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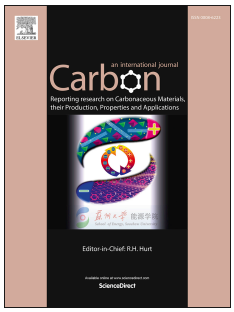

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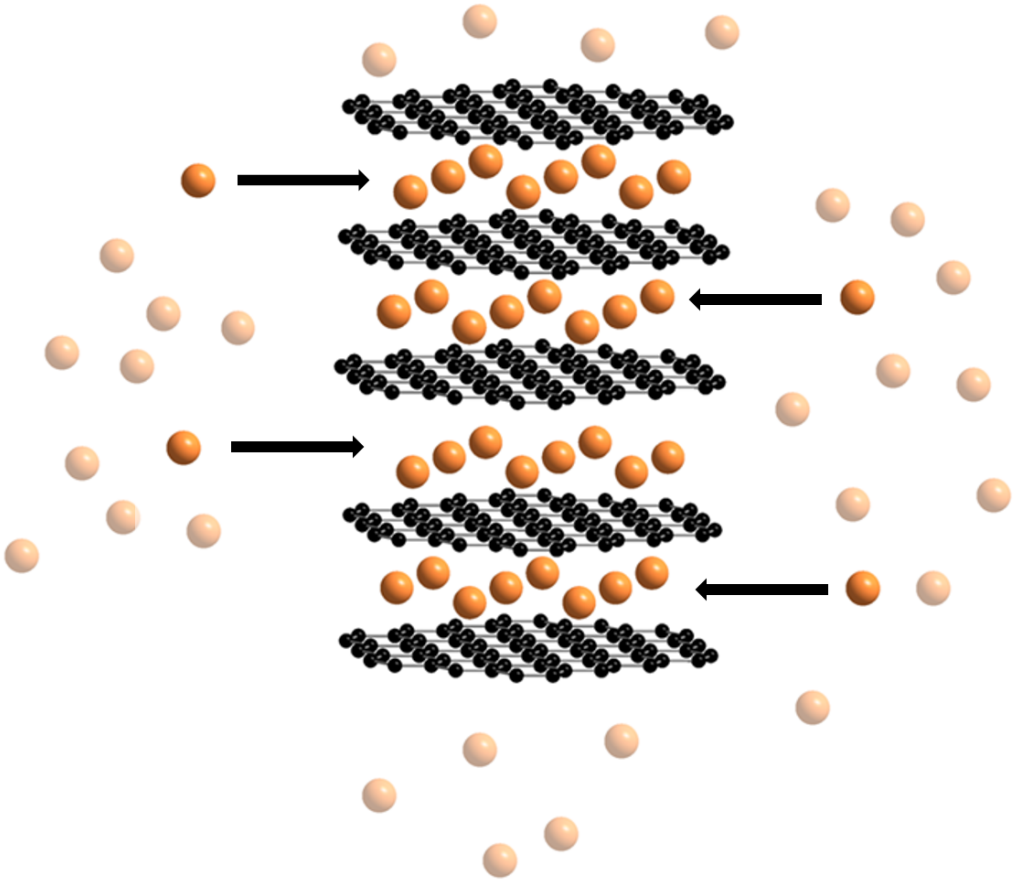

Crystal structure of first stage strontium-graphite intercalation compound

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Abstract

First stage strontium-graphite intercalation compound (GIC) is successfully synthesized using a recent method based on eutectic medium LiCl-KCl. The bulk compound is obtained after immersing a graphite platelet in strontium-molten salt solution at 450°C for several days. Using such bulk GIC, an accurate structural study is performed by applying X-ray diffraction techniques (00*l*, *hk*0 and rotating crystal method). It is validated that SrC_6, similarly to most MC_6 compounds, crystallizes in a hexagonal $P6_3/mmc$ space group with subsequent parameters a = b = 431 pm and c = 988 pm.

1. Introduction

Due to its strongly anisotropic structure, graphite is able to accommodate numerous chemical species in its van der Waals's gaps leading to Graphite Intercalation Compounds (GIC), according to an oxido-reduction topotactic reaction [1]. Depending on the amount of intercalated species, the GIC is characterized by its "stage": it is the number of graphene planes separating two successive intercalated layers. Thus, when all its van der Waals's gaps are occupied, the GIC belongs to the first stage.

