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Inass El Hajj, Lucie Speyer, Sébastien Cahen, L. Herbuvaux, P. Lagrange, et al.. Intercalation of barium into graphite by molten salts method: Synthesis of massive samples for crystal structure determination of BaC₆. Carbon, 2022, 186, pp.431-436. <10.1016/j.carbon.2021.09.073>. <hal-03397626>

HAL Id: hal-03397626

<https://hal.univ-lorraine.fr/hal-03397626v1>

Submitted on 22 Oct 2021

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Intercalation of barium into graphite by molten salts method: synthesis of massive samples for crystal structure determination of BaC₆

I. El Hajj, L. Speyer, S. Cahen¹, L. Herbuvaux, P. Lagrange, G. Medjahdi, C. Hérold

Université de Lorraine, CNRS, IJL, F-54000, Nancy, France

Abstract

A solid-liquid method is used to synthesize the first stage bulk BaC₆ graphite intercalation compound (GIC). This way of synthesis allows the preparation of bulk and massive samples useful for crystal structure determination. Through an eutectic medium LiCl-KCl, and by submerging a graphite platelet in barium-molten solution at 450°C for several days, the bulk BaC₆ compound is obtained and X-ray diffraction investigations allowed a complete structural study. The collected data certify that BaC₆ crystallizes in the hexagonal $P6_3/mmc$ space group with the following parameters $a = b = 430.6$ pm and $c = 1058.2$ pm.

1. Introduction

Graphite intercalation compounds (GIC) are an interesting class of materials for various theoretical and experimental studies, especially the first stage ones where all the van der Waals gaps of pristine graphite are occupied. In the last decades, these compounds have triggered the scientific community, especially due to their superconducting properties at low temperature. Numerous GIC with different intercalated species have been synthesized and reported in the literature. The donor type compounds involving alkali metals have firstly been described in 1926 [1]. A well-known example is the case of lithium intercalated into graphite [2], now used in the lithium-ion battery technology. Since, numerous donor-type GIC associating graphite with different metals have been investigated. Hence, some research has been focused on alkaline-earth metals and the understanding of their reactivity towards graphite.

¹ sebastien.cahen@univ-lorraine.fr

Institut Jean Lamour - UMR 7198 CNRS-Université de Lorraine
Campus ARTEM - 2 Allée André Guinier
B.P. 50840 F54011 Nancy Cedex

Several attempts have been made in hopes of intercalating alkaline-earth metals into graphite in pure and bulk sample form. Guérard *et al.* [3] have been the first ones to note the obtaining of BaC₆ samples using solid-vapor method. Nonetheless, the reaction remains incomplete except with micrometric single crystal graphite samples. In the 2000s, several studies have been conducted in order to obtain superconducting BaC₆ samples using the same solid-vapor route while modifying the experimental conditions. These results seem inconsistent, leading to the synthesis of a so-called homogeneous BaC₆ even if the presence of residual pristine graphite remains. It should be highlighted that only little crystallographic data have been provided to sustain these declarations [4-6].

Based on the work of Pruvost *et al.* concerning the use of Li-based molten alloy for intercalation reactions into graphite [7], Emery *et al.* studied the intercalation of some alkaline-earth metals and have elaborated a bulk first stage calcium-graphite intercalation compound using the same approach [8]. Then, in the Li-Ba-graphite system, the same authors have succeeded in obtaining a bulk first stage BaC₆ binary compound [9]. However, complementary studies are mandatory about this compound.

In the recent years [10-12], a novel method has been developed to obtain bulk and pure binary samples. On referring to the procedure proposed by Hagiwara *et al.* [13], consisting in using LiCl-KCl molten salts as a liquid medium to intercalate lanthanide into graphite, a tremendous success in producing fully intercalated first stage compounds such as EuC₆ and SrC₆ has been evidenced [10], [12].

Thus, the purpose of this paper is to synthesize a bulk and homogeneous first stage BaC₆ sample using the molten salts solid-liquid method. Then, thanks to the so-obtained massive sample starting from pristine pyrolytic graphite, a full structural study performed by means of X-ray diffraction techniques supported by complementary Raman spectroscopy analysis is presented, in order to definitively solve the crystal structure of this compound.

