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Chemical vapor transport for intercalation reactions: synthesis of a 1st stage DyCl₃ graphite intercalation compound

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Abstract

In this paper, we develop a chemical vapor transport process involving the gaseous species DyAl₃Cl₁₂ (g) in order to perform the intercalation of dysprosium trichloride into graphite. Even if it is known that such a reaction must be performed under chlorine atmosphere, this work reveals that an increase of the Cl₂ pressure in the synthesis reactor improves the intercalation yield. By combination of gravimetric measurement, EDX analysis and 00 l X-ray diffraction experiments, we evidence the synthesis of a novel 1st stage DyCl₃-Graphite Intercalation Compound (GIC). The sample obtained in this study is a mixture of 1st stage DyCl₃-GIC and 2nd stage AlCl₃-GIC. However, considering the 1st stage DyCl₃-GIC, the data collected in this work are in agreement with a 1c repeat distance of 982 pm and a C_{8.1}DyCl_{3.9} formula. Along the c -axis, the intercalated sheet is three-layered and exhibits a Cl-Dy-Cl stacking sequence existing in pristine chloride.

Keywords: Graphite; Intercalation Compounds; Chemical Vapor Transport; Lanthanide metal trichloride; X-ray diffraction

1. Introduction

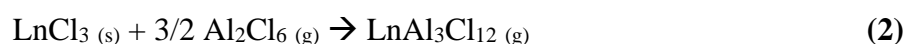
During the last decade, intercalation into graphite has been the subject of various theoretical and experimental studies. On the one hand, the scientific community still studies the intercalation of alkali metals and alkaline-earth metals into graphite. Indeed, the intercalation of lithium into graphite is well known as it is involved in the Li-ion battery

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technology. However, numerous works have been published concerning Li-based GIC in order to exhaustively characterize the staging phenomenon [1-3]. Moreover, regarding the need to develop post Li-ion technologies, the ability of sodium, potassium, magnesium or calcium to intercalate carbon-based materials and corresponding compounds can be considered [4-7]. On the other hand, since the Nobel Prize attributed to Novoselov and Geim in 2010 regarding their work on graphene, numerous kinds of 2D materials have been investigated regarding their synthesis and their structural and physical properties. Among the different classes of materials, carbon-metal compounds are one family represented for instance by MXene [8], intercalated graphene [9] and graphite intercalation compounds [10].

Since 1932 and the first intercalation of ferric chloride FeCl₃ into graphite by Thiele [11], numerous varieties of metal halides graphite intercalation compounds (MCl_x-GIC) have been synthesized and characterized regarding their structural and physical properties [12]. The main way of synthesis of such compounds consists in the reaction between pristine graphite and metal halide in the gas phase. By adjusting the reactant amount and the reaction temperature, it is easy to control the stage of the GIC, *i.e.* the ratio of van der Waals galleries filled by the intercalant species. Since the first work of Vickery *et al.* in 1957 [13], lanthanide trichlorides graphite intercalation compounds (LnCl₃-GIC) represent a hardly known class of compounds due to difficulties for preparing samples. If some authors mention the possibility to synthesize high-stage LnCl₃-GIC (with stage 2 < s < 4) by direct action of gaseous LnCl₃ (with Ln = Sm, Eu, Tb or Ho [14-17]), it appears tricky to prepare 1st or 2nd stage GIC.

Based on Stumpp's work [18-19], we developed in the laboratory a specific protocol called "heterocomplex way" consisting in the chemical vapor transport of lanthanide trichlorides towards graphite using aluminum trichloride as transport vector. This assisted way of intercalation allowed us to synthesize stage-2 LnCl₃-GIC using gaseous Al₂Cl₆ dimer as transport agent, with or without co-intercalation of this latter [20-22]. As oxidation of graphite and intercalation of LnCl₃ take place simultaneously, this way of synthesis requires processing under chlorine gas acting as oxidant atmosphere [16,23]. The successive steps occurring during the whole process can be written as followed:



Considering these previous results concerning LnCl_3 -GIC, we focused our effort on the synthesis of 1st stage LnCl_3 -GIC by adjusting reaction parameters and selecting appropriate lanthanide trichloride. On one hand, it appears necessary to increase the oxidation of graphite in order to reach a 1st stage GIC. On another hand, previous studies have revealed that heavy LnCl_3 ($\text{Ln} = \text{Dy} \rightarrow \text{Lu}$) which exhibit a lamellar structure are more easily intercalated into graphite. So, in this study, LnCl_3 is chosen among the aforementioned chlorides presenting in pristine state a pseudo-lamellar crystal structure with a chloride-lanthanide-chloride stacking sequence along its c -axis [21,24]. Moreover, the selected rare-earth metal trichloride needs favorable thermodynamic properties in order to form gaseous complexes with aluminum trichloride. Especially, the vapor pressure of the formed $\text{LnAl}_3\text{Cl}_{12}$ molecule in the gas phase must be sufficiently high in order to ensure subsequent LnCl_3 intercalation, what is observed only for a narrow range of temperature [25,26].

