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CHARACTERIZATION OF GRAPHITE INTERCALATION COMPOUNDS BY THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

Thermogravimetric analysis has been used to study the thermal properties of $M(NH_2)_2$ and graphite intercalation compounds of the system M–NH_3–graphite (M = Ca, Sr, Ba) and to characterize the intercalated species.

INTRODUCTION

Graphite has a layer structure with strong in-plane bonding but weak interactions perpendicular to the graphene layers [1]. The crystal structure as well as the electronic band structure of graphite allow the formation of graphite intercalation compounds (GICs), in which particular chemical species are inserted between the graphene layers [2,3]. If reaction parameters are varied then different stages can be obtained. Stage 1 GICs exhibit an alternating sequence of carbon and guest species layers; in stage 2 GICs every second carbon layer is followed by a guest species layer. This feature affords the possibility of investigating the two-dimensional properties of the intercalated species.

The alkaline earth metals calcium, strontium and barium are soluble in liquid ammonia. Depending on the concentration, blue (dilute) or bronze-coloured (concentrated) metal–ammonia solutions are obtained. These solutions react with graphite to form metal ammonia GICs (M–NH_3 GICs) of

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the general formula $M(NH_3)_xC_y$ [2,4]. Pure stage 1 and stage 2 GICs with varying compositions, as well as the pristine metal amides, were synthesized, and were investigated by thermogravimetric analysis (TGA). TGA was applied for the first time to study the thermal properties of these M–NH_3 GICs as a function of the composition and to characterize the intercalated species.

EXPERIMENTAL

Metal chips of calcium (99.8%, Ventron), strontium (99+%, Aldrich) or barium (99.5%, Ventron) were dissolved in liquid ammonia (99.8%, Linde) which had been dried with a Pb–Na alloy. The solutions were poured through a glass filter onto the graphite powder (99.93%, Kropfmühl, Bavaria; particle size < 50 μm or 60–100 μm) and stirred vigorously for 20 min at about -50 °C. Excess of the metal–ammonia solutions was decanted and then fresh ammonia was recondensed onto the samples to wash the GICs. This procedure was repeated several times until the ammonia rinsings were colourless. Finally, the ammonia was evaporated and the apparatus was transferred to a glove bag [2]. The pristine metal amides can be prepared easily by decomposing the metal–ammonia solutions [5]. These solutions were stored at -37 °C for two weeks using a platinum wire as a catalyst to accelerate the reaction

$$M + 2NH_3 \rightarrow M(NH_2)_2 + H_2 \qquad (1)$$

The H_2 which formed during this process was pumped off from time to time. The conversion was complete when the blue colour of the metal–ammonia solutions disappeared. All manipulations had to be carried out with special care [2] to avoid decomposition of the metal amides and the M–NH_3 GICs by moisture or oxygen. The M–NH_3 GICs were analysed to determine the M and NH_3 contents; the metal amides were characterized by chemical methods or X-ray diffraction measurements [5].

Thermogravimetric (TG) curves were recorded with a magnetic suspension balance (Sartorius, Göttingen, F.R.G.; model 2401). A complete isolation of the sample from the balance mechanism allowed TG measurements in corrosive environments [6]. The following parameters were used: heating rate from 20–400 °C, 0.63 K min^{-1}; from 400–1000 °C, 1.00 K min^{-1}; flow of nitrogen (99.999%), 0.3 l min^{-1}.

To compare TG curves of different samples within one plot, a relative weight loss was defined

$$\text{rel. weight loss} = \text{weight loss at } T_x/\text{total weight loss}$$

