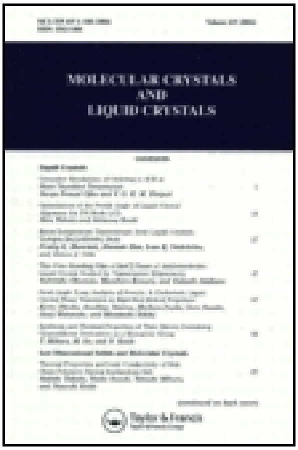

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A New Graphite Intercalation Compound Containing Sodium Associated with Oxygen

Mohammed El Gadi [a], Albert Hérold [a], Claire Hérold [a], Philippe Lagrange [a], Michèle Lelaurain [a] & Jean-François Marêché [a]

[a] Laboratoire de Chimie du Solide Minéral, (U.R.A. C.N.R.S. 158) B.P. 239, 54506, Vandoeuvre-lès-Nancy Cédex, France

Version of record first published: 23 Oct 2006.

To cite this article: Mohammed El Gadi, Albert Hérold, Claire Hérold, Philippe Lagrange, Michèle Lelaurain & Jean-François Marêché (1994): A New Graphite Intercalation Compound Containing Sodium Associated with Oxygen, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 29-34

To link to this article: http://dx.doi.org/10.1080/10587259408050078

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 29–34
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

A NEW GRAPHITE INTERCALATION COMPOUND CONTAINING SODIUM ASSOCIATED WITH OXYGEN

MOHAMMED EL GADI, ALBERT HÉROLD, CLAIRE HÉROLD, PHILIPPE LAGRANGE, MICHÈLE LELAURAIN AND JEAN-FRANÇOIS MARÊCHÉ
Laboratoire de Chimie du Solide Minéral (U.R.A. C.N.R.S. 158)
B.P. 239, 54506 Vandoeuvre-lès-Nancy Cédex, France.

Abstract A new second stage blue phase of donor-type with an interplanar distance of 745 pm has been synthesized by reaction of graphite with partly oxidized sodium. It contains oxygen in form of peroxide ions.

INTRODUCTION

In graphite intercalation chemistry, the behaviour of sodium strongly differs from that of the other alkali metals. It is well known that lithium and heavy alkali metals easily form the graphite intercalation compounds (GICS) of first stage LiC_6 or MC_8 (M = K, Rb, Cs). On the contrary, to date, no sodium GIC of stage lower than the fourth has been synthesized under normal pressure. After a series of several authors negative trials, the first synthesis of a well defined sodium GIC was carried out in 1958 by Asher and Wilson[1,2]. A mixture of sodium and graphite was heated at 400°C during 30 minutes under an helium atmosphere containing less than 10 ppm of oxygen, leading to a violet-coloured phase of 8th stage (NaC_{64}), which contains intercalated layers with the same "octal structure" than in the MC_8 first stage compounds of the heavy alkali metals.

Twenty years later, Métrot et al.[3] studied the reaction of sodium vapour with graphite in copper or stainless steel tubes sealed under vacuum. Pure phases of stage s, equal to 8, 7 and 6 with an average interplanar distance of 452 pm and of general formula NaC_{8s} have been synthesized at decreasing temperature (but with an adverse effect on the kinetics). Whereas at 400°C the compound NaC_{64} of stage 8 is formed in two weeks, at 135°C a mixture of compounds of stages 6, 5 and 4 and unreacted graphite was obtained after 4 months. These results confirm and extend those of Asher. Moreover, the decrease in stage with the reaction temperature clearly shows that the difficulty of sodium intercalation is mainly of a thermodynamic nature. This conclusion partly confirms that deduced by Dzurus et al.[4] from an electrostatic (or ionic) model of the GIC. Nevertheless, several observations indicate that the reaction of sodium and graphite often leads to irregular results. Thus, one can not exclude that small amounts of other elements such as O, H, N, ... play a role in intercalation, in agreement with some experiments of Dzurus et al.[4].