2. Experimental

2.1. Synthesis

The experiments are conducted in a glove box under purified argon due to the sensitivity of the reagents and products towards air and moisture. First, lithium and potassium chlorides (99%), used as solvent, have been individually outgassed for at least 24 h at 240°C under

secondary vacuum (10^{-6} mbar). The eutectic mixture is prepared in the glove box by mixing 58.2 and 41.8 mol % of LiCl and KCl respectively [14]. A total mass of 4 g of this blend is then introduced in a stainless-steel reactor and heated up at 450°C to ensure its melting. The suitable amount of barium (m_{Ba} about 200 mg; 99.9%, Sigma-Aldrich) for this quantity of molten salt is then added, which is around 2 at.%, meaning that the used metal is in excess compared to graphite (m_{graphite} about 10 mg). Subsequently, the solution is manually stirred for at least 15 minutes in the glove box. Once the metal is dissolved, a single platelet of pyrolytic graphite is immersed in the reactive liquid. The reactor is tightly closed with a Swagelok® plug and transferred in a metal enclosure under argon in order to safely perform the heat treatment outside the glove box. The whole device is heated up in a furnace and the reaction is performed for 12 days at 450°C . During this procedure, the oven undergoes regular swaying to guarantee the homogenization of the reactive medium. When the time span of the reaction is up, the sample is removed from the molten mixture inside the glove box, then scrapped and finally placed in a glass capillary sealed under argon, for X-ray characterizations.

2.2. X-ray experiments

The characterization methods are focused on XRD measurements, mainly performed with a Brüker D8 Advance diffractometer ($\lambda_{\text{MoK}\alpha 1} = 70.926$ pm) using a (θ , 2θ) configuration and enhanced with a Soller slit (2.5°). GIC prepared from extremely anisotropic pyrolytic graphite platelets are distinguished by a single-crystal behavior along the \vec{c} axis and considered as powder in the perpendicular (ab) plane. Hence, by changing the sample orientation on the diffractometer, the $00l$ and $hk0$ reflections can be separately recorded. The corresponding diffractograms allow the determination of a and b parameters of the elementary unit cell as well as the repeat distance I_C , the interplanar distance d_i and the stage s .

The quantitative analysis of $00l$ reflections allows the calculation of the experimental \vec{c} axis electronic density profile and hence contributes to the resolution of the stacking sequence of the atomic planes in this direction.

Elsewhere, a Brüker Kappa APEX duo diffractometer is used in order to measure the rotating crystal diffraction pattern equipped with a two-dimensional CCD APEX II detector and an X-ray micro-source (diameter spot 100 μm ; $\lambda_{\text{MoK}\alpha 1} = 70.936$ pm). A sample with small dimensions (hundreds of microns) is transferred into a Lindemann capillary (diameter = 0.5 mm), then placed on the Kappa goniometer and exposed to the X-ray source.

Thanks to this method, all reflections can be easily identified and the three-dimensional unit cell can be determined.

2.3. Raman analysis

Raman spectroscopy is mainly used in order to confirm the structure of the sample. It is carried out by using Jobin Yvon Horiba LabRAM HR spectrometer equipped with a He/Ne gas laser source and operating with a wavelength of 632.8 nm. The sample is cleaved in order to get a clean surface. Then, it is introduced in a quartz cell which is sealed under low helium partial pressure. The laser beam is then focalized on a selected area of the sample before recording the spectra.

3. Results and discussion

The obtained compound exhibits a shiny silver color related to the first stage binary barium-graphite intercalation compound. The X-ray diffraction pattern shown Figure 1 indicates individualized and intense 00*l* peaks that can be assigned to BaC₆.

