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Co-intercalation into graphite of lithium, potassium and barium using LiCl-KCl molten salt

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Abstract

The synthesis of a novel first stage GIC containing simultaneously lithium, potassium and barium through a solid-liquid reaction by molten salts method is described. Such a route has been largely developed in our laboratory for intercalation of metals into graphite. The interplanar distance of this quaternary compound reaches 950 pm and exhibits poly-layered intercalated sheets defined by X-ray measurements. The $\text{Li}_{0.2}\text{K}_{0.75}\text{Ba}_{0.6}\text{C}_6$ chemical formula of the compound is determined by ion beam analysis and this GIC is remarkably homogeneous. This GIC is the first poly-layered one containing barium.

Keywords

Graphite intercalation compound, molten salts, 2D materials, alkaline-earth metal, XRD, nuclear microprobe

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1. Introduction

Huge efforts are currently undertaken in order to prepare novel two-dimensional carbon-based materials such as graphene, graphenic materials or MXene. Another class of materials should not be forgotten, *i.e.* Graphite Intercalation Compounds (GIC) obtained by redox topotactic reactions between graphite and numerous chemical species [1]. During the last decade, abundant works have been focused on the intercalation of alkaline-earth metals into low-dimensional carbon-based materials. Different carbon-based materials have been tested, however graphite still constitutes an interesting 2D host versus these metals regarding the simple structure of graphite together with the complexity of bonding in GIC.

The first metal-GIC were synthesized from reaction of graphite with alkali metals in vapor phase. Lithium and heavy alkali metals, being strongly electropositive and having high vapor pressures, can be easily intercalated into graphite leading to binary first-stage GIC (meaning that all the van der Waals vacancies are occupied) using this synthesis route [2,3]. However, in the case of alkaline-earth metals, only a partial intercalation is obtained, as it is observed for example with strontium and barium [4]. In order to synthesize first stage alkaline-earth metal GIC intercalated into the bulk, other methods have been developed in our group, based on the use of molten reactive media. One of them, a solid-liquid method, consists in immersing graphite into a [lithium/alkaline-earth metal] molten alloy, for which lithium plays the role of an intercalation vector allowing the successive intercalation of the other metal [5]. By this method, for instance, high quality CaC_6 samples have been prepared which exhibit a superconducting behavior under a critical temperature of 11.5 K [6]. However, the Li-based molten alloy method presents limitations as some metals remain impossible to intercalate into the bulk [7]. That is why in the recent years, we have developed a new solid-liquid GIC synthesis route, involving reactions between graphite and a molten salts mixture [8]. Using such a way, we previously evidenced that the first step is the dissolution of the added metal by redox reaction with lithium chloride, leading to the formation of metallic lithium. The latter reacts with graphite allowing its intercalation. Then, thanks to the pre-opening of the van der Waals galleries by lithium, a second reaction occurs between Li-based GIC and the metallic elements contained in the reactive mixture. The alkaline-earth metal expels the intercalated lithium and replaces it in the graphitic galleries.

Following this mechanism, it has been possible to prepare SrC_6 , BaC_6 , EuC_6 as bulk compounds [9–12].

In the past years, several studies have pointed out the possibility to prepare superconducting calcium-based ternary GIC either by partial substitution of Ca with K or Sr [13,14] or by co-intercalation of lithium and calcium [15]. In the first case, the substitution induces a decrease in the critical temperature depending on the chemical composition, and a possible modification of the crystal structure of CaC_6 .

In the second case, the co-intercalation of lithium, using the molten lithium-based alloys method, led to ternary lithium-calcium-GIC [15]. Such GIC contain poly-layered intercalated sheets and $\text{Li}_3\text{Ca}_2\text{C}_6$ exhibits superconducting properties with a critical temperature very close to that of CaC_6 [16]. This latter route deserved to be explored with barium. Indeed, the study of the graphite-lithium-barium system only led to binary compounds, especially BaC_6 [17].

In the first stage compound which is superconducting under the very low critical temperature of 0.065 K [18], a substitution of barium atoms by K or Li would be interesting for studying the structure and composition of the so-obtained co-intercalation compound. Moreover, even if the critical temperature of a possible superconducting phase may not be promising, the effect of such a substitution is still intriguing.