The first donor-GIC syntheses date back to 1926 with the intercalation of the heavy alkali metals [2], using a solid-vapor method. The corresponding first stage GIC exhibit monoatomic intercalated layers and their chemical formula is written MC_8 (M = K, Rb, Cs). They were widely inspected mainly for their interesting chemical and physical properties, but pure and bulk materials remain especially appreciated for these studies.

Since this interesting achievement, other pure metals were intercalated too, but generally with increasing difficulties. Thus, sodium remains up to now resistant to form metal-rich GIC [3]. After the laborious success of synthesizing the first stage lithium compound (LiC_6) using the solid-vapor method [4], the intercalation tries of the alkaline earth metals were carried out,

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since these elements and lithium show various chemical likenesses. Based on the works of Guérard *et al.* [5], the intercalation of strontium (470°C) and barium (500°C) was performed using the same solid-vapor route, but the reactions remain greatly incomplete, except if the graphite samples are extremely small (millimetric scale). In addition, the more recent works of Kim *et al.* [6] and Heguri *et al.* [7], despite some sustained efforts, did not supply crystallographic evidences about the bulk nature of the sample. Consequently, it remains strongly difficult to prepare pure and bulk GIC with alkaline-earth metals according to this method.

Accordingly, Pruvost *et al.* [8] initiated a novel method in the purpose to prepare bulk alkaline earth GIC. This route consists in using lithium as an intercalation vector. In order to do this, a graphite platelet is immersed in a molten alloy (lithium-alkaline earth metal) at moderated temperature. Its composition is well chosen to work in a homogenous liquid regarding the corresponding phase diagram, so that the reaction product is a binary alkaline-earth metal GIC. This method succeeded in synthesizing high quality bulk binary compounds such as CaC_6 and BaC_6, but failed in preparing a pure and bulk first stage SrC_6 [9].

Furthermore, an interesting procedure was pursued by Hagiwara *et al*. [10] who mainly focused on lanthanides (Ln) and claimed the possibility of synthesizing LnC_6 GIC. Using a molten salts medium (LiCl-KCl eutectic), they simultaneously dissolve the metallic lanthanide and its corresponding $LnCl_3$ chloride and finally add graphite sample. Even if this study does not provide the actual proof of the successful formation of these binary compounds, the idea of using this molten eutectic as an intercalation medium is promising. Recently, the use of a solid-liquid method derived from the latter lead to the achievement of producing a fully intercalated first stage EuC_6 GIC [11]. As a matter of fact, native lithium immediately intercalates into graphite and is then progressively substituted with europium up to formation of the wanted EuC_6 compound [12]. Based on these works, several tries were carried out to prepare a pure and bulk first stage SrC_6 GIC.

Therefore, this paper aims to prove the possible synthesis of fully intercalated SrC_6 GIC samples by means of this original method. Thanks to these bulk samples, a complete structural study of the compound is carried out applying different X-ray diffraction techniques. It leads to the definitive determination of the crystal structure of SrC_6.

2. Experimental

2.1. Synthesis

The sensitivity of the reagents towards air requires working in a glove box under pure argon atmosphere (<1ppm in O_2 and H_2O). Firstly, LiCl and KCl chlorides (99%), used as solvent, have been individually outgassed for at least 24h at 240°C under secondary vacuum. The eutectic mixture is then prepared under argon using 59.2 mol% in LiCl [13] and 4 g of this blend is introduced in a stainless steel reactor and heated up at 450°C to insure its melting. For this amount of molten salt, 2 at.% of strontium (99.9%, Sigma-Aldrich) is added, the solution is then homogenized by manual stirring. So, the quantity of used metal is in excess versus graphite, *i.e.* 5 times higher than the suitable stoichiometry according to the intercalation reaction ($Sr + 6C \rightarrow SrC_6$). After dissolution of metal, a single pyrolytic platelet of graphite, attached to a tungsten support, is submerged in the liquid. The reactor is tightly closed with a Swagelok® plug and placed in a metal enclosure under argon in order to safely perform the heat treatment outside the glove box. The whole system is heated in a furnace and the reaction is carried out at 450°C for 12 days. Regular oscillations of the oven insure homogenization of the reactive medium. Lastly, the sample is extracted inside the glove box after melting of the chlorides blend, and the excess of salt on the surface is removed by scraping. The as-obtained sample is later placed in a suitable sample-holder for its characterization.