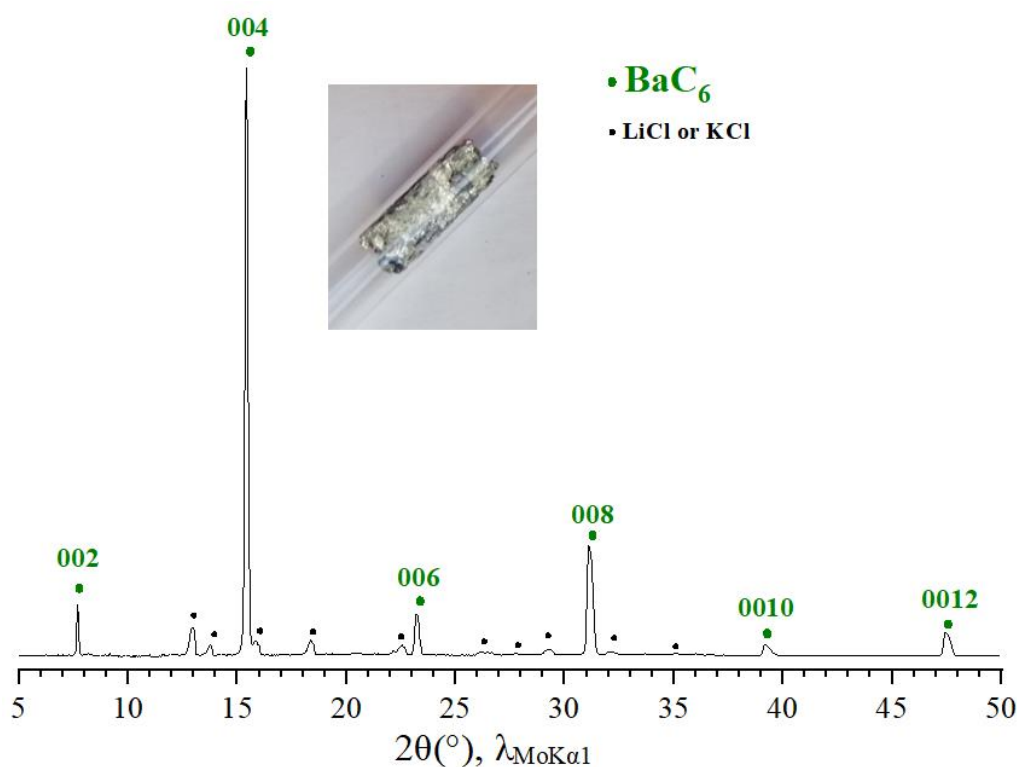


Figure 1. 00*l* X-ray diffraction pattern ($\lambda_{\text{MoK}\alpha 1} = 70.936$ pm) of the first stage BaC₆ compound ($I_c = 529.1$ pm).

ICCD numbers = LiCl: 00-004-0664; KCl: 00-041-1476

A picture of the bulk sample is attached to the diffractogram.

Except a minor amount of chloride salts on the surface, the diffractogram reveals the absence of any reflection due to residual metal, graphite, carbide or other intercalation compounds. This result confirms the synthesis of pure and bulk first stage BaC_6 compound. The repeat distance I_C extracted from this diffractogram is equal to 529.1 pm, slightly different from the one reported by Guérard *et al.* [3] who mentioned an I_C value of 525 pm. This tiny difference may be due to the involved way of synthesis involving different diffusion mechanism of barium atoms between graphene planes considering Ba atoms are intercalated using solid-gas or solid-liquid intercalation reactions. In the former, Ba atoms directly diffuse into graphite; in the latter, first lithium is intercalated into graphite, then substituted with barium. It is clear that this inter-diffusion between Li and Ba lead to some more textural defaults, increasing the I_C value.

The Fourier transform of the $00l$ structure factors, determined thanks to their corresponding experimental intensities, allows to plot the experimental electronic density profile which is in excellent agreement with a calculated one considering a three-layered model consisting in a monoatomic layer of barium between two graphene sheets (Figure 2).