Considering the aforementioned data, we present here the first results revealing the ability to prepare a novel barium-based graphite intercalation compound containing barium, potassium and lithium. A structural study is presented, which reveals poly-layered intercalated sheets between graphene planes. Such a stacking sequence is commonly observed for GIC synthesized using the molten alloy method but is obtained for the first time in the case of an intercalation reaction in a molten salts medium.

2. Materials and methods

2.1. Sample preparation

The novel Ba-based GIC is synthesized by reaction between a pyrographite platelet and barium dissolved in the molten LiCl-KCl eutectic medium. Regarding the instability of reactants and products versus air or moisture, the preparation of the intercalation reaction is realized in a glove box under pure argon atmosphere. In this work, the eutectic mixture is prepared with 58.2 and 41.8 mol % of LiCl (99%) and KCl (99%) respectively. After

an individual outgassing of the chloride salts for at least 24 h at 240°C under secondary vacuum, they are introduced in a stainless-steel reactor and heated up at 450°C to ensure the melting of the eutectic. A suitable amount of barium (99.9%, Sigma-Aldrich), which is 2 at.% so that the used metal is in excess versus graphite host, is then added to the 4g of molten chlorides. Subsequently, the solution is quickly stirred and a PGCCL platelet (PyroGraphite Comprimé Carbone Lorraine) is immersed in the liquid. The reactor is tightly closed with a Swagelok® plug and placed in a metal enclosure under argon. The intercalation reaction is performed outside the glove box for 12 days at 450°C. During the reaction, the oven undergoes some oscillations to guarantee the homogeneity of the reactive medium and the synthesis of this novel compound. Our preliminary experiments reveal that the initial solubilization of barium together with the oscillations of the furnace can impact the nature of the final product. At the end of the reaction, inside the glove box, the sample is removed from the molten mixture, scrapped and placed in a fitted sample-holder for further characterization. Even if hot centrifugating procedure has been tried, it appears that manual scrapping remains the best way for removing impurities attached on the surface of graphite. In this synthesis conditions, the recovered sample exhibits a huge dilation along its *c*-axis, and an unexpected indigo color different from those of graphite or BaC₆.

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

X-ray diffraction measurements are carried out with a Brüker D8 Advance diffractometer ($\lambda_{\text{MoK}\alpha 1} = 70.926 \text{ pm}$). The sample is placed in a glass capillary under argon. Being prepared from a pyrolytic graphite platelet, its crystallites have parallel *c*-axes and randomly oriented (*ab*) planes. Therefore, the sample can be considered as a single crystal along the *c*-axis and as a powder in the direction parallel to the graphene planes, which makes possible to record 00*l* and *hk0* reflections separately. The quantitative analysis of these 00*l* reflections allows the determination of the electronic density profile along the *c*-axis and the stacking sequence of the atomic planes [19].

2.2.2. Scanning electron microscopy (SEM)

Preliminary scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDXS) are performed with a JEOL JSM6010LA microscope operating at 20 kV in order to detect some (co)intercalation compound. For this experiment, the sample is stuck with

carbon tape on a sample-holder in the glove-box under argon atmosphere before to be rapidly introduced into the SEM analysis chamber.

