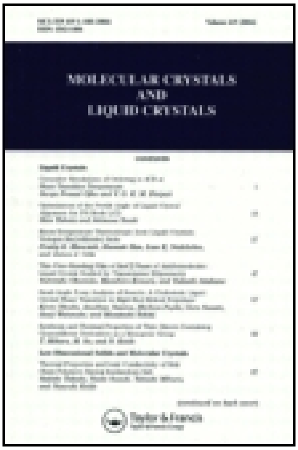

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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Version of record first published: 23 Oct 2006.

To cite this article: H. Alheid , M. Schwarz & E. Stumpp (1994): Electrochemical Preparation of Lanthanide-Ammonia Graphite Intercalation Compounds in Liquid Ammonia, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 191-196

To link to this article: http://dx.doi.org/10.1080/10587259408050103

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 191–196
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Printed in the United States of America

ELECTROCHEMICAL PREPARATION OF LANTHANIDE-AMMONIA GRAPHITE INTERCALATION COMPOUNDS IN LIQUID AMMONIA

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Abstract Graphite intercalation compounds (GICs) with the formula $C_xLn(NH_3)_y$, where Ln represents the elements La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu were prepared. Metallic solutions of these elements in liquid ammonia were obtained by anodic dissolution of the metals. The GICs were prepared by reaction of these solutions with graphite. The preparation prodecure is described. The samples were characterized by powder X-ray diffraction.

INTRODUCTION

Since the Craven and Ostertag work [1], the intercalation of lanthanide metals (Ln), with the exception of Eu and Yb, in graphite has not been the subject of research work . These authors prepared metal ammonia solutions of Gd, Tb, Dy, Ho, Er, and Tm in liquid ammonia by using an electrolysis technique to prepare metal-ammonia solutions. By reacting these solutions with graphite, lanthanide-ammonia graphite intercalation compounds (Ln-NH_3-GICs) were prepared. Only scant structural information can be found in this report.

We used this procedure to prepare new Ln-NH_3-GICs with Ln = La, Ce, Pr, Nd, Sm, Lu. Since the compositions of metal ammonia GICs with Gd, Tb, Dy, Ho, Er, and Tm are not well established and structural features remained uncertain we reinvestigated these systems.

PREPARATION OF LANTHANIDE-AMMONIA-GICS

The procedure was the same as that previously used to prepare Mg-NH_3- and Al-NH_3-GICs[2]. A glass apparatus, illustrated in Figure 1, was used to produce Ln-ammonia solutions by electrolysis. It was connected to a vacuum line. Ammonia having been carefully dried over a Na-Pb alloy, it was condensed into bulb A which was maintained at ca. -70 °C. Compartment A was filled with about 50 ml liquid ammonia. Since the electrolytic conductivity of liquid ammonia is very low, a conducting salt was dissolved, either NH_4ClO_4 or NH_4I, depending on the anode material,was used.

At the beginning of the current passage hydrogen, is evolved at the cathode :

$$2\ NH_4^+ + 2e \rightarrow 2\ NH_3 + H_2$$

Simultaneously, the anode is oxidized to form metal cations. When the ammonia ions are consumed, solvated electrons begin to evolve:

$$4\ NH_3 + e \rightarrow e(NH_3)_4$$

This reaction gives rise to the formation of blue clouds which diffuse into the solution. If the metal-ammonia solution is stable for at least several minutes the whole solution becomes blue.

The cathode consisted of a platinum sheet, and a rod of the metal to be dissolved served as the anode. To prepare GICs 500 mg graphite (purified natural graphite from Kropfmühl, Germany) of particle size < 50 µm were placed in tube A containing a Teflon-coated magnetic stirring bar. After the flask had been evacuated ammonia was condensed into compartment A. Then electrolysis was started. When the solution turned blue the graphite was periodically whirled up. The intercalation reaction was over when the solution remained blue. By tipping the vessel the supernatant liquid was decanted into the cooled sidearm B. For washing the product, ammonia was recondensed into A and then decanted back to B. This cycle was repeated several times. After evaporating ammonia the product was removed in a glove box.