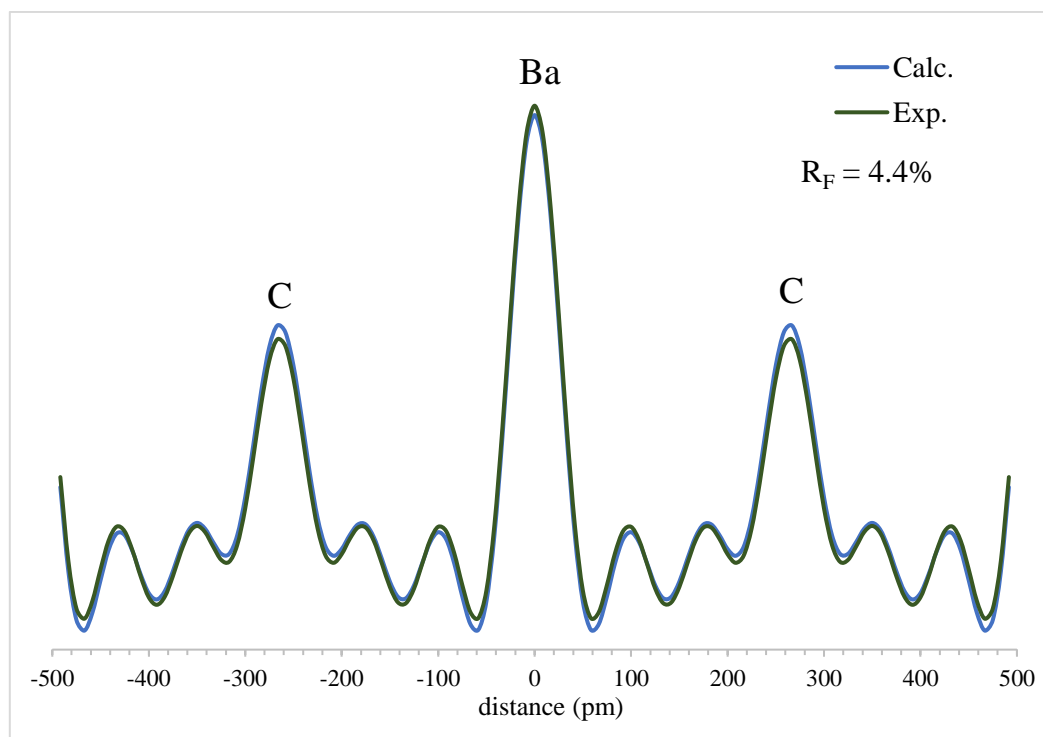


Figure 2. 1D \vec{c} axis electronic density profiles of the BaC_6 compound (calculated and experimental are drawn in blue and green respectively).

The structure factors of the corresponding experimental and calculated data are listed in **Table 1**. The residual factor evaluated by least square method is $R_F = 4.4\%$ after thermal agitation correction (Debye-Waller coefficient $B = 1.2 \text{ \AA}^2$) confirming the significant agreement between the experimental and calculated data. Thus, this modeling confirms the preparation of a bulk BaC_6 .

Table 1. Experimental and calculated structure factors of the $00l$ reflections used for the calculation of the electronic density profile of BaC_6 .

$00l$	θ ($^\circ$, $\lambda_{MoK\alpha 1}$)	d (pm)	I_C (pm)	F_{00l} exp.	F_{00l} calc.
002	7.68	529.3	529.3	20.1	29.7
004	15.40	265.5	531.0	100.0	100.0
006	23.20	176.3	528.9	35.2	35.0
008	31.30	132.2	528.8	72.7	69.8
0010	39.80	105.7	528.5	30.5	30.5
0012	47.45	88.1	528.6	54.8	55.8

The only divergent value that could be pointed out in **Table 1** is the structure factor referring to the 002 reflection. The calculated factor (29.7) is slightly different from the experimental one (20.1). This discrepancy can be explained by the X-ray absorption phenomenon that occurs for low diffraction angle either due to the heavy element (*i.e.* barium) contained in the sample and due to the pyrex glass capillary.

A typical Raman spectrum recorded on the BaC₆ sample is presented Figure 3.