2.2.3. Ion beam analysis

The chemical composition and homogeneity of the sample is studied by ion beam analyses using nuclear microprobe instrument in order to inquire about the composition of the samples and their homogeneity, in-depth (several tens of microns) as well as laterally. GIC samples were characterized with a 3 MeV proton $^1\text{H}^+$ ion beam. Particle detector was placed at an angle of 170° from the beam axis. For Cl, K and Ba, the only interaction considered is backscattering. With 3 MeV protons, (p, α) nuclear reactions exist for Cl and K, but their respective cross-sections are too weak to lead to significant signals. Scattering cross-sections of 3 MeV protons on Ba can be straightly calculated from Rutherford laws whereas it differs notably for Cl and K, up to 50% higher than Rutherford ones with numerous resonances [20,21]. For carbon, cross-sections are more than an order of magnitude higher than Rutherford one and very well documented [22] s. Finally, for lithium, cross-sections for both backscattering and $^7\text{Li}(p,\alpha)^4\text{He}$ nuclear reaction [23,24]. Accordingly, one recorded spectrum (with a lateral resolution of few micrometers due to the $3 \times 3 \mu\text{m}^2$ ion beam size) contains information concerning the aforementioned elements mapped on areas of size $200 \times 200 \mu\text{m}^2$. The collected data are then treated using the SimNRA software for spectra simulation [25]. The sample is described as a stacking of several layers of given compositions and thicknesses. The final simulated spectrum is then composed of the superimposed contributions of all the interactions, with each isotope of each element of each sublayer of the defined solid. Since all the physical parameters of the interactions are imposed by the beam conditions (detection geometry, cross-sections, stopping powers,...), simulated spectra are fitted on experimental ones only by adjustment of sample definition.

3. Results and discussion

First observations using SEM were carried out on the synthesized Ba-based GIC, in association with EDXS measurements recorded on different zones of the sample (spot 001, 002 and 003 on Figure 1). EDX spectra giving similar results, only one representative spectrum is presented here.

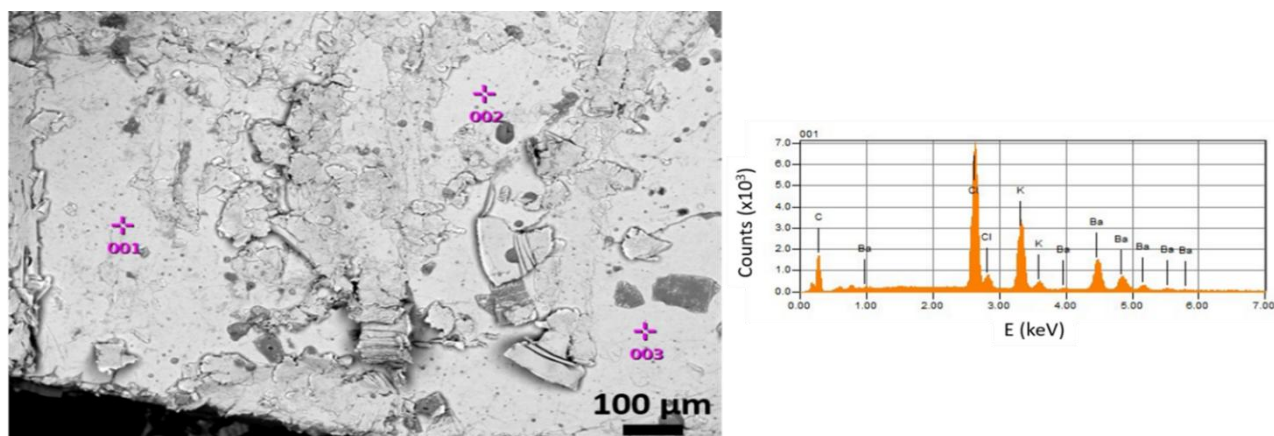


Figure 1. SEM micrograph (backscattered electrons imaging) and EDX spectrum (recorded on spot 001)

As seen on the SEM micrograph, the sample exhibits some heterogeneities on its surface, mainly due to residual chlorides hard to remove thoroughly by manual scraping. Besides carbon, EDXS indicates the presence of chlorine, potassium and barium, some of these elements being intercalated into graphite.

However, as lithium cannot be detected by EDXS and to go further in the study of the chemical composition, ion beam analyses have also been performed using nuclear microprobe instrument. It has already been demonstrated that such an analysis can provide a representative chemical composition of a sample intercalated into the bulk beneath are the surface impurities [26].

Data corresponding to the ion beam analysis of the Ba-based GIC is given Figure 2.