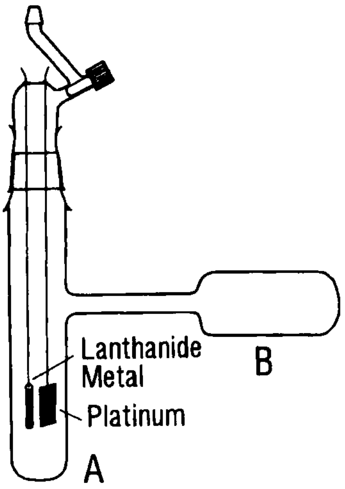

FIGURE 1. Apparatus for the preparation of metal-ammonia solutions and metal-ammonia GICs in liquid ammonia

For analysis a part of the sample was burnt in oxygen. The amount of Ln was determined from the remaining Ln_2O_3. A second part was heated in concentrated H_2SO_4. In this solution ammonia was determined by the standard Kjeldahl method. The X-ray reflections of the samples were recorded with a diffractometer using CuKα radiation

RESULTS AND DISCUSSION

The prepared samples are ternary GICs with the general formula $C_xLn(NH_3)_y$. All the samples are black in colour and were found to decompose rapidly on exposure to air. The extent of intercalation essentially depends on the stability of the solvated electrons for each metal-ammonia solution. While in the case of Gd and Tm the blue solutions formed at the cathode became colourless very rapidly, Sm and Er gave deep-blue solutions which proved to be stable for a time of several minutes up to half an hour. The compositions of representative samples are given in Table 1. Due to the low stability of the metal-ammonia solutions of Ce, Gd and Tm, these metals gave GICs with the lowest metal contents. Considering the chemical similarity of the Ln metals, it is not clear which factors are responsible for the stability of the Ln-ammonia solutions. In aqueous solutions the redox potentials of the Ln^{3+} ions decrease regularly from Ce (-2.48 V) to Lu (-2.26 V). It can be supposed that the same trend can be found in the case of liquid ammonia. Samples showing X-ray patterns conform to a single phase structure have rarely been obtained though preparations under varied experimental conditions have been performed on each Ln metal. The products were mostly mixtures of stage 3 and 4, or stage 4 and 5.

For each Ln-NH_3-GIC a typical sample is listed in Table 1 which also gives the c-axis repeat distances (d_i) as determined from the 00ℓ reflections. The distance between two graphene layers, which are separated by one intercalate sheet (d_1), is related to the identity period (d_i) of a nth stage structure according to the equation: $d_1 = d_i - (n-1)335$ (in pm). The d_1 values thus determined for the Ln-NH_3-GICs are in the same range as that found for alkaline earth-ammonia-GICs [3,4] as well as in Eu-NH_3-GICs and Yb-NH_3-GICs [5].

Our results for Gd through Tm are not consistent with those of Craven and Ostertag. They reported much higher metal contents. For example, they found the Tm:C ratio to be 1:17.8. In view of the low stability of the Tm-ammonia solutions it is unlikely that all Tm found in the samples was intercalated. Probably their samples were contaminated with appreciable amounts of thulium amide.

TABLE 1. Compositions of lanthanide-ammonia GICs and c-axis repeat distances

Compound	d_i stage3 (pm)	d_i stage 4 (pm)	d_i stage 5 (pm)	d_I* (pm)
$C_{39.5}La(NH_3)_{4.3}$	1281			611.0
$C_{80.9}Ce(NH_3)_{4.9}$		1618.5		613.5
$C_{20.6}Pr(NH_3)_{2.5}$	1297.6			627.6
$C_{23.9}$ $Nd(NH_3)_{3.5}$	1275.4			605.4
$C_{30.2}Sm(NH_3)_{1.3}$	1268.5			598.5
$C_{68.5}Gd(NH_3)_{4.1}$			1947.5	607.5
$C_{32.3}Tb(NH_3)_{3.6}$	1252.2			582.2
$C_{33}Dy(NH_3)_{3.5}$	1257.2	1592.2		587.2
$C_{46.7}Ho(NH_3)_{3.7}$	1256.3			586.3
$C_{69}Er(NH_3)_{4.0}$		1601.3		595.1
$C_{86.3}Tm(NH_3)_{4.1}$				
$C_{43}Lu(NH_3)_{3.8}$			1935.1	595.1

*) d_I is the distance of two graphene sheets separated by the intercalate

Figures 2-4 show the diffractograms of Ln-NH_3-GICs.