2.2. X–ray experiments

X-ray diffraction (XRD) measurements are performed with a Bruker D8 Advance diffractometer (λ(MoKα1) = 70.926 pm). The sample is sealed in a glass capillary under argon. Since the evaluated samples are originated from pyrolytic platelets, the obtained GIC have crystallites whose $\vec{c}$ axes are parallel to each other while the ab planes are randomly oriented. Thanks to this texture, the sample behaves as a single crystal along the $\vec{c}$ axis and as a powder in the direction parallel to the graphene planes. Therefore, by changing orientation, the separate record of 00*l* and *hk*0 reflections is possible. The quantitative analysis of these

00*l* reflections allows the resolving of the $\vec{c}$ axis experimental electronic density profile leading to the determination of the stacking sequence of the atomic planes [14].

Rotating crystal pattern is also measured by Bruker Kappa APEX duo diffractometer with X-ray micro-source (diameter spot 100 µm; λ(Mo) = 70.926 pm) with a 2-dimensional CCD APEX II detector. Using this method, *hk*0 and *hkl* strata are easily identified and help to determine the three-dimensional order.

3. Results and Discussion

In order to prepare a bulk first stage strontium-GIC, 2 at.% of Sr are dissolved in the molten salt and heated under 450°C for 12 days with continuous homogenization. The platelet is then extracted and scraped to reveal a shiny silver color associated to the bulk SrC_6 compound (*Fig.1*).

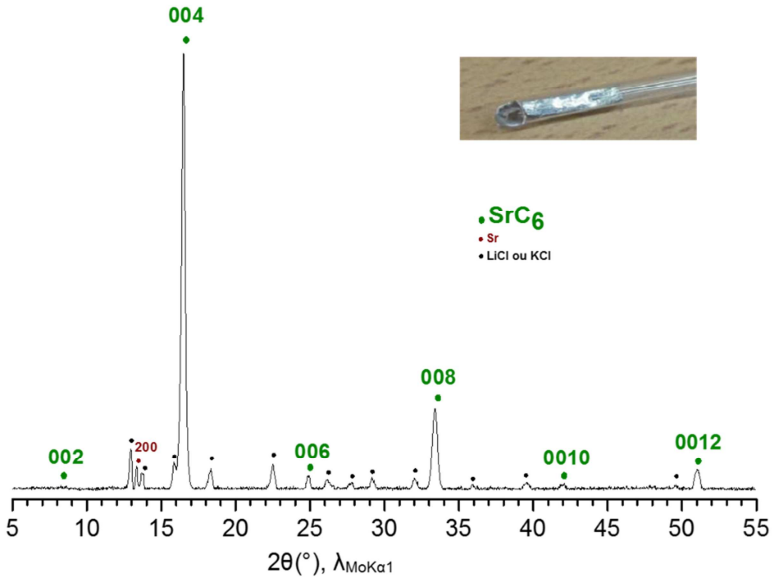

Fig. 1. 00*l* X-ray diffraction pattern ($\lambda_{MoK\alpha1}$ = 70.926 pm) of the first stage SrC_6 GIC (I_C = 494 pm). A picture of the bulk sample is associated to the diffractogram.

Its corresponding 00*l* diffractogram is presented in *Fig. 1*. It shows intense and individualized reflections which positions easily give the value of the repeat distance I_C of the compound, equal to 494 pm and quite identical to previous results [5] [12]. It is also important to notice the absence of reflections attributed to graphite, carbide and other intercalation compounds. This result indicates the synthesis of bulk SrC_6 compound, even if small peaks are observed referring to the minor presence of LiCl, KCl and strontium.

The $\vec{c}$ axis electronic density profile of the compound is given *Fig. 2*. This experimental profile is compared to a calculated one obtained from a one-dimensional model considering a monoatomic strontium layer between two graphene planes.