It is well known that the volume of an alkali metal GIC is smaller than the sum of the volume of the pristine materials. Thus, one can hope to synthesize GIC very rich in metal by compressing graphite with the molten metal. In the case of the sodium-graphite system, the first experiments by Belash et al.[5] have led to compounds NaC_2 and NaC_3 near 35 - 45 kBar between 450 - 700°C. More precise determinations by Avdeev et al.[6] using volume measurements under 40 kBar at 300°C led to a $NaC_{2.6}$ phase of stage one with an interplanar distance of 704 pm. According to the authors, the sodium intercalated sheets are three-layered. Udod and Genchel [7] have described a red NaC_4 compound and an orange NaC_3 phase with interplanar distances of 799 and 803 pm synthesized under 43 kBar at 750°C and 840°C respectively. From the intensities of the *00l* X-Ray reflections, the authors conclude that the intercalated sodium sheets are two-layered.

Intercalated sheets containing two sodium layers or more can also be stabilized by association of the alkali metal with one or two other elements. Indeed, Billaud and Hérold [8] have synthesized graphite-sodium-baryum intercalation compounds by heating graphite with Na-Ba alloys of different compositions. The C/(Na+Ba) ratio is 7 to 8 for the richest compound which is of stage 2, with an interplanar distance of 738 pm. The in-plane lattice of the intercalated sheets is hexagonal and parallel to that of graphite, but not commensurate, with a parameter of 636 pm.

As shown by Guérard et al.[9], sodium hydride reacts with graphite in a sealed glass tube, leading to compounds of stage 1 to 8, of formula $C_{2.5s}NaH$ to $C_{4.5s}NaH$ (s = stage) and with an interplanar distance variable from 730 to 760 pm.

Other GIC containing sodium associated with hydrogen and nitrogen have been prepared by Billaud and Hérold [10]. The synthesis was carried out by heating near 400°C in a stainless steel reactor graphite, sodium and uranium containing some hydrogen and nitrogen. The third stage was isolated and its analysis has given the formula $C_{10.7}Na(NH_2)_{0.5}$. The interplanar distance is 752 pm, the in-plane lattice of the intercalated sheets is hexagonal with a parameter of 1230 pm, five times the parameter of graphite. The large interplanar distance and the low value of the C/Na ratio (which would be 3.57 for a first stage) suggest that the intercalated sheets contain two sodium layers.

More recently, a new blue GIC of stage one with an interplanar distance of 921 pm, containing sodium cations associated with hydroxide anions, has been synthesized by dipping pyrographite samples or single crystals during several hours in the blue liquid formed by melting sodium with its hydroxide [11, 12]. The two-layered intercalated sheets, with a square in-plane lattice of parameter a equal to 341 pm, partly preserve the structure of the free hydroxide in its quadratic form.

EXPERIMENTAL

Recently we have synthesized a new blue GIC, by heating near 470°C during one or two days, in a nickel or stainless steel reactor, a pyrographite sample or a single crystal immersed in liquid sodium previously exposed to the atmosphere or to air diluted with argon. The new phase, which is not very reactive, can be separated from the excess of alkali metal by washing with alcohol or water.

The e/e_0 ratio of the sample thickness after and before intercalation which is included between 1.6 and 2, and the repeat distance I_c equal to 1080 pm deduced from the *00l* X-Ray reflections allow to conclude that the compound belongs to the second stage.

The same phase was synthesized by reaction of a pyrographite platelet with pure sodium mixed with sodium peroxide under an atmosphere of pure argon in a glove box : thus, this phase contains mainly graphite, sodium and oxygen. Its analysis was carried out as follows:

- the amount of graphite is determined by weighing the pristine sample
- the weight uptake after intercalation gives the sum : Na + O
- the sodium amount is obtained by burning the sample in air at 600°C in a silver crucible and titrating the ash with HCl 0.1 N
- the O amount is obtained by difference.

The average formula determined on four samples is $C_{4.75\pm0.05}Na_1O_{0.35\pm0.05}$. A qualitative analysis using the X-Ray dispersion accessory of a transmission electron microscope has shown that the composition of the new blue phase is quite homogeneous.

