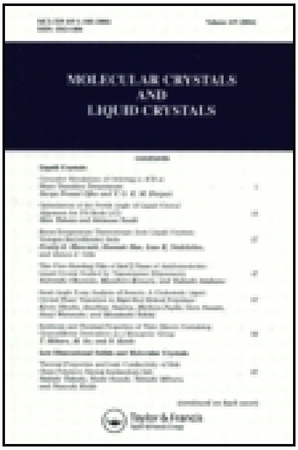

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Thermal Desorption of Graphite Intercalated by $SbCl_5$

Ludmila Matzui [a] & Ludmila Vovchenko [a]

[a] Kiev Taras Shevchenko University, Vladimirskaya str. 64, Kiev, 252033, Ukraine

To cite this article: Ludmila Matzui & Ludmila Vovchenko (2000): Thermal Desorption of Graphite Intercalated by $SbCl_5$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 313-318

To link to this article: http://dx.doi.org/10.1080/10587250008025485

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 313-318
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Thermal Desorption of Graphite Intercalated by $SbCl_5$

LUDMILA MATZUI and LUDMILA VOVCHENKO

Kiev Taras Shevchenko University, Vladimirskaya str. 64, Kiev 252033, Ukraine

The paper presents the results of investigations of thermal desorption of intercalation compounds Gr-$SbCl_5$. The influence of the particle size of pristine graphite, the heating rate and concentration of intercalant on the character of deintercalation process have been investigated. The obtained data were discussed in the frame of thermodynamic theory of stability of intercalation compounds.

Keywords: graphite; intercalation compounds; thermal desorption; stage transition

INTRODUCTION

It is known that the heating of graphite intercalation compounds leads to intercalant escape from the graphite layers and under certain conditions of heating it results in essential changes in macrostructure - exfoliation. In spite of the wide application of thermoexfoliated graphite in industry a comparatively small number of publications is devoted to the investigations of the conformities of this process and the mechanism of intercalant thermal desorption from GIC [1-4].

This work presents the data obtained from investigations in the process of intercalant escape from GIC with $SbCl_5$ and its dependence on intercalant concentration, heating rate, particle size of pristine graphite.

RESULTS AND DISCUSSION

The pristine material used for intercalation was natural graphite with particle sizes of 160 μm, 300 μm, 315 μm and 400 μm from Zavalievsk deposit. The graphite was intercalated with $SbCl_5$ by a standard method to stage-2 and 3. The mass loss during heating at constant rate in the air was measured on thermogravitometer with precision of 0.01 mg. The phase composition of the samples after intercalation and heating was determined by X-ray method.

The influence of intercalant concentration has been investigated for the samples of stage-2 and 3 Gr-$SbCl_5$. Fig.1 shows the differential mass decrease dM_{GIC}/dT of the samples as a function of temperature, the rate of heating is 2.5 K/min.

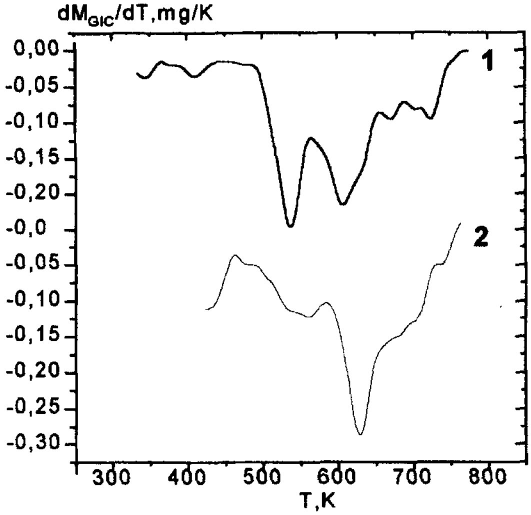

FIGURE 1 $dM_{GIC}/dT=f(T)$ for Gr-$SbCl_5$ samples under slow heating to 773 K with constant rate 2.5 K/min.: 1 - Gr-$SbCl_5$ compound of stage-2; 2- Gr-$SbCl_5$ compound of stage 3.