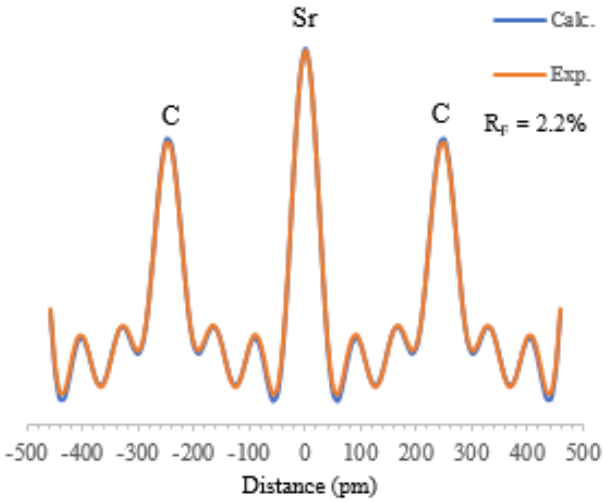

Fig. 2. 1D **c**$^{\rightarrow}$ axis electronic density profiles of the SrC_6 compound
(calculated and experimental are drawn in blue and orange respectively).

Table 1 points out the corresponding experimental and calculated data. The residual factor calculated by least square method is R_F = 2.2% indicating the excellent agreement between the experimental and the calculated data. This result confirms the success in preparing a bulk SrC_6 using this method.

Table 1. Experimental and calculated structure factors of the 00*l* reflections
used for the calculation of the electronic density profile of SrC_6.

00*l*	**θ (°, *λMoKα1*)**	**d *(pm)***	**I_C *(pm)***	**F_{00l} exp.**	**F_{00l} calc.**
002	8.25	492.6	493	5.2	7.0
004	16.49	247.2	495	100.0	100.0
006	24.89	164.5	494	22.1	21.2
008	33.40	123.4	494	70.1	66.8
0010	42.01	98.9	495	19.1	19.2
0012	51.01	82.3	494	53.4	53.2

The study of *hk*0 and *hkl* reflections of the compound corroborates its structure and stoichiometry. *Fig. 3* exhibits the *hk*0 diffraction diagram of the compound along with some reflections related to the superficial LiCl, KCl and Sr. The intrinsic weakness of the *hk*0 reflections artificially enhances in this configuration the intensities of LiCl, KCl and Sr diffraction peaks which actually correspond to minor impurities.

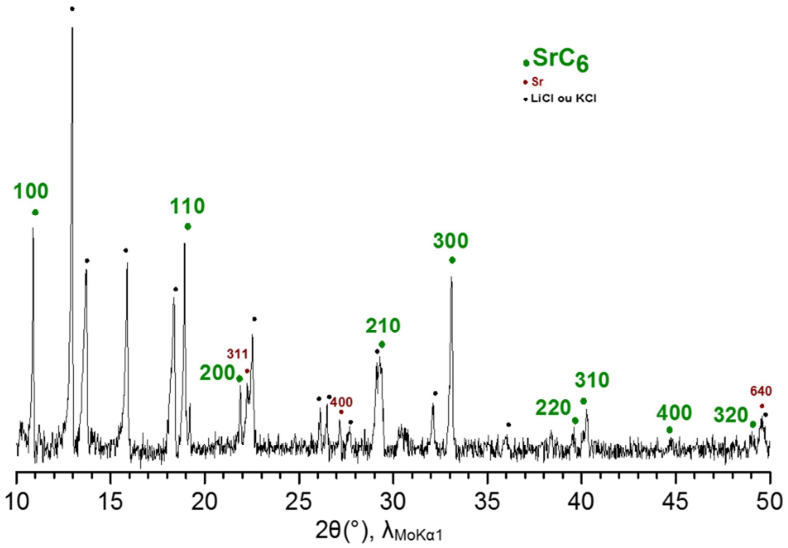

Fig. 3. *hk*0 X-ray diffraction pattern ($\lambda_{MoK\alpha1}$ = 70.926 pm) of the first stage SrC_6 GIC (I_C = 494 pm).