Based on all these criteria, we experiment the intercalation of dysprosium trichloride into graphite by “hetero-complex way” under oxidizing conditions. This paper deals with synthesis details and structural properties of the obtained GIC.

2. Materials and Methods

In a glove box under dry air, anhydrous powders of DyCl_3 (purity 99.9% provided by Aldrich®) and AlCl_3 (purified by sublimation under chlorine) are mixed together in an agate mortar. Chloride mixtures ($m_{\text{DyCl}_3} = 450$ mg; $m_{\text{AlCl}_3} = 90$ mg) and graphite ($m_{\text{C}} = 30$ mg) are introduced separately in a two bulbs Pyrex tube [27] sealed under pressure of chlorine $P_{\text{Cl}_2} = 0.8$ atm. A pyrolytic platelet of graphite is cut out in a Highly Oriented Pyrolytic Graphite block (HOPG - Union Carbide - 5 x 0.5 x 0.2 mm) and used for structural characterization. It is important to use such a small sample that allows to favor the diffusion of the intercalated species into graphite. As the mass of the platelet is low, and regarding the adequate molar ratio between graphite and dysprosium trichloride, some graphite powder is added but is not considered for structural characterizations. Indeed, it is well known that two different varieties of graphite will behave differently versus the expected intercalated species, leading to different GIC. After sealing, the glass ampoule is placed in a two-heating zone furnace for 3 weeks under temperature gradient of 10 K with graphite positioned on the hotter zone in order to avoid any condensation phenomenon on the surface of graphite. Regarding the work of

Wang *et al.* concerning the thermodynamic stability of $\text{DyAl}_3\text{Cl}_{12}$ gaseous complex, the optimal intercalation temperature is evaluated to be 778 K [26,28] which is the imposed temperature on the graphite zone. Further details concerning the way of synthesis can be retrieved in [21].

Elementary composition of the sample is evaluated by combination of weight uptake measurements and Energy Dispersive X-ray Spectroscopy (Philips CM20 Transmission Electron Microscope operating at 200 kV equipped with EDX detector). EDXS allows the evaluation of the chemical composition of the intercalated species (atomic content in Dy, Al, and Cl). Then, gravimetric measurements is used to determine the mass variation $\Delta m/m_0$ (Δm is the weight uptake and m_0 the initial mass of graphite) of the graphite pristine host, leading to the formula of the GIC.

X-Ray diffraction experiments are performed using a $\theta/2\theta$ Inel goniometer equipped with a molybdenum anticathode ($\lambda_{\text{MoK}\alpha 1} = 70.926$ pm). By adjustment of the intercalated platelet orientation of the goniometric head, it is possible to record specifically the $00l$ reflections. The indexation of the $00l$ pattern lead to determine the the c -axis repeat distance I_c . Finally, the quantitative analysis of the collected intensities allows the modeling of the stacking sequence of the GIC along the c -axis [29].

3. Results

3.1 $00l$ X-ray diffraction

Using the intercalated pyrolytic platelet of graphite, it is possible to record separately the $00l$ X-ray diffraction pattern presented in Figure 1.