The intensities of the *00l* X-Ray reflections were measured and the experimental Fourier transform of the corresponding structure factors was compared to the theoretical one calculated for a five-layered model taking into account the chemical formula (figure 1). The best fitting of the two curves is obtained for the layers sizes and densities indicated in figure 1. In particular, the distance between the two oxygen layers (152 pm) is very close to that of the two oxygen atoms in the peroxide ion (150 pm). Thus, it is probable that oxygen is contained in the intercalated sheets in form of O_2^{2-} ions.

A flat camera X-Ray diagram (figure 2) shows that the in-plane unit cell of the intercalate is hexagonal, turned of ± 0.7° with respect to the graphene sheets axes but not commensurate. A precise determination of the a parameter from the ***hk0*** reflections has led to a value of 636 pm which is close to that of the Na_2O_2 unit cell (620.8 pm). This result confirms the presence of peroxide ions in the intercalated sheets.

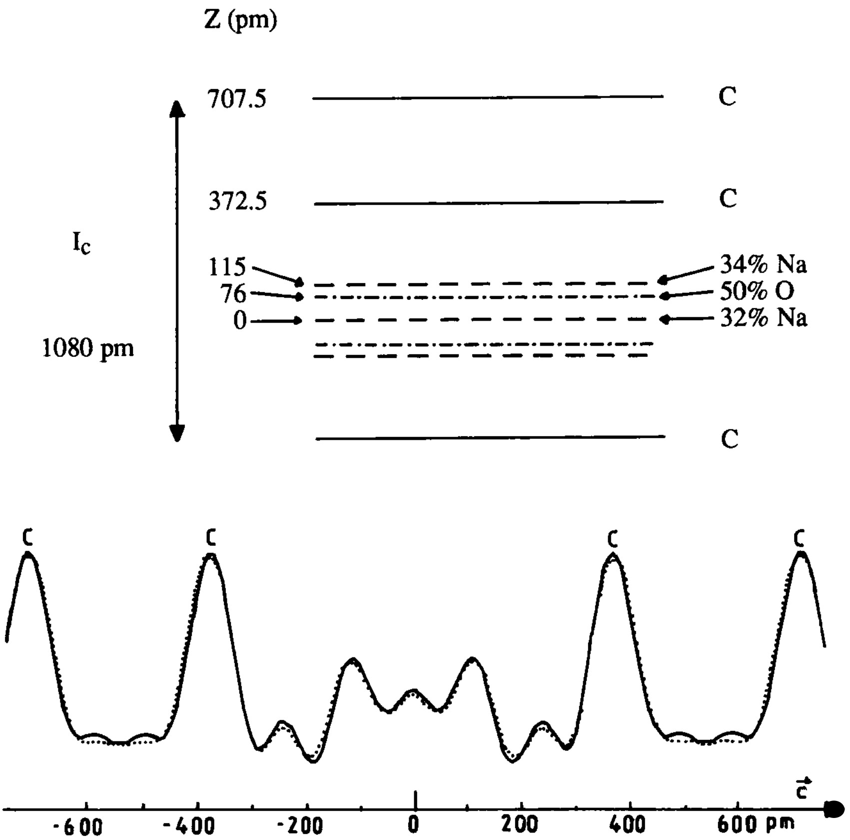

FIGURE 1 Five-layered sheet model
Electronic density profiles along the c-axis
(solid line : calculated; dashed line : experimental).

Intensity measurements of the X-Ray reflections along *hk* lines of the graphene and intercalate sublattices allow to propose the sequence AαBAαBAαB of the graphene sheets A, B and the intercalate sheets α.

The coefficient of thermal expansion is close to zero between 10 and 100 K as for all GICs, and of 40.10^{-6} between 200 and 300 K, as for KC_8.

The increase of the in-plane carbon-carbon distance which is 0.7 pm, allows to calculate a charge transfer to the graphene layers of 0.038 electron per carbon atom using the Pietronero-Strässler [13] relationship. On the other hand, if we suppose that the sodium atoms are completely ionized, the charge transfer calculated from the chemical formula is 0.137 e^-/C. The comparison between these two values suggests that the sodium ionization remains incomplete in the intercalated sheets, in agreement with the rather high first ionization potential of the sodium which is higher of about 20 percent than that of potassium.

