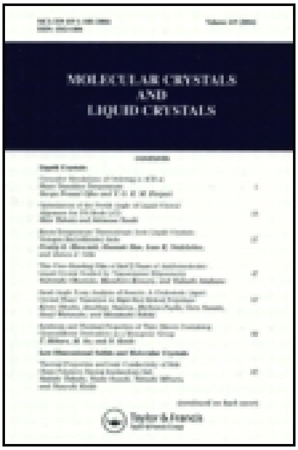

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Lotfi Reghai [a] & Herve Fuzellier [a]

[a] Laboratoire de Chimie du Solide Mineral CNRS. URA 158 Université de Nancy, I BP 239 54 506, Vandoeuvre-les-Nancy, France

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REACTION OF AMMONIA WITH GRAPHITE-POTASSIUM COMPOUNDS

LOTFI REGHAI and HERVE FUZELLIER
Laboratoire de Chimie du Solide Mineral CNRS.URA 158 Université de Nancy I
BP 239 54 506 Vandoeuvre-les-Nancy France

Abstract Reaction of ammonia vapor with a KC_8 GIC and treatment (vacuum and heating) produces a new second stage GIC : $K(NH_3)_{0.5}C_8$ with di = 815 pm. The stage 1 GIC can be obtained by reaction with potassium vapor. Similar treatment with KC_{24} leads to a stage 2 GIC : $K(NH_3)_{1.3}C_{24}$ with a smaller di = 648 pm. Synthesis conditions and organisation of the intercalated layers are discussed.

INTRODUCTION

About forty years ago, Rüdorff[1] and Rubisch[2] prepared ternary graphite intercalation compounds (GIC) with potassium and ammonia using two different methods:

- immersion of graphite powder in a metal ammonia solution
- reaction of liquid or vapor ammonia with the KC_8 GIC .

Both techniques yield ternary compounds $K(NH_3)_{2.0}C_{12s}$ (stage s = 1 or 2) with an interlayer distance about 650 pm.

More recently Solin and co-workers [3,4] have carefully studied the synthesis conditions of these GIC from KC_{24} with ammonia vapor in the pressure range 0 to 9.5 atm. They noted a dependence of the sandwich thickness (651 to 663 pm) with the composition $K(NH_3)_xC_y$, $0<x<4.33$ and the charge transfer : $f = 0.95$ for a stage 1 compound with x = 4.33.

EXPERIMENTAL

The binary lamellar compounds were prepared by using the usual "two bulb" method from distilled potassium and highly oriented pyrolytic graphite (HOPG). The KC_8 or KC_{24} samples were transferred from their Pyrex glass tube in the reaction vessel in a stainless steel glove box with purified argon atmosphere. The composition of these compounds was determined by weighing the HOPG pieces and the binary byproducts. Commercial grade ammonia was purified by condensing it onto potassium at -70°C, pumping off residual hydrogen; this procedure was repeated twice before warming up and stocking ammonia gas over anhydrous diphosphore pentoxide. The reaction vessels include a Young teflon stopcock and a rectangular glass tube containing the compound, apparatus convenient for X ray diffraction ((00l) lines) or in situ contactless electrical resistivity measurements. Composition of the ternary compounds was determined by chemical analysis at the CNRS analysis center.

REACTION OF NH_3 VAPOR WITH KC_8

Rubisch[2] observed exfoliation of the binary GIC during reaction with ammonia, even at 0°C. To avoid this phenomena, we used a low ammonia pressure ($P = 0.6$ atm) to react with KC_8 GIC (Figure 1.A) at room temperature or -20°C. In this latter case, the reaction process is slower (about 1h) and thickness increase is smaller. The reaction product is a mixture of two phases:

- a first stage ternary compound T_1 with $d_i = 646$ pm similar to Rüdorff compound
- a new first stage compound α with a large intercalate thickness: $d_i = 933$ pm.