RESULTS AND DISCUSSION

Thermal behaviour of alkaline earth metal amides

The amides decompose in two steps. The first corresponds to the conversion of the amides into imides, and the second to the formation of the nitrides. The degradation of $Ca(NH_2)_2$ and $Ba(NH_2)_2$ leads to thermally stable mixed crystals that are composed of metal amide and imide [5]. This characteristic was not observed for $Sr(NH_2)_2$. The TG curve of $Ca(NH_2)_2$ (Fig. 1) shows an initial decomposition at 25 °C followed by a slower degradation at 330 °C which indicates the existence of a mixed crystal. CaNH, which is thermally stable in the temperature range from 480 °C to 620 °C, reacts to give Ca_3N_2. The formation of the nitride is complete at 850 °C. The weight loss can be attributed to the following reactions

$$Ca(NH_2)_2 \rightarrow CaNH + NH_3 \qquad (2)$$

$$3CaNH \rightarrow Ca_3N_2 + NH_3 \qquad (3)$$

The $Sr(NH_2)_2$ (Fig. 2) is more thermally stable than $Ca(NH_2)_2$. It does not start to decompose below 350 °C. At 490 °C the reaction is complete. The $Ba(NH_2)_2$ starts to lose ammonia at 220 °C (Fig. 1). The TG curve shows a shoulder indicating the formation of a mixed crystal resembling the $Ca(NH_2)_2$–CaNH system. In contrast to the behaviour of alkaline earth metal carbonates, the thermal stability of the amides does not increase regularly with the atomic number of the metal. Thus, $Sr(NH_2)_2$, which forms no mixed crystals on decomposition, was found to be the most stable compound in this series.

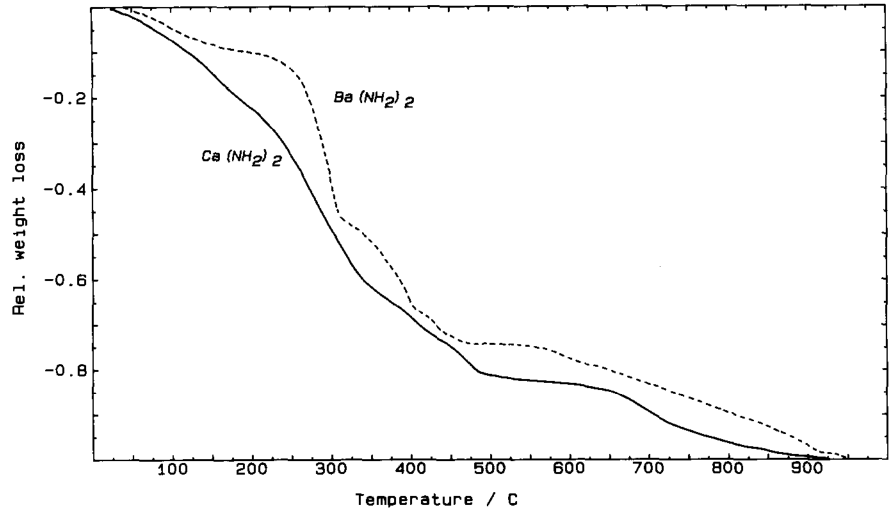

Fig. 1. TG curve of $Ca(NH_2)_2$ (———) and $Ba(NH_2)_2$ (— — —).

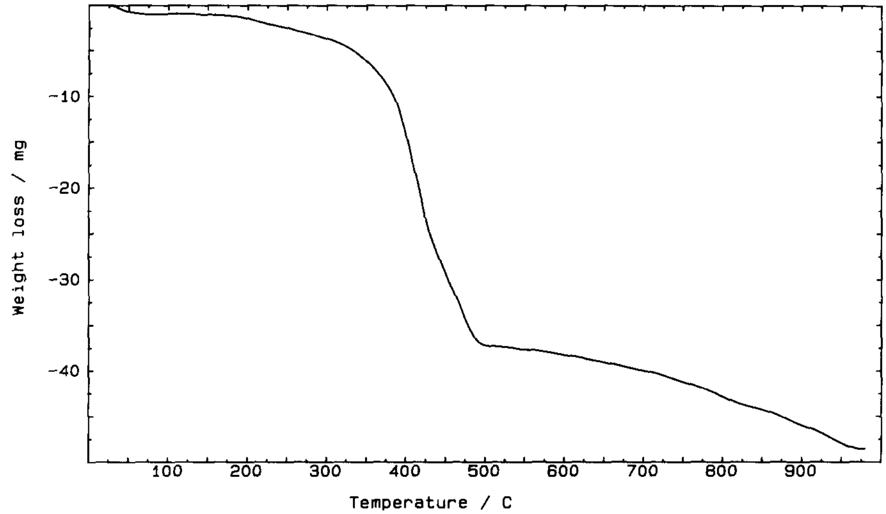

Fig. 2. TG curve of $Sr(NH_2)_2$.