The analysis of these data for above samples has shown that there are several temperature ranges characterized by intensive mass losses. For the samples of stage-2 the first peak of mass loss is observed at ~540 K. As X-rays studies of

Gr-$SbCl_5$ of stage-2 heated to ~600 K show, sometimes the reflections corresponding to stage-2 disappear from diffractogramms and instead the reflections pattern characteristic of stage-3 appear. This indicates the transition from stage-2 to stage-3 in the samples at ~540 K. On $dM_{GIC}/dT=f(T)$ dependence for the samples of stage-3 there are no peaks in this temperature range. The second temperature range in which a sharp loss of mass is observed is (620-630) K. The peak of mass loss at this temperature is observed both for the samples of stage-2 and stage-3. X-ray studies performed after annealing at this temperature show that the produced samples are mainly compounds of stage-4. This indicates that at the temperatures (620-630) K the transition from stage-3 to stage-4 takes place. The analysis of absolute values of mass losses and phase composition of the samples heated above 770 K has shown that this temperature leads to complete deintercalation of GIC with $SbCl_5$.

The influence of pristine graphite particle size on characteristics of deintercalation process has been studied for stage-2 GIC with $SbCl_5$ prepared from graphite powders with particle sizes of 60 μm, 200 μm, 315 μm, and 400 μm. It was shown that the primary mass losses at the temperature below T~500 K, when transition from stage-2 to stage-3 is observed, are maximal for the sample with the smallest particle size. Intercalant desorption from particles surface results in changes of sample's mass on heating to T~500 K, but the stage of the compound was not changed, as it has been shown by X-ray studies. The temperature of transition from stage-2 to stage-3 for GIC on the basis of fraction 160 μm powder is 523 K, which is somewhat lower that the corresponding temperature (528-533) K for the samples of large fractions. The relative values of mass loss during stage transitions were practically identical for the samples of pristine graphite with particle sizes 200 μm, 315 μm, 400 μm and these values were ~10% and 18% for stage transitions from stage 2 to stage-3 and from stage-3 to stage-4 respectively. For powders with 160 μm in particle size these values were 8% and 14 % respectively which were somewhat lower than those for other samples.

The influence of heating rate on the character of deintercalation process and characteristics of the samples has been studied for Gr-$SbCl_5$ powders of fraction 400 μm at the rates of 2.5 K/min, 5 K/min, 20 K/min. Fig. 2 presents the mass losses and $dM_{GIC}/dT=f(T)$ dependences for different rates of heating. As it is seen from the figure the first minimum on $dM_{GIC}/dT=f(T)$ curves characteristic for transition from stage-2 to stage-3 in GIC is observed at the temperatures (535-540) K and does not depend on heating rate. However, as it is clear from figure 2(b) the character of peaks for different rates of heating is different. At V=2.5 K/min there is a vivid minimum on the $dM_{GIC}/dT=f(T)$ curve at T=540K and its width is ~ 40 K. At the rate V=5 K/min the peak symmetry is broken and the ratio of $(dM_{GIC}/dT)_{580\,K}$ to $(dM_{GIC}/dT)_{530\,K}$ is reduced. For these samples the maximal value of mass loss reaches 15% at T~ 530 K which is consistent with the theoretically estimated change in mass for transition from stage-2 to stage-3. At the rate of heating V=20 K/min the first minimum on the $dM_{GIC}/dT=f(T)$ curve is essentially extended and it may be treated as superposition of two peaks (at T~530 K and T ~620 K). For the sample heated at the rate V=20K/min the mass loss at 630K corresponds to the mass loss characteristic of transition from stage-3 to stage-4. The temperature of the second maximum on $dM_{GIC}/dT=f(T)$ curve, which has been shown by X-ray analysis to correspond to transition from stage-3 to stage-4 in the samples heated at low rates (2.5 K/min. and 5 K/min), is practically the same and was 610 K. The minimum on $dM_{GIC}/dT=f(T)$ in case of heating at V=5K/min is not sharp in comparison with minimum observed for sample heated with V=2.5K/min. Further heating of the samples at these rates gives a number of peaks on $dM_{GIC}/dT=f(T)$ curves which correspond to the regions with intensive mass losses. However, their amplitude and the interval between them decreases as the temperature is increased. That is, the temperature interval of higher stages existence becomes narrower. At the temperature above 800K, as X-ray studies have shown, the samples heated at these rates consist of practically pure graphite with a small amount of impurities of higher stages (7-9). At high heating rates which correspond to thermal shock (100-200) K/min after heat treatment at 800 K the diffractogramms of the samples show in addition to intensive lines of pure graphite also the weak intensity reflections