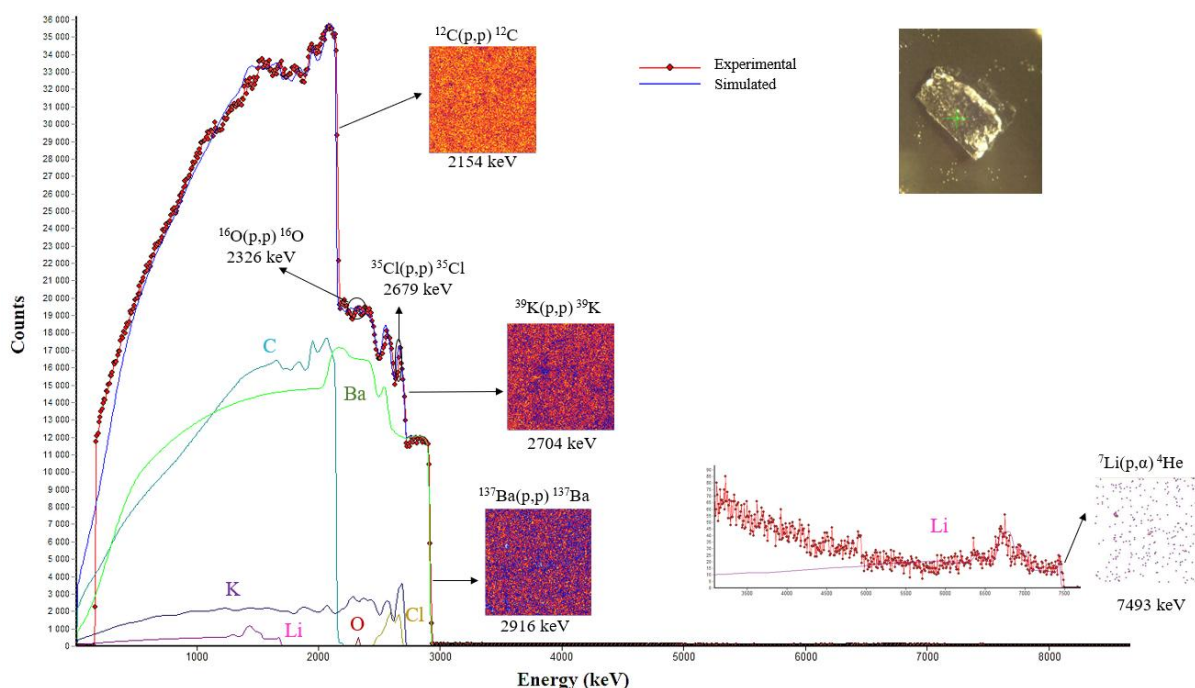


Figure 2. Recorded RBS/NRA spectrum of the Ba-based GIC and its simulation. Each individual elementary contribution to the simulation is drawn. Red spots: experiment; blue solid line: simulation. Inset shows a sample picture on the sample-holder of the microprobe instrument.

The measurement gives information on the in depth-elementary repartition (several tenth of microns). As the presence of an element in the bulk of the sample corresponds to a step on the spectrum, here Cl (also detected by EDXS) and O are only located on the surface of the sample as peaks are recorded on the spectrum. This presence on the surface is due to post-synthesis residual chlorides and surface oxidation due to air exposure when transferring the sample into the microprobe instrument.

Then, RBS contributions of carbon, potassium and barium show intense steps, what is expected for a graphite sample intercalated by K and Ba into the bulk. Moreover, the corresponding elementary maps for these elements reveal a homogeneous lateral distribution of these elements, in agreement with the synthesis of a GIC fully intercalated into the bulk.

Finally, a small amount of lithium is detected seen with the ${}^7\text{Li}(p, \alpha){}^4\text{He}$ nuclear reaction in the high energy region of the spectrum. It looks like this element is also homogeneously distributed in the GIC, in-depth and laterally.

All these elements are homogeneously intercalated between graphene layers and the corresponding quaternary GIC exhibits a $\text{Li}_{0.2}\text{K}_{0.75}\text{Ba}_{0.6}\text{C}_6$ chemical formula. The monophasic nature of the sample is indeed confirmed by X-ray analysis.

The $00l$ X-ray diagram of the compound (Figure 3) reveals a significant series of ten $00l$ reflections (002 to 0011). They are indexed considering a first stage compound with a repeat distance $I_c = 950$ pm. Although the sample has been manually scrapped, some very weak additional peaks are due to the superficial presence of LiCl and KCl. The 003 reflection is exceptionally intense. Indeed, the intensities of the 006 and 007 reflections, that are the 2nd and 3rd more intense, achieve respectively 10.8 and 6.2% only of the intensity of the 003 one. All the other reflections are still weaker. This is especially unusual in a $00l$ X-ray diffractogram of a GIC.