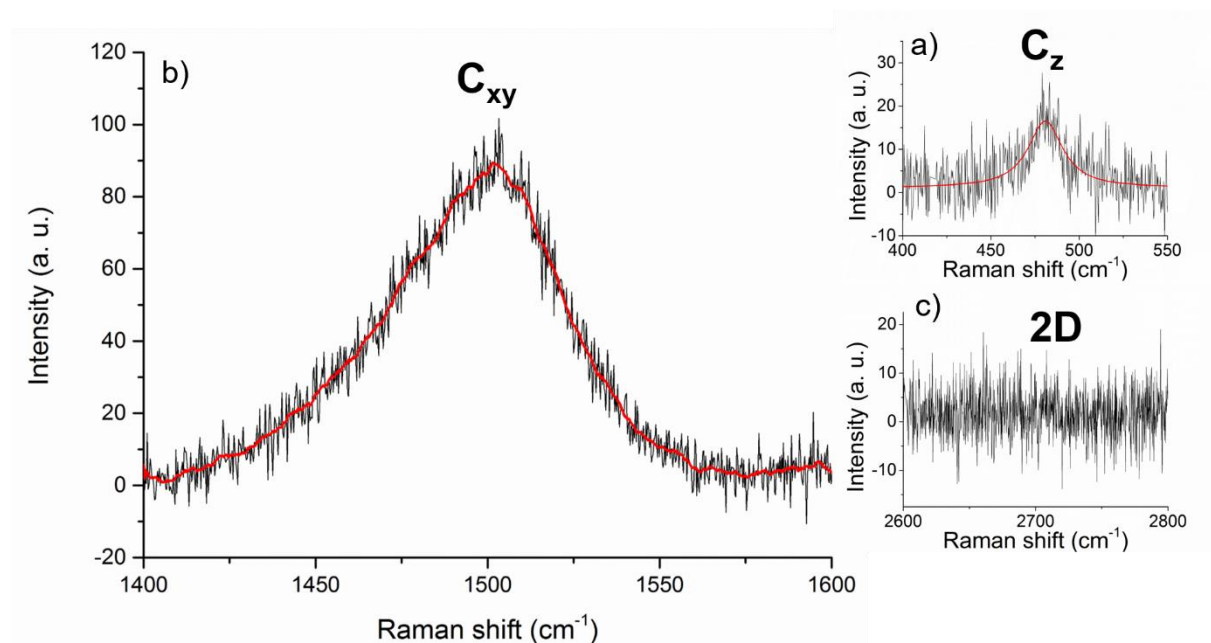


Figure 3. Raman spectrum ($\lambda = 632.8$ nm) of the BaC₆ compound: a) C_z band b) C_{xy} region c) graphite 2D band region.

Three particular zones are studied and show the presence of the C_z peak at 481 cm⁻¹, a broad C_{xy} band located around 1500 cm⁻¹ and the absence of the 2D band of pristine graphite which should be observed around 2700 cm⁻¹. These three features are specific to stage-1 binary compounds [15-18] and support the X-ray diffraction observations. More specifically, the C_z peak corresponds to an out-of-plane vibration mode of carbon atoms in stage-1 GIC [15,17,18], and its position depends of the nature of intercalant. The value of 481 cm⁻¹ obtained after curve fitting with a Lorentzian peak is in excellent accordance with the one reported by Dean *et al.* for BaC₆ sample [18]. The broad and asymmetric C_{xy} band is the result of the E_{2g} vibration mode which corresponds to an in-plane bond-stretching mode. In stage-1 GIC, this mode is broadened and shifted in comparison with the G band of pristine graphite due to the presence of the intercalate [17,18]. Then, the whole results extracted from Raman analysis confirm the BaC₆ nature of the sample together with its bulk intercalation.

The investigation of the binary compound is pursued with the study of its *hk0* and its *hkl* reflections in order to identify the unit cell parameters. The analysis of *hk0* diffraction pattern (Figure 4) shows relevant peaks corresponding to the BaC₆ compound accompanied with some very weak reflections related to LiCl or KCl.

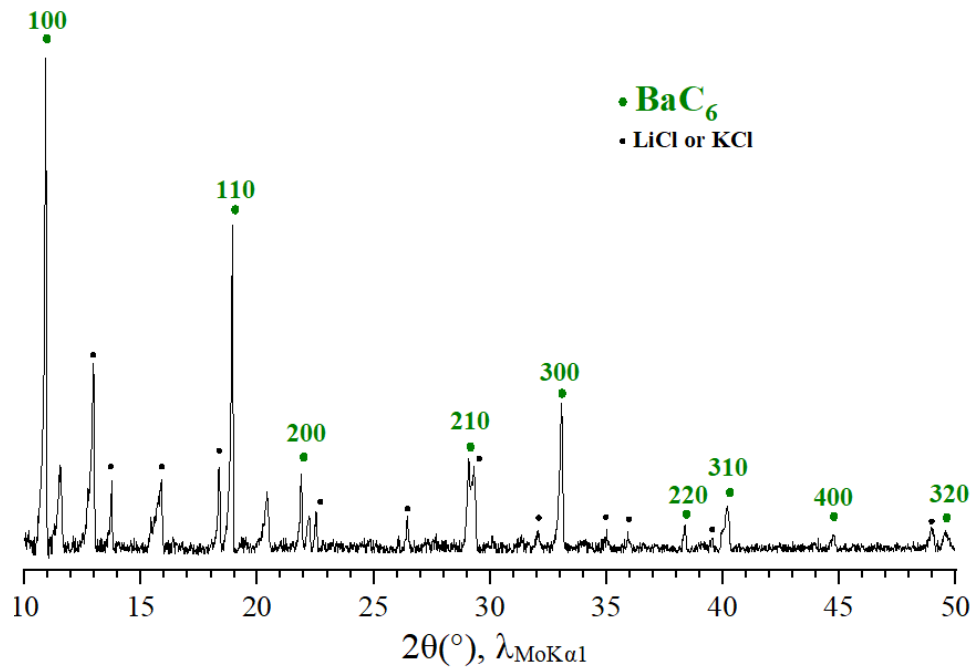


Figure 4. $hk0$ X-ray diffraction pattern ($\lambda_{\text{MoK}\alpha 1} = 70.926$ pm) of the first stage BaC_6 compound ($I_c = 529.1$ pm)