Thermal behaviour of alkali earth metal–ammonia GICs

The TG curves of Sr–NH_3 GICs and Ba–NH_3 GICs resemble those of Ca–NH_3 GICs. Therefore only the Ca compounds will be discussed in detail. The following degradation steps were observed

(1) loss of NH_3 and H_2 from the intercalated species to form amides;
(2) decomposition of the amides to give imides;
(3) formation of nitrides;
(4) reactions of nitrides with graphite.

The first degradation step of the inserted species leads to intercalated metal amides. Comparing the thermal properties of intercalated and pristine amides, we found the former to be more stable (Fig. 3). This effect, which is observed for many intercalated substances, is caused by strong interactions between the inserted species and the graphene layers. The formation of mixed crystal phases, which are due to the exchange of imide anions for amide anions in the amide lattices, requires the existence of three-dimensional systems. In GICs the intercalate forms only a two-dimensional lattice, thus no mixed crystals can occur or be observed. The degradation of the amides leads to expanded and partly decomposed graphite flakes which are called exfoliated graphite compounds. The formerly intercalated species are now finely dispersed on the large graphite surface; therefore the conversion of the imides into nitrides is accelerated compared with the pristine substances. The final small weight loss is related to the reaction of Ca_3N_2 with dispersed graphite to form $Ca(CN)_2$ and $CaCN_2$, as well as their decomposition [7].

The thermal behaviour of M–NH_3 GICs changes distinctly with increasing metal content of the samples. The TG curve of a mixed stage 1 and stage

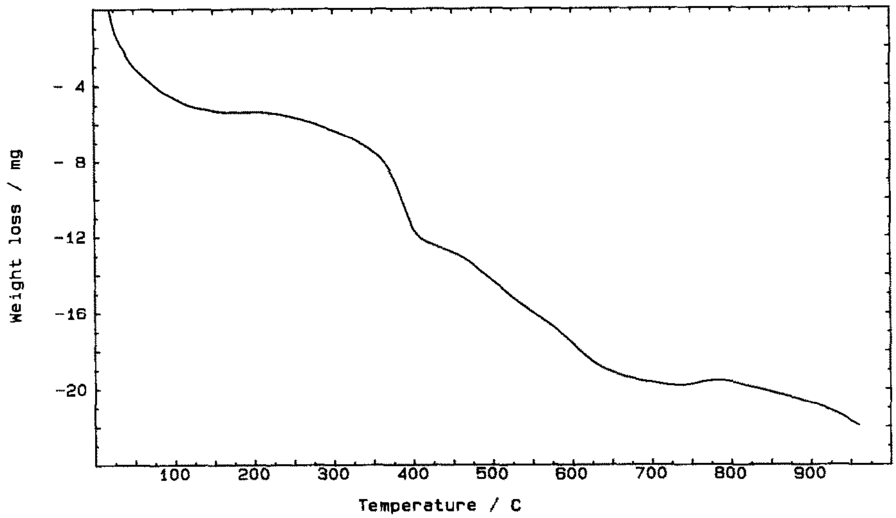

Fig. 3. TG curve of Ca–NH_3 GIC (stage 2).

2 Ca–NH_3 GIC displays only small plateaux, indicating thermally stable intermediate products (Fig. 4). No plateaux are observed within the TG curve of stage 1 M–NH_3 GICs with a high metal content. It is surprising, however, to note that at 720 °C a weight increase occurs (Fig. 5). After considering several reactions to explain this behaviour, we concluded that the reaction of Ca metal with N_2 was the most likely. To prove this assumption, pristine Ca metal was heated in flowing N_2. The TG curve showed a very similar weight gain at 700 °C, due to the formation of Ca_3N_2.