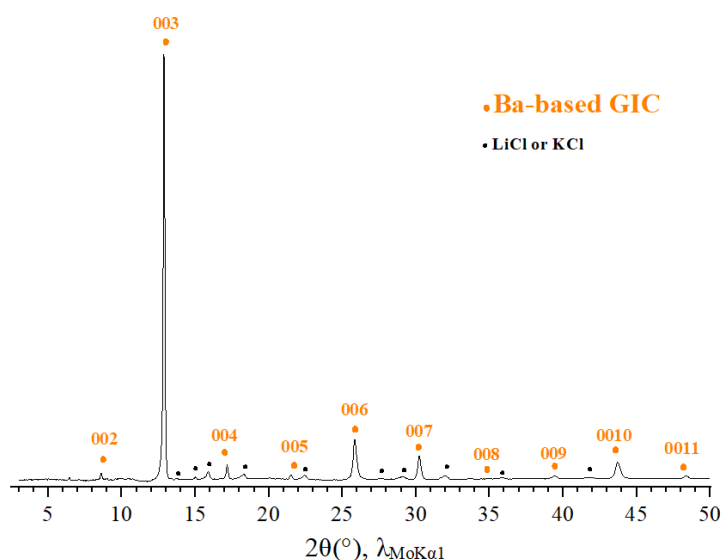


Figure 3. $00l$ X-ray diffractogram of the novel Ba-based GIC

The measurement of these intensities allows to calculate the structure factor of each reflection and thus the evolution of the electronic density by Fourier transform of this set. This calculation leads to the experimental c -axis electronic density profile of the compound. A theoretical profile is then drawn based on a c -axis atomic stacking model which of course considers the chemical composition of the compound. The best fit between experimental and calculated profiles allows to determine the c -axis atomic stacking of this novel Ba-based GIC (Figure 4 and Table 1).

