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

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Kazimierz Kaûki [a] & A. Waldemar Morawski [a]

[a] Institute of Inorganic Chemical Engineering, Technical University of Szczecin, ul. Pułaskiego 10, 70-322, Szczecin, Poland

Version of record first published: 23 Oct 2006.

To cite this article: Kazimierz Kaûki & A. Waldemar Morawski (1994): Preparation of K-Bi-Graphite Under Nitrogen, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 59-64

To link to this article: http://dx.doi.org/10.1080/10587259408050083

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 59–64
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Printed in the United States of America

PREPARATION OF K-Bi-GRAPHITE UNDER NITROGEN

KAZIMIERZ KAŁUCKI AND A. WALDEMAR MORAWSKI
Institute of Inorganic Chemical Engineering, Technical University of Szczecin, ul. Pułaskiego 10, 70-322 Szczecin, Poland

Abstract The ternary graphite intercalation compounds (GICs) of K-Bi-graphite have been synthesized. The preparation method under inert gas (nitrogen) and at atmospheric pressure has been tried. The intercalation of K-Bi alloy to the graphite has been successfully performed. The resulted K-Bi-GIC was quite air stable. Proposed preparation method is easier to carry out than under vacuum.

INTRODUCTION

Graphite Intercalation Compounds (GICs) are widely investigated in recent years with respect to the large possibility to design crystallographic and electronic structure and also their potential application. Since discovery of ternary GICs[1-3] they often have been studied because most of them become superconductors at low temperatures [4]. The more recent of these compounds are those obtained with bismuth. The bismuth possess electropositivity close to 2 and form alloy with the alkali metals. A wide range of new ternary compounds has been synthesized with the chemical formula MBi_xC_{4n}, in which M = K, Rb or Cs; n = stage index and $x \approx 0.6$. The K-Bi--graphite samples described by Lagrange et al.[5] have been obtained by heating K-Bi alloy with HOPG under vacuum. The resulted K-Bi-GIC was quite air stable.

Above method of K-Bi-GICs synthesis under vacuum is inconvenient from technological point of view. Therefore the purpose of this work is to try to prepare of K-Bi-GICs under nitrogen atmosphere.

EXPERIMENTAL

The samples preparation was carried out in a Pyrex glass ampoule which is shown in Figure 1. The binary K-Bi alloy was preprepared by reaction of metallic potassium with metallic bismuth at the temperature of 320 °C for 72 hours in ampoule filled with purified gaseous nitrogen. Then at the temperature of 20 °C the powdered Sri Lanka graphite was supplied

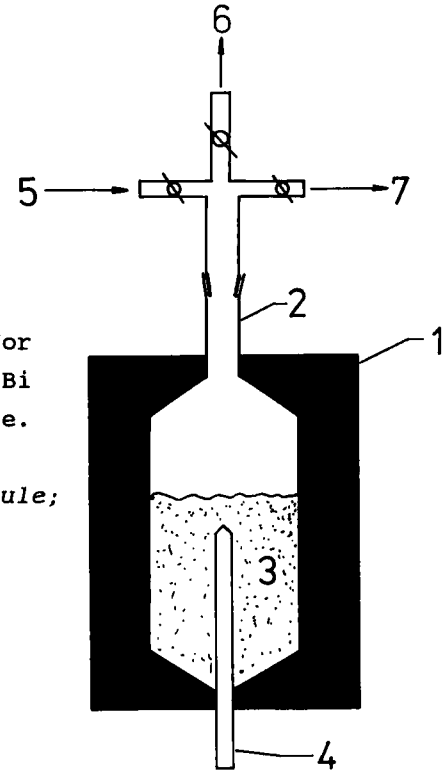


FIGURE 1 The Pyrex ampoule for preparation of both K-Bi alloy and K-Bi-graphite.