The *hk*0 reflections can be easily indexed using a commensurate hexagonal two-dimensional unit cell inspired from the model of Lagrange *et al.* [15] with **a** parameter of 431.4 pm close to $a_G\sqrt{3}$ (a_G the lattice parameter of graphite equals to 246 pm). Another and frequently used notation for this 2D unit cell is $(\sqrt{3}x\sqrt{3})$ *R*30°, which reveals its rotation by 30° with respect to the graphene one (*Fig. 4).*

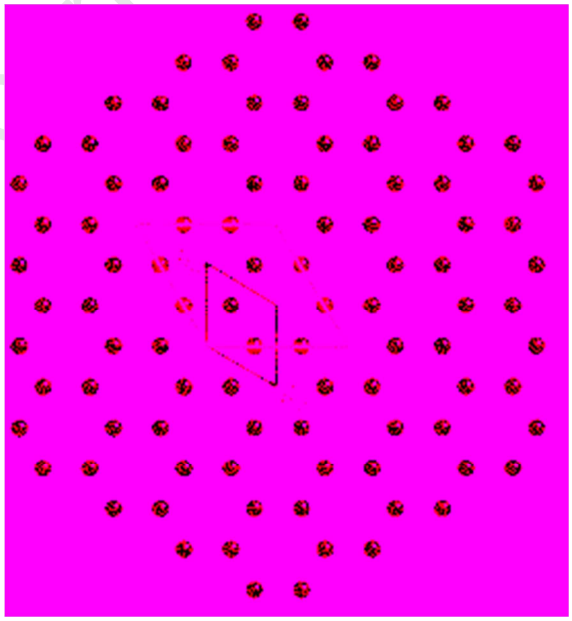

Fig. 4. 2D unit cells of graphene (____) and SrC_6 compound (____) rotated by 30 °.

In order to gather some information about the 3D structure, a notably approach consists in performing a diffraction pattern by the rotating crystal method. The whole *hkl* strata are effortlessly identified and indexed (*Fig. 5*).

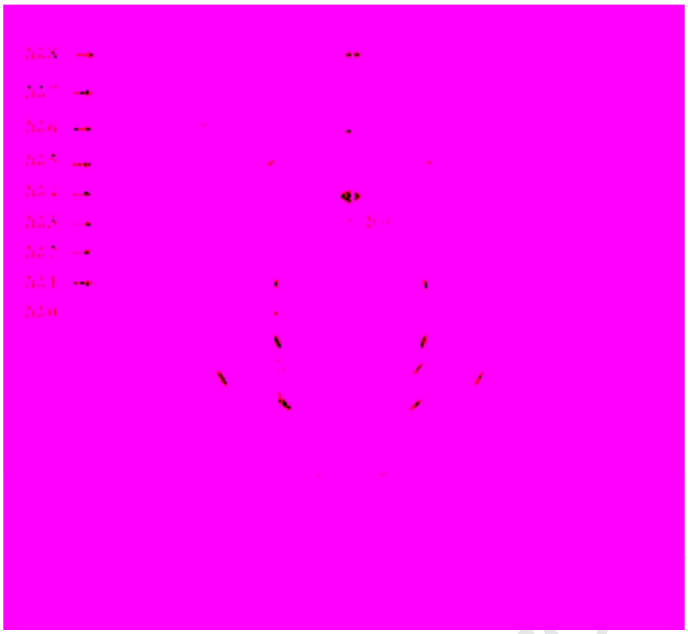

Fig. 5. Rotating crystal pattern obtained by X-ray diffraction (Mo anticathode) of the SrC_6 compound.

We can also observe in the perpendicular direction the [*hk*] rows whose first one is attributed to [10] with an inter-reticular distance of 373 pm for the (100) reflection, corresponding to a value of **a** parameter equal to 430.7 pm, close to $a_G\sqrt{3}$. This result, matching with a hexagonal unit cell, comes out as an additional confirmation of the SrC_6 stoichiometry.

Furthermore, the intensities of the 00*l* spots of the GIC, especially 004, 006 and 008 reflections, and the presence of the 200 reflection of Sr are in conformity with the results presented *Fig. 3*. These 00*l* reflections obey to a diffraction condition $l = 2n$ (n = integer number). There is also agreement between *hk*0 diffraction pattern (*Fig.3*) and the equatorial strata.