Rüdorff's results must be taken in account with reaction of liquid NH_3 on KC_8 :

$$3\ KC_8 + 4\ NH_3 \text{ --------- } 2\ K(NH_3)_2C_{12} + K\ \text{(solvated)}$$

Intercalation of ammonia in the intercalated potassium layer produces a lower K density layer and expulsion of potassium. In our case, these expelled K atoms react with ammonia gas to create an intercalated layer with a higher potassium density than observed in KC_8, which suggests the formation of a double K layer similar to that in $KHgC_4$ or $KTl_{1.5}C_4$ [5,6].

To increase the proportion of the new phase, we used a primary vacuum treatment (Figure 1.B) which produces a mixture of T_1 ($d_i = 638$ pm) and α' ($d_i = 820$ pm): in both samples the NH_3/K ratio becomes smaller. Under high vacuum appears a new phase β (Figure 1.C) which is the second stage corresponding to the α phase. By heating the mixture at 70°C, a pure second stage compound $K(NH_3)_{0,5}C_8$ denoted as β is obtained (Figure 1.D): its interlayer distance $d_i = 815$ pm corresponds to a 3 sheets intercalated layer ($K\text{-}NH_3\text{-}K$).

Synthesis of the corresponding first stage compound needs additional potassium which can be obtained either by a bronze potassium-ammonia solution or by potassium liquid or vapor (vacuum and heating required). With liquid ammonia only the phases mixture $T_1 + \alpha$ can be obtained. Moreover, this β compound can react with potassium vapor at 220°C to prepare a new first stage compound, $K(NH_3)_{0.25}C_4$, with an interlayer distance $d_i = 837$ pm less than that of the α compound.

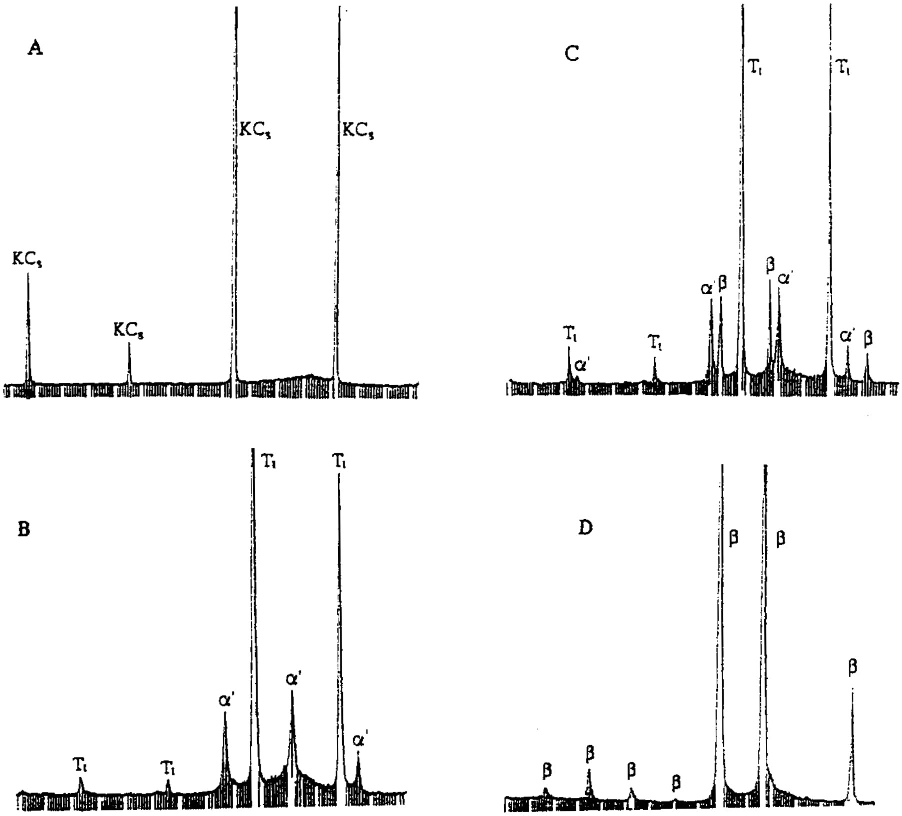

FIGURE 1 (00l) X ray diffractograms (Mo) : (A) KC$_8$ binary GIC

(B) phases mixture obtained after reaction with NH$_3$ followed by vacuum

(C) under high vacuum stage 2 β appears

(D) pure β compound after heating at 70°C for 18 h.