1 - electric furnace; 2 - ampoule;
3 - sample; 4 - thermowell;
5 - nitrogen; 6 - outlet;
7 - vacuum.

to the reactor and the temperature up to demanded temperature was increased. The following duration of the reaction and temperatures were used:

Sample	Temperature, ^{o}C	Reaction time, hrs
A	380	264
B	440	380
C	460	384

The resulted samples were analyzed by X-ray powder diffraction method and X-ray fluorescence spectroscopy using HZG-4 diffractometer and VRA-30 spectrometer. The surface morphology of samples were also observed by scanning electron microscopy of JEOL JSM-6100 type.

RESULTS

The total composition of samples is listed below:

sample "A" - $KBi_{0.9}C_{6.7}$
sample "B" - $KBi_{0.22}C_{6.32}$
sample "C" - $KBi_{0.1}C_{16.14}$

When compare chemical composition of K-Bi-graphite against background of preparation temperature one can observe the lowering of bismuth concentration with increasing preparation temperature. In addition, X-ray powder diffraction spectrums of sample "B" and "C" exhibit higher number of peaks than the spectrum of sample "A". The complicated and nonuniform phases composition of K-Bi-graphite in samples "B" and "C" is to be suspect.

On the contrary, the sample of "A" prepared at lower temperature, gives more homogeneous phase of intercalate with distinct (001) family of reflection values (Figure 2): 2640 pm (001); 1320 pm (002); 880 pm (003); 660 pm (004); 528 pm (005); 440 pm (006); 377 pm (007); 330 pm (008); 293 pm (009); 264 pm (0010);.....165 pm (0016). The reflections of (008) and (0016) were the most intensive.

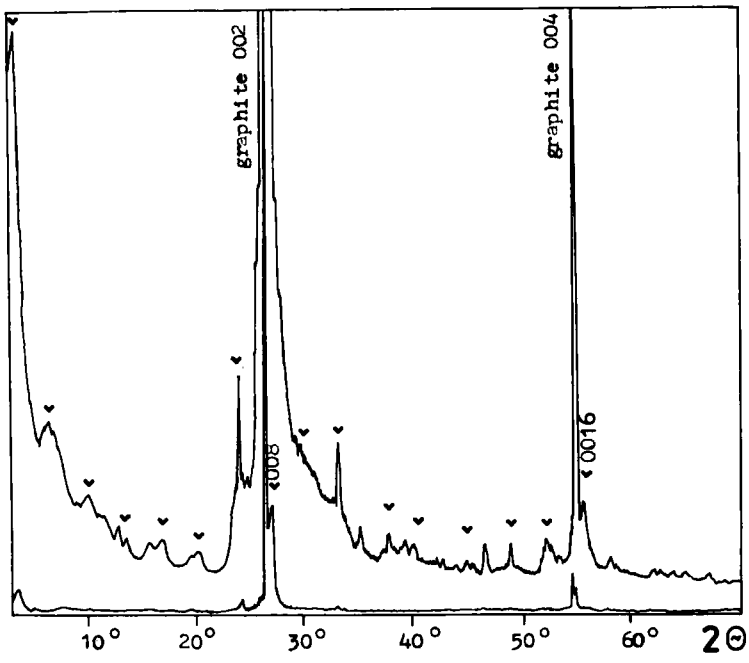


FIGURE 2 X-ray powder diffraction spectrums of K-Bi-GICs (sample"A"). The family of (00l) reflections is marked above the peaks. CoK_{α} radiation.