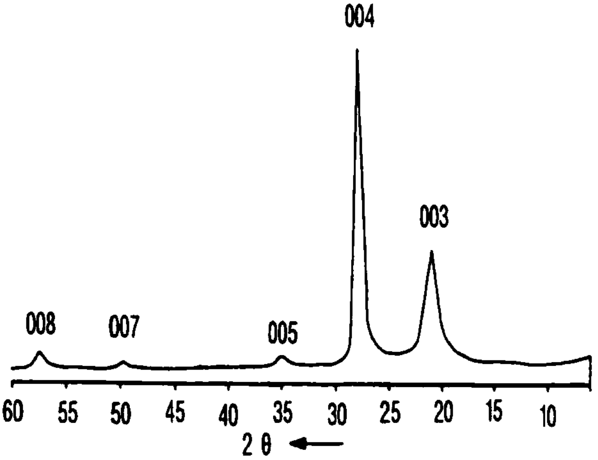

Figure 2. X-ray diffractogram of $C_{20.6}Pr(NH_3)_{2.5}$ (stage 3). CuKα radiation.

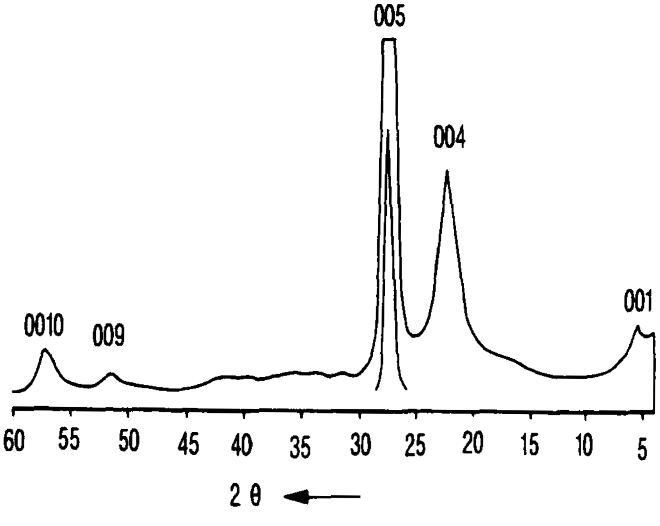

Figure 3. X-ray diffractogram of $C_{69}Er(NH_3)_{4.0}$ (stage 4). CuKα-radiation

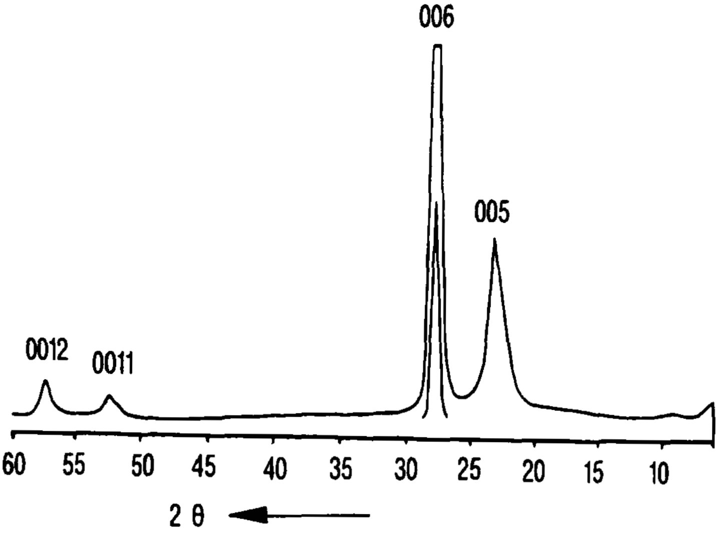

Figure 4. X-ray diffractogram of $C_{94}Ho(NH_3)_{6.4}$ (stage 5). CuKα-radiation

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