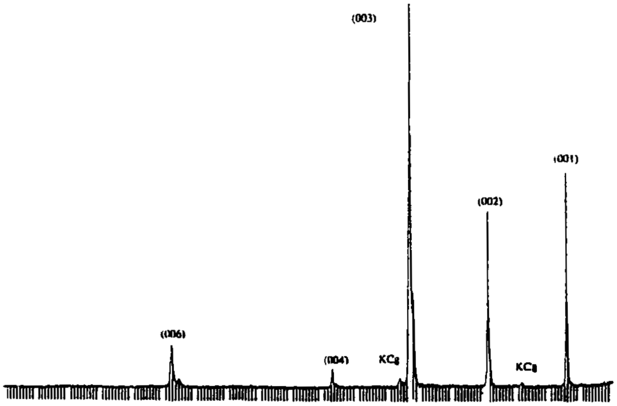

FIGURE 2 (00l) lines of X ray diffractogram (Mo) of the α compound K(NH$_3$)$_{0.25}$C$_4$

When the β compound is kept at 370°C with potassium vapor (T_K = 250°C), a second stage compound is obtained. It presents the same d_i = 540 pm as the first stage GIC prepared by Akusawa [7] by deamoniation of T_1 followed by reaction with K vapor.

REACTION OF AMMONIA GAS WITH KC_{24}

The reaction of ammonia gas with KC_{24} GIC (Figure 3.A) was realized with a low ammonia pressure (P = 0.6 atm). After reaction with ammonia vapor, a mixture of the well known ternary compounds $T_1 + T_2$ can be identified (Figure 3.B).Under vacuum, the mixture exhibit a larger amount of stage 2 compound. Treatment at 70°C for 18 h leads to a pure second stage compound $K(NH_3)_{1,3}C_{24}$ denoted as T'_2(Figure 3.C)

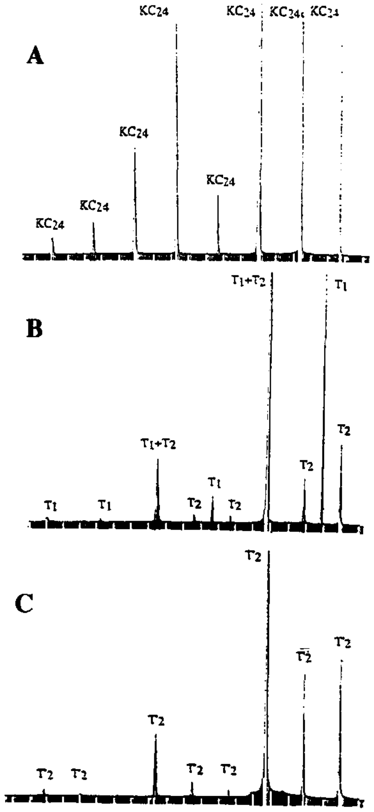

FIGURE 3 X ray diffraction patterns ((001) lines) (A) KC_{24} binary GIC

(B) phases mixture (T_1+ T_2) after reaction with NH_3 vapor

(C) T'2 compound after treatment under vacuum and heating at 70°C with an interlayer distance d_i = 648 pm.similar to that observed by Rüdorff during intercalation of K-NH_3 solutions in graphite at low temperature. Usually these ternary GIC present a liquid like intercalated layer, but in our conditions, it exhibits a two dimmensional organisation deduced from the crystallographic study.