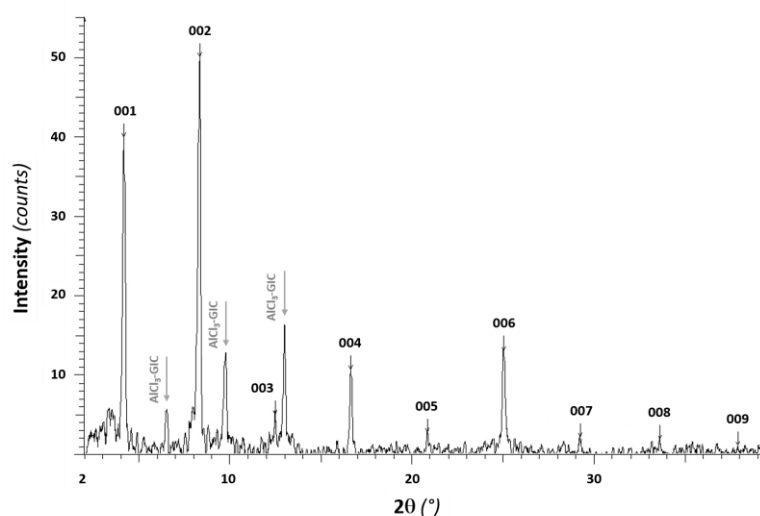


Figure 1: $00l$ X-ray diffraction pattern ($\lambda_{\text{Mo-K}\alpha 1} = 70.926$ pm) of the DyCl_3 -GIC.

The latter reveals two series of individualized reflections. The first family including the highest intensity lines can be indexed considering a repeat distance along the c -axis $I_c = 982$ pm. Other $00l$ peaks are indexed considering a stage-2 AlCl_3 -GIC with mean c -axis repeat distance $I_c = 1256$ pm and deduced interplanar distance equals to 921 pm.

Assuming a first stage DyCl_3 -GIC, such a repeat distance leads to an interplanar distance d_i equals to 982 pm, which can be compared with values retrieved in the literature for various intercalated lanthanide trichlorides reported in Table 1.

LnCl_3	Stage (s)	I_c (pm)	d_i (pm)	Reference
(Sm \rightarrow Lu) Cl_3	2-4	1295-1965	960	[19]
Sm Cl_3	2	1294	959	[20]
Eu Cl_3	2	1328	993	[15]
Gd Cl_3	2	1329	994	[20]
Tb Cl_3	2	1305	970	[20]
Dy Cl_3	2	1314	979	[21]
Ho Cl_3	2	1313	978	[22]

Table 1: c -axis structural data retrieved from the literature concerning various LnCl_3 -GIC.

First, the work of Stumpp refers to an mean interplanar distance of 960 pm [19], slightly lower than the one determined in this work but higher than the value of 940-950 pm classically admitted for AlCl_3 or transition metal chlorides intercalated into graphite [30]. Mainly, the value determined by Stumpp *et al.* is attributed to the presence of co-intercalated aluminum trichloride together with the obtaining of high-stage LnCl_3 -GIC. The d_i value of samarium-based GIC is also low, but this result is also easily explained by massive co-intercalation of AlCl_3 . Finally, regarding heavier LnCl_3 , their interplanar distance is closed to the one determined in this work, especially considering the second stage DyCl_3 -GIC. So, we can conclude that a 1st stage DyCl_3 -GIC has been successfully synthesized. This result underline the need to realize such an intercalation reaction under oxidative conditions. Indeed, previous works leading to 2nd stage LnCl_3 -GIC were realized under chlorine pressure $P_{\text{Cl}_2} = 0.5$ atm whereas in this work, the pressure is increased of 60% and reaches 0.8 atm. This experimental parameter appears as a key point in order to reach the saturation of graphite, *i.e.* the formation of first stage compounds.

3.2 Chemical composition

EDXS analysis performed on intercalated platelet confirms that both dysprosium and aluminum are intercalated into graphite (Fig. 2).

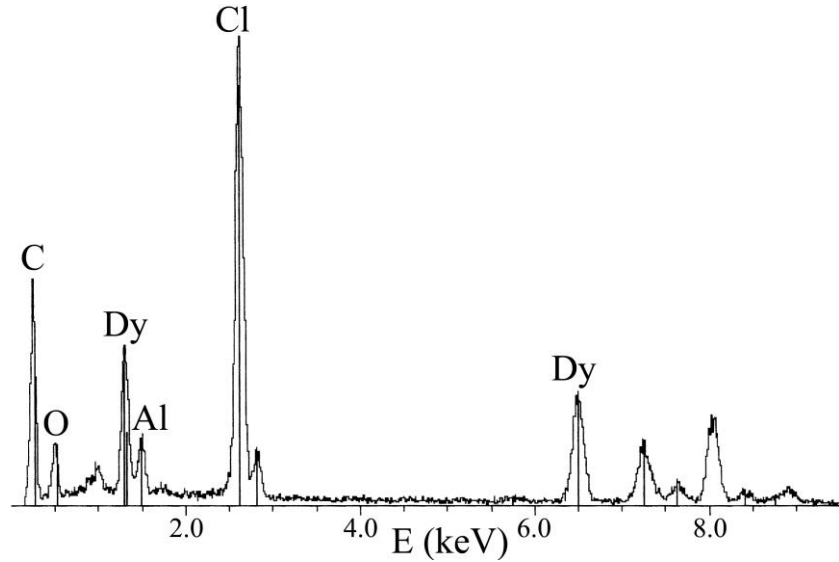


Figure 2: EDX spectrum of 1st stage $C_{10.4}Dy_{0.64}Al_{0.36}Cl_{3.70}$ GIC.