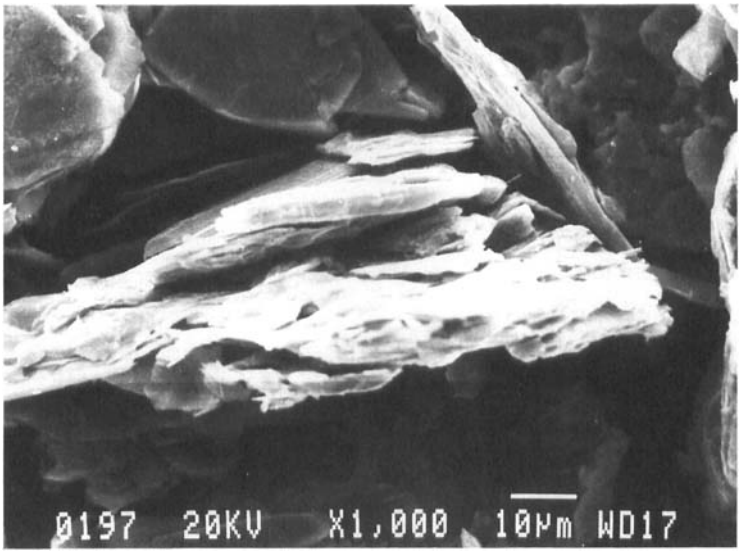
Also the decrease of (002) reflection of graphite in comparison to the (002) reflection of pure graphite is noticeable, e.g. from 117 to 76 $X10^3$ imp/s. It corresponds to the phases mixture with domains of pure graphite and K-Bi-GIC. Obtained $KBi_{0.9}C_{6.7}$ is probably of stage 3 of "α" phase, similar to described by Lagrange et al.[5]. The total thickness of interplanar distance can be calculated as: 987 pm ("α" phase) + + 334 pm (graphite) = 1321 pm.

Representative, well-formed lamellar structure obtained in sample "A" is shown in Figure 3. The stratification of graphite plates along (001) direction is evidently observed.

The presence of nitrogen in reactor space do not disturb K-Bi alloy intercalation reaction into the graphite . It is because range of temperature (above of 300 ^{o}C) cause the desorption of gaseous nitrogen out of interplanar space of

graphite. In that cause the affinity of K-Bi alloy to the amphoteric graphite electron system is higher than affinity of nitrogen to the same electron system.

a)



b)

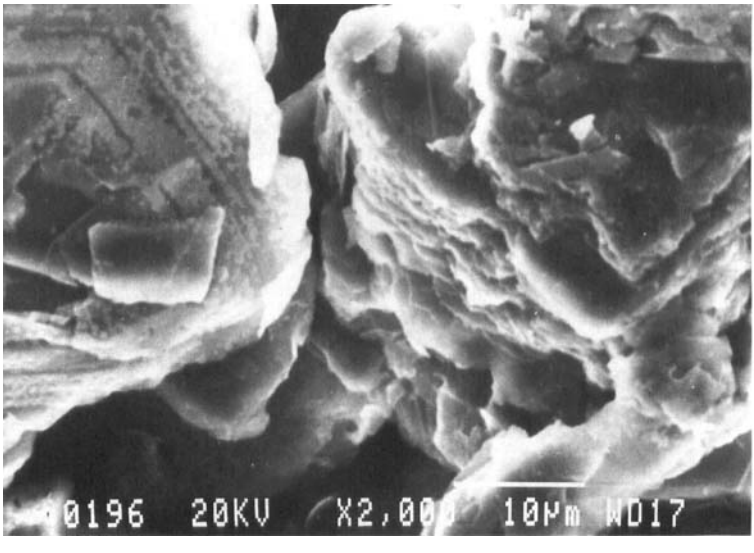


FIGURE 3 SEM micrographs of the obtained K-Bi-GIC (sample "A"). a) x1000; b) x2000

CONCLUSIONS

Presented results indicate that is possible to synthesize of K-Bi-graphite intercalation compounds of periodic structure under an inert gases and suggests that the layered structure of the intercalate is rather complex and depend on the synthesis conditions.

At lower temperatures obtained K-Bi-GICs are more homogeneous and form mixture of third stage of K-BI-GICs with interplanar distance of 1320 pm and free graphite.

Above preparation method is easier to carry out than under vacuum and presence of nitrogen in reaction space do not disturb intercalation reaction.

Several applications of such K-Bi-GICs can be expected, for instance as catalyst of dehydrogenation reactions.

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