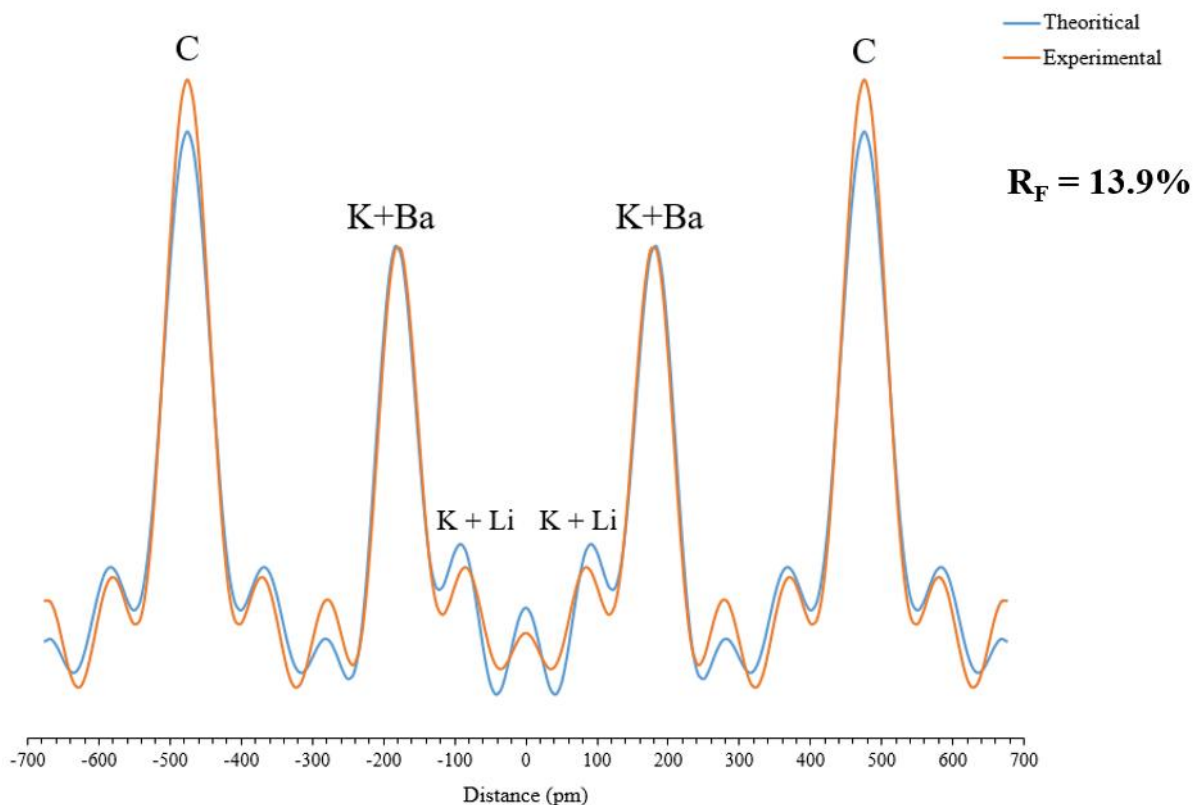


Figure 4. Electronic density profile of the Ba-based GIC along the c-axis

Table 1. Data concerning the stacking sequence of 1st stage Ba-based GIC

Element	C	K	Ba	K	Li	Li	K	Ba	K	C
<i>z</i> (pm)	-475	-213	-174	-96	-96	96	96	174	213	475
Atomic content	3.0	0.196	0.30	0.179	0.11	0.11	0.179	0.30	0.196	3.0

In a first approach, the intercalated species K and Ba are distributed into six atomic planes according to the (K-Ba-K-K-Ba-K) sequence. Potassium planes are in contact with the graphene ones, and are furthermore very close to barium ones. It is sensible to think that these K and Ba planes constitute thick symmetrical single layers, containing K and Ba atoms tightly nested inside. In addition, two other potassium planes are located near to the center of the intercalated sheet which is however empty itself. In other words, the intercalated sheet is almost four-layered, in accordance with the (K,Ba)-K-K-(Ba,K) *c*-axis sequence.

Concerning the position of the Li atoms, it remains difficult to determine it because lithium scatters extremely weakly due to a poor electronic cloud (three electrons only). However, it seems that the best modelling solution consists in positioning these Li atoms in the same planes as the central potassium ones.

It is interesting to compare the *c*-axis structure of this GIC with those of two other ternary intercalation compounds, graphite-potassium-oxygen and graphite-potassium-sulphur, that reveal several similarities between them. These latter GIC are ternary compounds containing three-layered intercalated sheets (K-O-K and K-S-K) [27,28]. Such stackings do not differ significantly from the previous four-layered one. For instance, for both of these ternaries, the most intense reflections on *00l* XRD patterns are the 003 ones and then the 006 ones. This is also observed in the present study for the Ba-based GIC. A schematic comparison between these three compounds is given Figure 5 and Table 2.