Additional investigation shows the absence of the 001 reflection together with the presence of the 101 one. This reveals that the repeat distance I_C (494 pm) is equal to half the **c** lattice parameter (988 pm). This feature must be associated to the AαAβAα stacking sequence (A = carbon layer; α and β = strontium layers) along the $\vec{c}$ axis. This set of collected data demonstrates that SrC_6 crystallizes in a hexagonal structure with a $P6_3/mmc$ space group and lattice parameters: a = b = 431 pm and c = 988 pm. Wyckoff's atomic positions are consequently listed below, and the representation of the SrC_6 compound is given in *Fig. 6.*

Carbon: 12 atoms 12i $(1/3, 0, 0)$

Strontium: 2 atoms 2c $(1/3, 2/3, 1/4)$

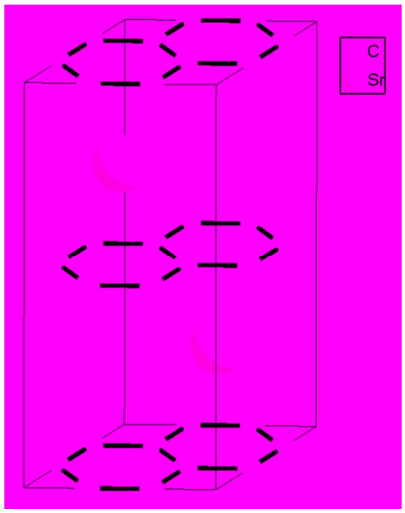

Fig. 6. Hexagonal unit cell ($P6_3/mmc$ space group) of SrC_6 compound with a = b = 431 pm and c = 988 pm.

Consecutively, it is possible to calculate structure factors and intensities of the *hkl* reflections. They are gathered in *Table 2*.

Table 2. Structure factors and intensities of SrC_6 reflections.

hkl	**d_{hkl} (pm)**	**Structure factors**	**F_{hkl}**	**I_{calc}**
001	988	0	0	0
002	494	$12f_C - 2f_{Sr}$	-7.71	0.45
100	373	$-f_{Sr}$	-32.86	18.30
101	349	$-\sqrt{3}\,f_{Sr}$	-56.21	100.00
003	329	0	0	0
102	298	f_{Sr}	31.37	26.43
103	247	$\sqrt{3}\,f_{Sr}$	51.77	59.16
004	247	$12f_C + 2f_{Sr}$	102.1	38.35
110	215	$-6f_C + 2f_{Sr}$	38.36	14.04
111	210	0	0	0
104	206	$-f_{Sr}$	-28.18	14.44
112	197	$-6f_C - 2f_{Sr}$	-72.99	92.56
005	197	0	0	0
200	186	$-f_{Sr}$	-27.14	6.02
201	183	$\sqrt{3}\,f_{Sr}$	46.67	34.91
113	180	0	0	0
202	174	f_{Sr}	26.4	10.58
105	174	$-\sqrt{3}\,f_{Sr}$	-45.73	31.76
006	164	$12f_C - 2f_{Sr}$	-21.88	1.13
203	162	$-\sqrt{3}\,f_{Sr}$	-44.3	27.46
114	162	$-6f_C + 2f_{Sr}$	36.54	18.69
106	150	f_{Sr}	24.7	7.84
204	149	$-f_{Sr}$	-24.56	7.65
115	145	0	0	0
210	141	$-f_{Sr}$	-23.93	6.82
211	139	$-\sqrt{3}\,f_{Sr}$	-41.24	40.06

007	141	0	0	0
212	135	f_{Sr}	23.47	12.53
205	135	$\sqrt{3}\, f_{Sr}$	40.65	18.81
116	130	$-6f_C - 2f_{Sr}$	-58.19	36.92
107	132	$\sqrt{3}\, f_{Sr}$	40.09	17.71

Regarding the intensities, there is a very good match between calculated values in Table 2 and the experimental ones observed in 00*l* and *hk*0 diagrams (*Fig. 1* and *3* respectively) as well as in rotating crystal pattern (*Fig. 5*).

4. Conclusion

Several attempts were made in order to obtain bulk SrC_6 GIC by exploring different synthesis routes. The solid-liquid method using LiCl-KCl eutectic mixture has proved its efficiency of synthesizing bulk first stage binary compounds with several metal in different families: alkali, alkaline-earth and lanthanides. Especially, we succeeded in obtaining a fully intercalated first stage SrC_6 GIC.

An extensive structural study was carried out for the first time on such a bulk sample. It is definitively shown that SrC_6 crystallizes in a hexagonal unit cell with the $P6_3/mmc$ space group (as most MC_6 compounds) with a = b = 431 pm and c = $2I_C$ = 988 pm.

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Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: