thanks to the Transmission Electron Microscope (MET). Scanning Electron Microscopy (SEM) observations were performed using a HITACHI 54800 FEG equipped with an Energy Dispersive X-ray (EDX) spectrometer. In this case, the platelet of the sample is fixed on the sample holder using a carbon scotch. Various sample regions are scanned and M/As atomic ratio is collected. Electrical measurements were performed both parallel and perpendicular to the graphitic planes. All HOPG samples required for electrical conductivity were cut out of a single cylindrical graphite with σ_a and σ_c being equal to $(1.2 \pm 0.2) \times 10^4$ and $(7.7 \pm 0.5)\ \Omega^{-1}\,cm^{-1}$, respectively. They were disk shaped with the dimensions; diameter $\varphi = 4$ mm and a thickness ranging between 0.2 and 0.5 mm. The in-plane electrical resistivity has been measured using a conductive contactless method developed by McRae et al. in the laboratory [17]. This technique is well suitable for air-sensible samples, since any sample transfer to atmosphere is necessary. Indeed, the sample is placed under vacuum into a sealed glass tube, which allows carrying out in-situ measures. On the other hand, c-axis resistivity measurements were performed using a direct four-contact point probe method, also developed in the laboratory [18].

3. Results and discussion

3.1. Investigation in the graphite-heavy alkali metal-arsenic graphite systems

By controlling both the composition of the binary alloy and the reaction temperature, it is possible to synthesize a whole series of ternary GICs formulated MAsxC4s, where s = stage and $0 < x \leq 1$. For all three heavy alkali metals, two or more varieties of the phases exist, designated α, β, γ distinguished by their inter-planar distance di. The new synthesized compounds are summarized in Table 1. The stage number varies from 1 to 4 and the interplanar distance from 950 to 1110 pm. The Chemical formulas indicated in this table were provided by the elemental chemical analysis using the atomic absorption spectroscopy. The samples conditioned in glass capillary after reaction, are systematically characterized by X-ray diffraction experiments. The examination of the X-ray patterns allows the determination of the nature of the phase(s) present in the sample, the repeat distance (distance between two successive intercalated graphitic intervals) and the stage number (number of carbon layers comprising between two successive intercalated galleries). In fact, the stage value, sample dilatation and repeat distance of a GIC are linked by the following equation; $s = I_C/[335 \times (1 + \Delta e/e)]$, where 335 value designates the graphitic interval distance (in pm) of the graphite before intercalation, Ic is the repeat distance, and $\Delta e/e$ is the c-axis relative dilatation of the sample measured before its conditioning in the capillary tube. Fig. 1 illustrates the typical 00l X-ray patterns recorded. As it can be seen, they reveal the formation of GICs without any reflection of pristine graphite, emphasizing the high chemical activity of the reactive alloys towards graphite. After the reaction, the sample also undergoes microscopic examination by the use of the SEM-EDS microscope in order to investigate the composition of the sample at the nanoscale. The typical EDS (Energy Dispersive Spectroscopy) spectrum analysis recorded is given in Fig. 2. Clearly, it shows that the sample contains a large amount of arsenic and cesium.



001	θ_{Mo} (°)	d_i (pm)
001	2.06	986.5
002	4.12	493.6
003	6.20	328.3
004	8.25	247.1
005	10.35	197.4
006	12.45	164.5

001	θ_{Mo}(°)	di (pm)
001	1.94	1047.5
003	5.83	349.1
004	7.77	262.3
005	9.72	210.0
006	11.72	174.5
007	13.70	149.7

Fig. 1. (00l) X-ray diffraction pattern of: (a) the first stage α-G-Rb-As phase with $I_C = 987$ pm, (b) the first stage α-G-Cs-As phase with $I_C = 1045$ pm ($\lambda\ Mo_{K\alpha 1} = 70.923$ pm).

Table 1
The heavy alkali metal-arsenic-graphite ternary compounds. 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 mn	950	950	$KA_{s0,60}C_4$
	2 α	32	630	6 h	1285	950	–
	3 α	30	630	24 h	1620	950	$KA_{s0,60}C_{12}$
	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 mn	987	987	$RbAs_{0,6}C_4$
	2 β	40	610	72 h	1375	1040	$Rb_{0.8}AsC_8$
	3 β	53	630	240 h	1710	1040	–
	2 γ	32	640	17 h	1400	1065	$RbAsC_8$
G-Cs-AS phases	1 α	32	650	20 mn	1050	1050	$CsAs_{0,6}C_4$
	2 β	38	640	120 h	1415	1080	$Cs_{0.8}AsC_8$
	4 β	59	600	144 h	2080	1075	–
	1 γ	55	610	24 h	1110	1110	CsAsC4
	2 γ	50	620–630	48 h	1445	1110	CsAsC8

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