Previously, we mentioned that $00l$ reflections revealed that no more graphite was persisting in the final sample. Here, it appears that the position of some $hk0$ reflections of BaC_6 are equivalent with those of pristine graphite. Moreover, all reflections can be indexed considering the hexal unit cell of BaC_6 . For instance, d_{110} of BaC_6 matches with d_{100} of graphite, or d_{300} of BaC_6 is equivalent to d_{110} of graphite. So, this X-ray pattern displays the commensurability of the intercalated metallic sheet in respect with the graphene network. Lagrange *et al.* [19] ensured a detailed mathematical approach about exhaustive commensurability versus graphene to sustain the compatibility between the two-dimensional lattice of graphite and the intercalated sheets. Therefore, every GIC exhibiting commensurability owns planar unit cell parameters obtained by combination of the graphite ones, with a_g the lattice parameter of graphite equals to 246.1 pm. In this work, the a and b parameters, calculated from the $hk0$ pattern, are equivalent to $a_g\sqrt{3}$, hence a value of 430.6 pm. The 2D unit cell of the BaC_6 compound (Figure 5) exhibits a 30° rotation regarding the graphitic one, allowing to express the lattice by $(\sqrt{3}\times\sqrt{3}) R30^\circ$.

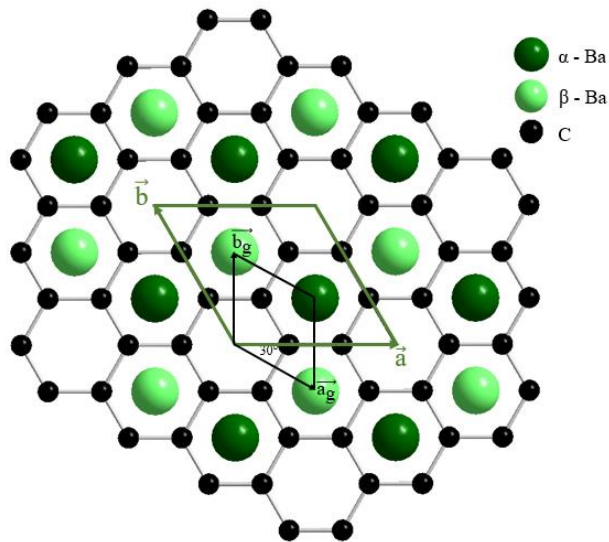


Figure 5. 2D unit cells of graphene (—) and BaC₆ compound (—) rotated by 30°. α - Ba and β - Ba correspond to Ba atoms belonging to different van der Waals gaps.

The structural study is completed thanks to a rotating crystal pattern (Figure 6) disclosing the hkl reflections and consequently allowing the determination of the c parameter. The entire strata were easily identified and indexed. Compared to the $00l$ and $hk0$ X-ray diagram, the similarities in distance and intensities are undoubtedly found. In fact, the $hk0$ strata is used to confirm the value of a parameter. According to the 110 reflection, the reticular distance is 215 pm, therefore the value of a is 430.6 pm, close to aforementioned $a_g\sqrt{3}$, confirming the commensurability notion and approving the hexal 2D unit cell previously stated.