By combination of the atomic ratio Dy/Cl, Al/Cl and Dy/Al retrieved from EDX, and considering the weight uptake of graphite after intercalation, the global composition of the sample is $C_{10.4}Dy_{0.64}Al_{0.36}Cl_{3.70}$.

Considering the Dy/Al atomic ratio, we assume that the sample is composed for two third of 1st stage $DyCl_3$ -GIC and one third of 2nd stage $AlCl_3$ -GIC. Considering this ratio and regarding the chemical composition of corresponding GIC ($C_{8.65}DyCl_{3.86}$ deduced from 2nd stage GIC [20] and $C_{18}AlCl_{3.3}$ retrieved from [18]), it is possible to propose an expected composition $C_{11.7}Dy_{2/3}Al_{1/3}Cl_{3.68}$ in very good agreement with the aforementioned experimental composition. So, this analysis confirms the presence in the sample of mainly 1st stage $DyCl_3$ -GIC with a minor fraction of 2nd stage $AlCl_3$ -GIC. It should be noted that in this sample, the excess of chlorine is remarkably high, what illustrates the important electronic charge transfer between host graphite and metallic chlorides playing the role of electron acceptor. This is attributed to the highly electropositive nature of dysprosium regarding its electronegativity value on Pauling's scale ($\chi_{Dy} = 1.22$).

3.3 Stacking sequence of stage-1 DyCl₃-GIC

Considering exclusively the $00l$ reflections attributed to 1st stage DyCl₃-GIC, the stacking sequence of the GIC is investigated by quantitative analysis of the $00l$ reflections [29]. The modeling of the electronic density profile can be elucidated by comparing $00l$ structure factors issued from modeling (F_{00l}^{calc}) with those calculated from experimental data (F_{00l}^{exp}). Here, the stacking sequence adopted by the intercalated chloride is determined to be a three-layered intercalated sandwich chlorine-metal-chlorine between graphene planes. The crystallographic data are given in Table 2, and the compared experimental and theoretical 1D c -axis electronic density profiles are superimposed in Figure 3.

$00l$	2θ (°)	d_{00l} (pm)	I_c (pm)	F_{00l}^{exp}	F_{00l}^{calc}
1	4.1	985	985	52.3	52.3
2	8.3	492	984	76.1	76.3
3	12.5	327	981	-27.1	-28.7
4	16.6	245	980	49.6	49.5
5	20.8	196	980	28.0	35.6
6	25.1	164	984	100.0	100.0
7	29.2	140	980	54.3	53.9
8	33.6	123	984	37.6	55.2
9	37.9	109	981	-32.2	-0.8

Table 2: Experimental and calculated structure factors of the $00l$ reflections used for the calculation of the electronic density profile of 1st stage DyCl₃-GIC.