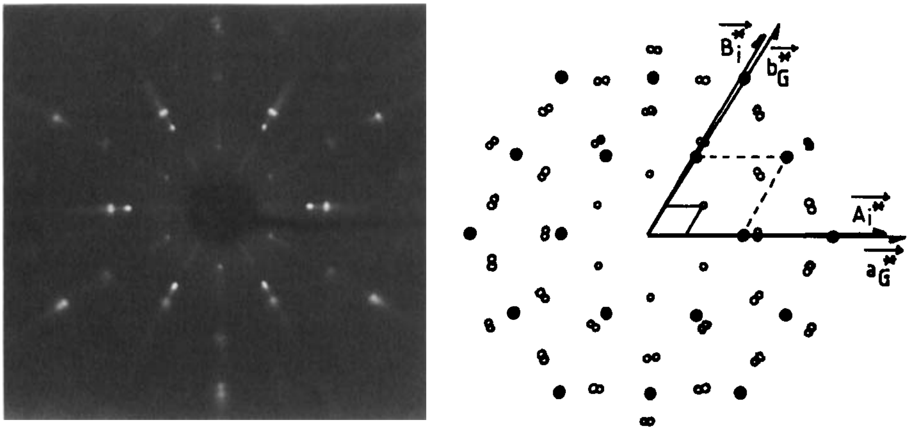

FIGURE 2 X-Ray flat camera diagram and reconstitution in the reciprocal space of the two hexagonal lattices : graphite (- - -) and intercalate (——).

CONCLUSIONS

The new blue GIC of stage 2 containing sodium and oxygen is original by the existence of three sodium layers and of peroxide ions in the intercalated sheets.

The air stability of the new blue phase, which is much higher than those of the binary alkali metal compounds, is probably a consequence of the low mobility of the sodium atoms in the galleries, due to the strong sodium-oxygen bonds. It should favorize the study of the physical properties of this original GIC.

Moreover, one can think that this new phase often plays a role in the attack of the carbon materials by sodium. In industrial conditions, sodium is often more or less oxidized, either by reaction with oxides or with gases containing a small amount of oxygen.

ACKNOWLEDGEMENT

The authors wish to thank Dr. Berger (Le Carbone Lorraine, Gennevilliers) for supplying pyrographite "PGCCL" samples.

REFERENCES

1. R.C. Asher and S.A. Wilson, Nature (London), 181, 409 (1958).
2. R.C. Asher, J. Inorg. Nucl. Chem., 10, 238 (1959).
3. A. Métrot, D. Guérard, D. Billaud and A. Hérold, Synth. Met., 1, 363 (1979/80).
4. M.L. Dzurus, G.R. Hennig and G.L. Montet, Proc. 4th Conf. Carbon (Buffalo, 1960), p.165.
5. I.T. Belash, A.D. Bronnikov, O.V. Zharikov and A.V. Palnichenko, Solid State Comm., 64, 1445 (1987).
6. V.V. Avdeev, V.A. Nalimova and K.N. Semenenko, Synth. Met., 38, 363 (1990).
7. I.A. Udod and V.K. Genchel, High Pressure Research, 8, 581 (1992).
8. D. Billaud and A. Hérold, Bull. Soc. Chim. Fr.,131 (1978).
9. D. Guérard, N.E. Elalem, C. Takoudjou and F. Rousseaux, Synth. Met., 12,195 (1985).
10. D. Billaud and A. Hérold, Carbon, 16, 301 (1978).
11. A. Hérold, M. Lelaurain and J.F. Marêché, C. R. Acad. Sc. Paris, Série II, 312, 361 (1991).
12. A. Hérold, M. Lelaurain and J.F. Marêché, Mater. Sc. Forum, 91-93, 89 (1992).
13. L. Pietronero and S. Strässler, Phys. Rev. Lett., 47, 593 (1981).