CRISTALLOGRAPHIC STRUCTURE ALONG THE C AXIS

Contrary to the usual compounds T_1 and T_2 whose intercalated layers are desorganised[8], these new phases α , β and T_2 are well crystallised at room temperature.

The (00l) diffraction patterns have been analyzed using a two or three sheet intercalated layer model. The structure factors of the (00l) reflexions have been calculated to know their signs and to represent the Fourrier transforms of these data.

The electronic distribution picture, along the graphite c axis, confirms the validity of the three sheets model for the α and β compounds.

Our last evaluation for the β compound, with central ammonia molecules and lateral potassium atoms distant 120 pm from the ammonia sheet, gives a reliability factor of 14.5% when using the experimental composition $K(NH_3)_{0.6}C_8$ (Figure 4).

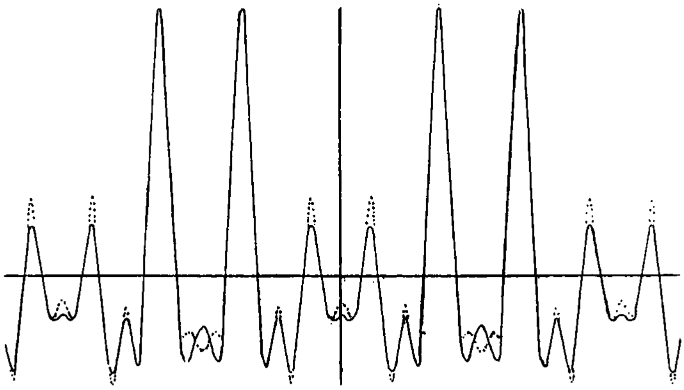

FIGURE 4 Electronic density along c axis for the β compound.
(dashed line : experimental, dotted line : calculated)

For the α compound$K(NH_3)_{0.3}C_4$, the distance K-NH_3 is 132 pm and the reliability factor of 12.7%.

In the case of the T'_2 compound, the best agreement (R = 10.9 %) between experimental and calculated values correspond to a single layer of potassium atoms and ammonia molecules corresponding to the experimental composition $K(NH_3)_{1.5}C_{24}$ (Figure 5).

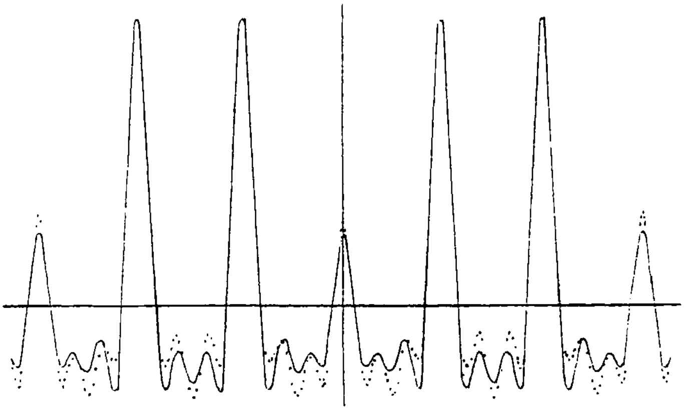

FIGURE 5 Electronic density along c axis for the T'$_2$ compound (dashed line : experimental, dotted line : calculated)

CONCLUSION

Ternary compounds graphite-potassium-ammonia cover a range of compositions attributed to a continuous substitution of K atoms by NH_3 molecules. Two dimensional organisation appears in the intercalated monolayer at low temperature, about the melting point of ammonia for $NH_3/K = 2$. For higher ratios, this 2D organisation appears at room temperature ($NH_3/K = 1,3$). When the potassium content increases ($NH_3/K = 0,5$) the intercalated layer can be modelled by a three sheet model in which ammonia molecules stabilize the instable potassium double layer corresponding to the limiting compound KC_4.

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