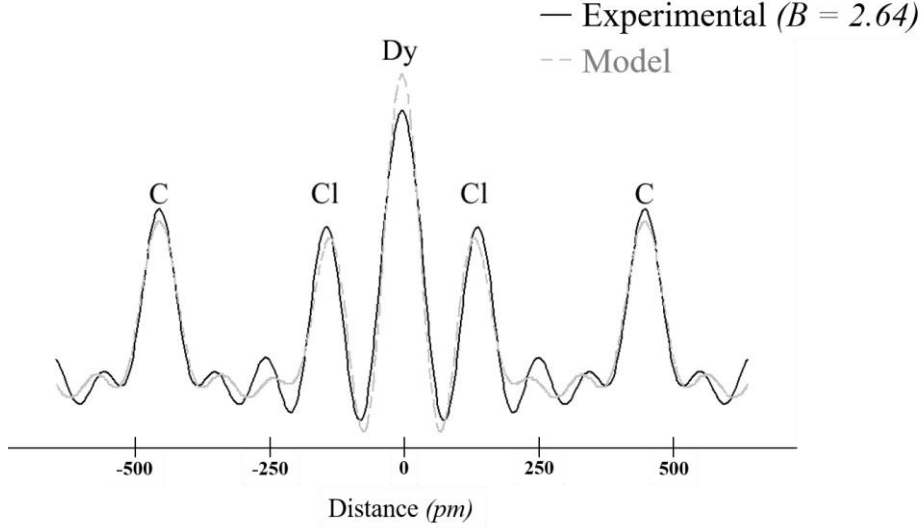


Figure 3: 1D c -axis electronic density profiles of the 1st stage DyCl_3 -GIC. Calculated and experimental profiles are drawn in grey dash lines and black line respectively.

The characteristics of the different atomic planes constituting the intercalated sheet (position along the c -axis, atomic content) are summarized in Table 3.

Element	C	Dy	Cl
z_i (pm)	± 4.91	0	± 1.54
n_i (atoms)	4.05	1	1.96

Table 3: structural model proposed for stage-1 DyCl_3 -GIC.

The determined general formula is $\text{C}_{8.1}\text{DyCl}_{3.9}$ ($R_F = 2.9\%$ for $B=2.64$).

In this model, the comparison between experimental and calculated $00l$ structure factors leads to residual factor $R_F = 2.9\%$ with nine reflections taken into account for calculation. This R_F value attests of an accurate determination of the c -axis stacking sequence. A Debye-Waller coefficient B has been set at $B = 2.67$ in order to reconstitute thermal agitation. In the work of Leung *et al.* [29], the Debye-Waller factor is described as follow:

$$B_j = 8 \cdot \pi^2 \langle Z^2 \rangle \quad (4)$$

with $\langle Z^2 \rangle$ the mean-squared thermal displacement of the layers normal to the diffracting planes in \AA^2 .

Regarding the modeled stacking sequence, several common points can be highlighted by comparison with 2nd stage DyCl_3 -GIC and 2nd stage HoCl_3 -GIC, as reported in Table 4. Such

a comparison is not suitable with Sm, Gd, and Tb-based GIC as these compounds are co-intercalation compounds with aluminum trichloride which impacts the stacking sequence.

GIC	Ln-Cl distance (LnCl ₃ thickness) (<i>pm</i>)	C-Cl distance (<i>pm</i>)	<i>d_i</i> (<i>pm</i>)	Composition
1 st stage DyCl ₃	± 154	337	982	C _{8.1} DyCl _{3.90}
2 nd stage DyCl ₃	± 149	338	974	C _{17.3} DyCl _{3.86}
2 nd stage HoCl ₃	± 157	331	976	C _{24.8} HoCl _{3.78}

Table 4: comparison of the *c*-axis stacking sequences between 1st stage DyCl₃ GIC with 2nd stage DyCl₃ and HoCl₃-GIC.

It clearly appears that the lanthanide-chloride distance between atomic planes is almost the same, leading to equivalent thickness for intercalated sheets. This result is in agreement with the fact that Cl-Ln-Cl stacking sequence existing in pristine chlorides (AlCl₃ isotype structures [24]) is maintained after intercalation. Moreover, the distance between positively charged graphene planes and negatively charged chlorine planes is almost constant for dysprosium-based GIC. For the holmium-based GIC, the distance is shorter, in agreement with a smaller ionic radius for Ln³⁺ ion together with a lower excess of chlorine. Finally, it can be noted that the interplanar distance is a bit higher for the 1st stage GIC which exhibits a higher Ln/C atomic ratio.

4. Conclusions

In this study, we report for the first time the synthesis of a first stage DyCl₃-GIC synthesized by chemical vapor transport process (“hetero-complex way”). The possibility to obtain such a rich 1st stage GIC is ensured by a reaction performed under strongly oxidative conditions, with a high pressure of chlorine P_{Cl₂} in the reactor. The 1st stage DyCl₃-GIC has been characterized by crystallographic analysis combined with gravimetric measurements and EDX analysis. First stage DyCl₃-GIC exhibits a repeat distance *I_c* = 982 pm, in agreement with the values mentioned in the literature for other lanthanide trichlorides GIC. The Fourier transform of its 00*l* structure factors confirms that stage-1 DyCl₃ is obtained. The stacking sequence of the intercalated sheet along the *c*-axis consists in a Cl-Dy-Cl three-layered sandwich pre-existing in pristine chloride.

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.

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