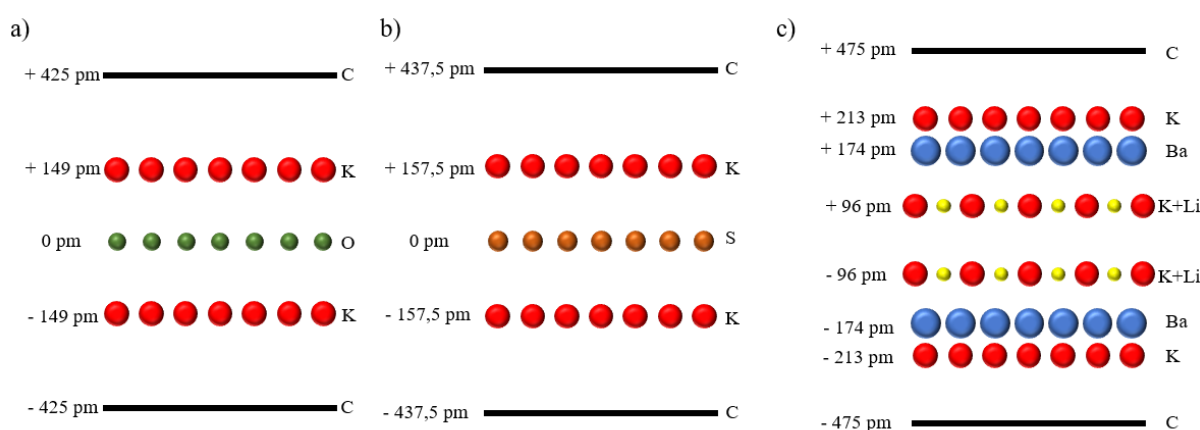


Figure 5. Comparison between a) $\text{KC}_{3.7}\text{O}_{0.08}$, b) $\text{KC}_3\text{S}_{0.25}$ and c) Ba-based GIC

Table 2. Comparison between $\text{KC}_{3.7}\text{O}_{0.08}$, $\text{KC}_3\text{S}_{0.25}$ and Ba-based GIC

GIC	$\text{KC}_{3.7}\text{O}_{0.08}$	$\text{KC}_3\text{S}_{0.25}$	$\text{Li}_{0.2}\text{K}_{0.75}\text{Ba}_{0.6}\text{C}_6$
I_c (pm)	850	875	950
Distance K – K (pm)	298	315	426
Distance C – K (pm)	276	280	262

The repeat distance of the graphite-potassium-oxygen and graphite-potassium-sulphur compounds reaches respectively 850 pm and 875 pm, slightly lower than that of this compound for which the value is 950 pm. This can be explained by the presence of a smaller amount of oxygen or sulphur atoms between potassium planes, in comparison with the K-Ba-Li intercalated species whose central layer contains 0.55 metallic atoms.

Moreover, in the intercalated sheet, the distance between both potassium planes is 298 pm in the case of graphite-potassium-oxygen compound, increasing to 315 pm in the case of sulphur-containing compounds, up to 426 pm in the studied compound. This high value can be explained by the presence of electropositive species in the central part of the intercalated sheet, which tend to put the potassium planes more distant. On the contrary, the electronegative species such as oxygen or sulphur bring these potassium planes closer.

It is also noteworthy to compare the distance between the graphene plane and the adjacent potassium one in these compounds, the reference value being 267.5 pm in the binary KC_8 GIC. This distance progressively increases from potassium-oxygen GIC (276 pm), to potassium-sulphur GIC (280 pm) up to 281.5 pm in the case of mean position of the K-Ba layer, the intercalated sheets becoming more complicated with a stronger internal cohesion.

4. Conclusions

GIC are well-known compounds studied regarding their nice structure-properties correlations and some of their applications in current life. Among these GIC, researchers are especially interested in superconducting phases associating graphite and a metallic element or alloy located in the van der Waals galleries. In most cases, the metallic element is an alkali or an alkaline-earth metal.

In this work, we evidence the ability to synthesize a barium-based GIC using the molten salts method. Interestingly, a quaternary compound has been obtained whereas most of the complex GIC are more often ternary. 00I quantitative analysis confirm that all metallic elements are intercalated. This first stage Ba-based GIC has been isolated and its structural investigation has been performed. It is shown that a pseudo four-layered (K,Ba)-(K,Li)-(Li,K)-(Ba,K) intercalated sheet is stabilized between graphene planes, with a repeat distance I_C equals to 950 pm and a $Li_{0.2}K_{0.75}Ba_{0.6}C_6$ formula, *i.e.* a particularly metal-rich $M_{1.55}C_6$

compound. It should be highlighted that this work constitutes the first synthesis of a barium-based GIC different from the well-known BaC_6 binary compound. It is also the first time that a poly-layered GIC is obtained by solid-liquid reaction in molten salts medium. Currently, the $\text{Li}_{0.2}\text{K}_{0.75}\text{Ba}_{0.6}\text{C}_6$ composition is a matter-of-fact. Henceforth, additional detailed investigations must be realized in order to determine the in-plane structure of the GIC, the intercalation mechanism allowing the stability of such a phase, and the physical properties of this novel GIC. The influence of the experimental parameters on the final composition of the GIC should also be investigated.

Statment and declarations

Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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