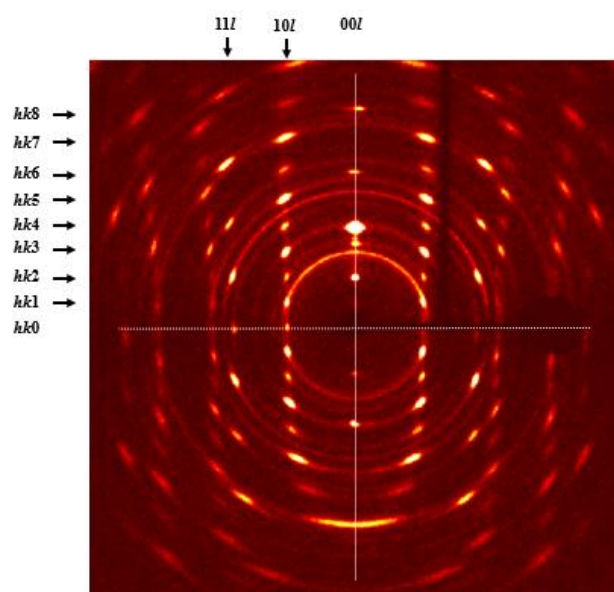


Figure 6. Rotating crystal pattern obtained by X-ray diffraction ($\lambda_{\text{MoK}\alpha 1} = 70.926$ pm) of the BaC₆ compound.

The $00l$ reflections (002, 004, 006 and 008) are all distinguished with their respective intensities, especially the highly intense 004. The absence of $00l$ reflections for l an odd number confirms that these reflections obey to diffraction conditions $l = 2n$ ($n \neq 0$). Another interesting observation regarding the odd l numbers is their existence in the hkl strata (101 for example) implying that the c parameter is twice higher than the repeat distance I_c , thus its value is 1058.2 pm. This also indicates the stacking arrangement along the \vec{c} axis, $A\alpha A\beta A\alpha\dots$ (A = graphene layer; α and β = barium layers).

All these information prove that BaC_6 crystallizes in the hexagonal system with a $P6_3/mmc$ space group, with lattice parameters: $a = b = 430.6$ pm and $c = 1058.2$ pm. Wyckoff's atomic positions are subsequently pointed out, and the representation of the BaC_6 compound is given in Figure 7.

Carbon	12 atoms	12i	$(\frac{1}{3}, 0, 0)$
Barium	2 atoms	2c	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$

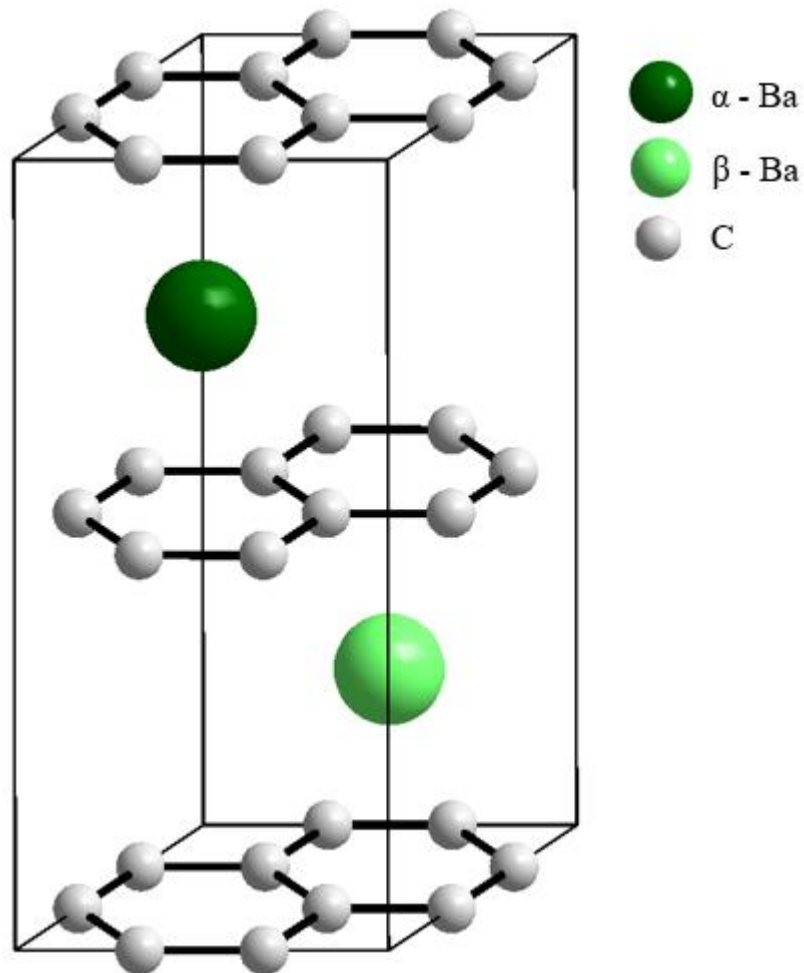


Figure 7. Hexagonal unit cell ($P6_3/mmc$ space group) of BaC₆ compound with $a = b = 430.6$ pm and $c = 1058.2$ pm.