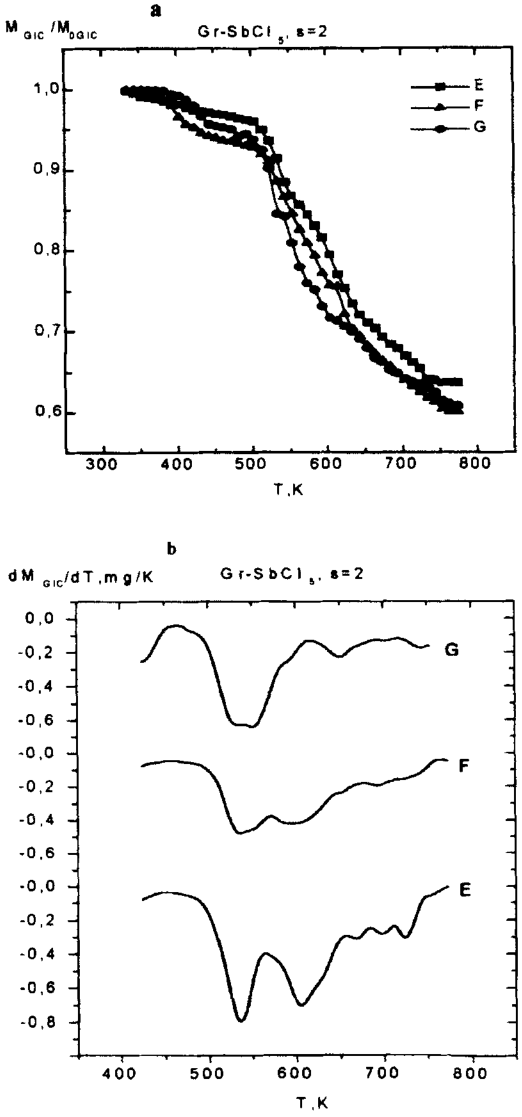

FIGURE 2 The change of mass (a) and $dM_{GIC}/dT=f(T)$ (b) for Gr-$SbCl_5$ samples with particle size 400μm under heating with constant rate to 773K: E - 2.5K/min, F - 5 K/min, G - 20 K/min.

only from stage-2 or stage-3, the reflections from higher stages are not present.

Thus, the investigations of thermal desorption in Gr-$SbCl_5$ of stage 2 and 3 have shown that mass losses have the step character: there are a few ranges of intensive mass losses. According to the thermodynamic theory of stability[4] for each stage of the compound there is such temperature T^*_S heating above which leads to transformation the intercalant into unstable, or metastable, state. The GIC tends to pass into stable state. According to the kinetic theory for intercalation [5] the rate of transition V_S from stage S into stage (S+1) is finite. If the rate of heating $V_T>V_S$, the transition from stage S into stage S+1 cannot be completed, since during the time interval required for stage S+1 formation the temperature of the sample reaches the temperature of stability of intercalant in the layer for S=1 stage ($T_{(S+1)}^*$) and the transition into S=2 stage has more advantages from the standpoint of thermodynamics. At high heating rates or under thermal shock (in case of GIC with $SbCl_5$ this rate is V>150 K/sec) the time required to cover the temperature interval from temperature of stability of initial stage T_S^* to the ternary temperature of intercalant T_C is considerably less than the time necessary for stage transition of intercalant and for its diffusion toward the sample's boundaries. The escape of intercalant mass takes place in the whole volume of the sample resulting in its exfoliation.

Acknowledgment
The work has been carried out according to Project N1089 of Science and Technology Center in Ukraine.

References

[1] Chung D.D.L. *Carbon* **25,** 361 (1987).
[2] Ho C.T., Chung D.D.L. *Carbon* **28,** 825 (1990).
[3] Mazieres G., Colin G, Jegoudez J., Setton R. *Carbon* **14,** 176 (1978).
[4] Kharkov E.I., Lysov V.I., Matzui L. Yu., Vovchenko L.L. 9th ICIMTEC-World Forum on New Materials, Simposium 1, P. Vincenzini, A. Dogli Esposti.(Editor). Techna Srl. 199 (1999).
[5] Anderson S.H., Chung D.D.L. *Carbon* **25**, 377 (1987).