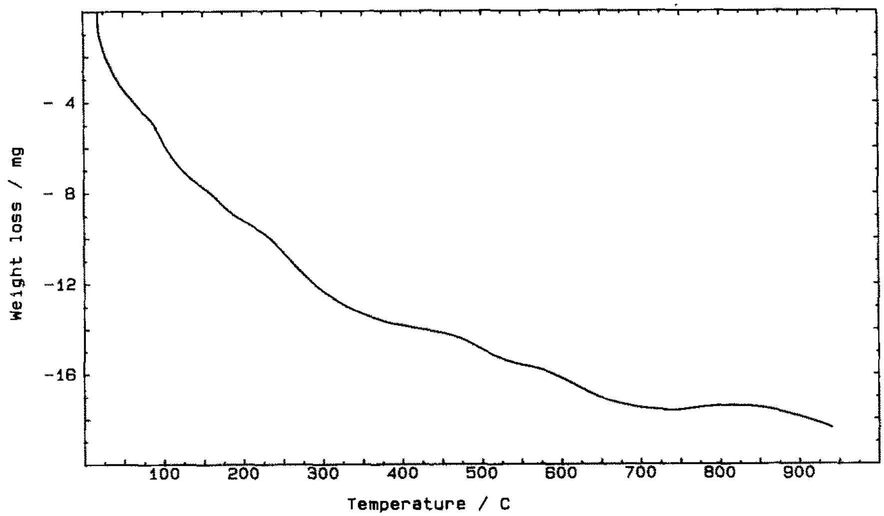

Fig. 4. TG curve of Ca–NH_3 GIC (stages 1 and 2).

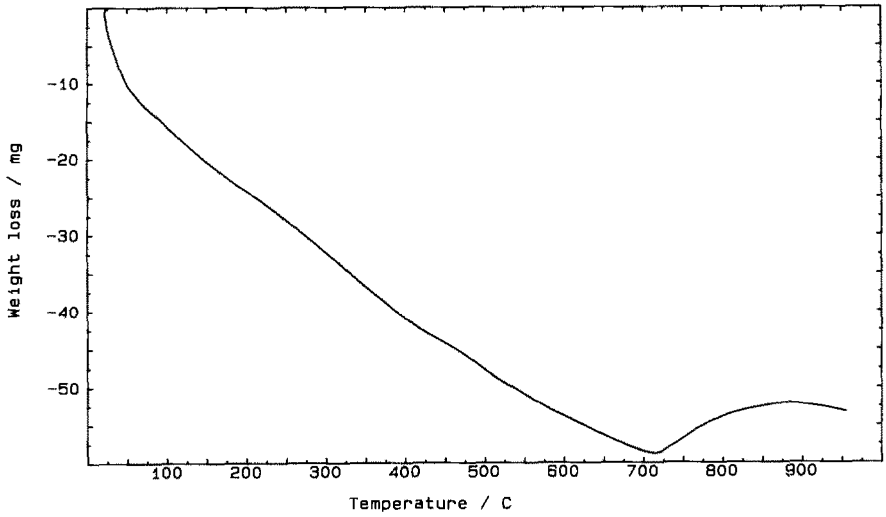

Fig. 5. TG curve of Ca–NH_3 GIC (stage 1; high metal content).

Thus the intercalate of stage 1 M–NH_3 GICs with a high metal content is very probably composed of co-intercalated free metal and metal ammine domains. Stage 2 M–NH_3 GICs, however, consist only of metal ammine species.

CONCLUSION

For the first time the thermal properties of metal–ammonia GICs (M–NH_3 GICs) have been studied by TGA. The thermal behaviour of these compounds changes noticeably with the composition. The decomposition of stage 2 M–NH_3 GICs resembles that of the pristine metal amides, thus the intercalate is composed of metal ammine. Stage 1 GICs with a high metal content show TG curves which reveal that the intercalated material is made up of free, co-intercalated metal and metal ammine domains. Thus TGA has proved to be a powerful tool to study and explains the thermal properties of M–NH_3 GICs.

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