The structure factors and intensities of the hkl reflections can subsequently be calculated after the determination of the lattice parameters. The corresponding data are given in **Table 2**.

Table 2. Structure factors and intensities of BaC₆ reflections.

<i>hkl</i>	<i>d_{hkl}</i> (pm)	Structure factors	<i>F_{hkl}</i>	<i>I_{calc}</i>
001	1058	0	0.00	0.00
002	529	12 <i>f_C</i> - 2 <i>f_{Ba}</i>	-40.67	5.96
100	373	- <i>f_{Ba}</i>	-48.87	18.08
101	352	- $\sqrt{3}$ <i>f_{Ba}</i>	-83.74	100.00
003	353	0	0.00	0.00
102	305	<i>f_{Ba}</i>	46.93	27.09
103	256	$\sqrt{3}$ <i>f_{Ba}</i>	77.78	62.09
004	265	12 <i>f_C</i> + 2 <i>f_{Ba}</i>	135.17	32.31
110	215	-6 <i>f_C</i> + 2 <i>f_{Ba}</i>	66.19	18.69
111	211	0	0.00	0.00
104	216	- <i>f_{Ba}</i>	-42.57	15.50
112	199	-6 <i>f_C</i> - 2 <i>f_{Ba}</i>	-100.46	79.27
005	212	0	0.00	0.00
200	186	- <i>f_{Ba}</i>	-40.37	5.95
201	184	$\sqrt{3}$ <i>f_{Ba}</i>	69.51	3.68
113	184	0	0.00	0.00
202	176	<i>f_{Ba}</i>	39.45	10.65
105	184	- $\sqrt{3}$ <i>f_{Ba}</i>	-69.57	34.83
006	176	12 <i>f_C</i> - 2 <i>f_{Ba}</i>	-47.45	2.58
203	165	- $\sqrt{3}$ <i>f_{Ba}</i>	-66.52	28.17
114	167	-6 <i>f_C</i> + 2 <i>f_{Ba}</i>	62.24	25.02
106	159	<i>f_{Ba}</i>	37.86	8.79
204	152	- <i>f_{Ba}</i>	-37.12	8.03
115	151	0	0.00	0.00
210	141	- <i>f_{Ba}</i>	-35.83	6.83
211	140	- $\sqrt{3}$ <i>f_{Ba}</i>	-61.81	40.25
007	151	0	0.00	0.00
212	136	<i>f_{Ba}</i>	35.26	12.71
205	140	$\sqrt{3}$ <i>f_{Ba}</i>	61.85	20.18
116	136	-6 <i>f_C</i> - 2 <i>f_{Ba}</i>	-83.10	35.38
107	140	$\sqrt{3}$ <i>f_{Ba}</i>	61.88	20.24

This table reports data in good agreement with the aforementioned analysis. Among the 00*l* reflections, 004 is the most intense one, which is well suited with the 00*l* diffractogram (Figure 1) and the data collected in Table 1. Likewise, the intensities of the odd reflections along the \vec{c} axis such as 001, 003... are zero, which is in agreement with the information recovered from the rotating crystal pattern (Figure 6). The intensities of the *hk*0 reflections are weaker than the 00*l* ones, as already observed. Finally, the 101 reflection is the most intense one, as reported the literature [5].

4. Conclusion

For the first time, a massive bulk and fully intercalated binary BaC₆ compound has been synthesized thanks to a solid-liquid method involving a LiCl-KCl eutectic molten salt as a reaction medium, which has already been highlighted for the successful elaboration of several other bulk binary compounds. Using such a massive sample, an extensive structural study becomes possible. Various X-ray diffraction measurements and complementary Raman spectroscopy analysis allowed an extended structural study of the as-obtained BaC₆ sample. This study confirms that BaC₆ crystallizes in a hexagonal unit cell with the *P63/mmc* space group with $a = b = 430.6$ pm and $c = 2I_C = 1058.2$ pm.

Declaration of 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.

Funding source

The authors claim that no funding sources are involved in this research article.

Acknowledgments

The authors want to thank Sébastien Hupont, Hervé Rinnert and the Optics-Laser Competence Center of the Institut Jean Lamour for formation session on Raman device and fruitful discussions.

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