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

Transport Properties of A Graphitized Polyimide Film and Its Stage-2 $FeCl_4^-$ Intercalation Compound

B. Nysten [a], J.-P. Issi [a], H. Shioyama [b], M. Crespin [b], R. Setton [b] & F. Beguin [b]

[a] Unité Pcpm, Université Catholique de Louvain, place Croix du Sud, 1, B-1348, Louvain-la-Neuve, Belgium

[b] Crmd, Cnrs-Université d'Orléans, 1B, rue de la Férollerie, F-45071, Orléans CEDEX 2, France

Version of record first published: 23 Oct 2006.

To cite this article: B. Nysten , J.-P. Issi , H. Shioyama , M. Crespin , R. Setton & F. Beguin (1994): Transport Properties of A Graphitized Polyimide Film and Its Stage-2 $FeCl_4^-$ Intercalation Compound, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 55-60

To link to this article: http://dx.doi.org/10.1080/10587259408051666

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 55–60
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

TRANSPORT PROPERTIES OF A GRAPHITIZED POLYIMIDE FILM AND ITS STAGE-2 $FeCl_4^-$ INTERCALATION COMPOUND

B. NYSTEN and J.-P. ISSI
Unité PCPM, Université Catholique de Louvain, place Croix du Sud, 1
B-1348 Louvain-la-Neuve, Belgium

H. SHIOYAMA, M. CRESPIN, R. SETTON and F. BEGUIN
CRMD, CNRS - Université d'Orléans, 1B, rue de la Férollerie
F-45071 Orléans CEDEX 2, France

Abstract The temperature variation of the thermal conductivity, the electrical resistivity and the thermoelectric power of a graphitized polyimide film has been measured in the temperature range $2 < T < 300$ K. The effect of electrochemical intercalation with $FeCl_4^-$ ions has also been studied. The thermal conductivity results confirm the high degree of graphitization that may be obtained with polyimide films. It shows how intercalation increases the structural disorder and how the intercalate substantially contributes to the thermal conductivity at low temperatures. The electrical-resistivity and thermoelectric-power measurements reveal that the density of free carriers is about three times lower in stage-2 $FeCl_4^-$ solvated intercalation compounds obtained by an electrochemical way than in stage-2 $FeCl_3$ compounds synthetized by a classical method.

INTRODUCTION

Polyimide films are known to transform into soft carbon films when heat-treated at temperatures around 1000°C.[1] When further treated above 2800°C, these films are transformed into highly crystallized graphite films.[2]

Recently the insertion of $FeCl_4^-$ ions into graphite has been realized electrochemically in a solution of $FeCl_3$ in concentrated HCl.[3] This method allows the synthesis of stage-2 compounds. It has been applied to a graphitized polyimide film in order to increase its electrical conductivity.

In the present study, we will compare the transport properties of a pristine graphitized polyimide film and of its $FeCl_4^-$ stage-2 intercalation compound. We shall show that the measurement of the transport properties is a powerful tool for the characterization of the crystalline and the electronic structure of these materials.

EXPERIMENTAL

The graphitized polyimide film has been prepared from a Novax film (Mitsubishi Chemicals Ind. Ltd.). It was first carbonized at 900°C under flowing nitrogen between two alumina plates. It was then graphitized at 3000°C between two graphite blocks under a flow of argon.

A sample from this film was electrochemically intercalated in a solution composed of 2.5 moles of $FeCl_3$ and 1.75 moles of HCl in 6 moles of H_2O with a ramping rate of 0.1 V sec^{-1}. A stage-2 compound was obtained with a c-axis repeat distance, I_c, equal to 1.271 nm. The formula of the compound determined from the transferred charge during intercalation and confirmed by elemental analysis was $C_{28}FeCl_4^-$. Elemental and thermogravimetric analyses also showed that each $FeCl_4^-$ ion in the interlayer spaces is solvated by about two co-intercalated molecules (HCl or H_2O).

The transport properties (thermal- and electrical-conductivity and thermoelectric power) of the pristine and the intercalated films were measured as a function of temperature between 2 and 300 K.

RESULTS AND DISCUSSION

The thermal conductivity of the graphitized film presents a behaviour comparable to that of HOPG (Fig. 1(a)).

TABLE I Structural parameters of the graphitized and the intercalated films determined by the fit of the thermal conductivity data compared to those of graphitized vapor-deposited fibers (HTT=3400°C) : L_a, the in-plane coherence length, L_c, the out-of-plane coherence length, and A, the parameter proportional to the point defect concentration.

Samples	L_a [nm]	L_c [nm]	A [10^{-24} m^2]
VDF	6819	321	2.3
Pristine	2650	450	0.98
$FeCl_4^-$ st.2	320		44

This confirms the high degree of crystallinity that may be obtained on

graphitized polyimide films. The in-plane and the out-of-plane coherence lengths, L_a and L_c, were determined using a model developed to analyze the thermal conductivity of graphitic materials.[4] They were respectively equal to 2.65 μm and 0.45 μm (Tabl. I). The analysis also enables the determination of a parameter related to point defect scattering, A, which is proportional to the defect concentration ($A \approx 3.3\ 10^{-22}\ C\,(1 - C)\,(\Delta m/m)^2$ where C is the defect concentration). The value corresponds to a low concentration of point defects.

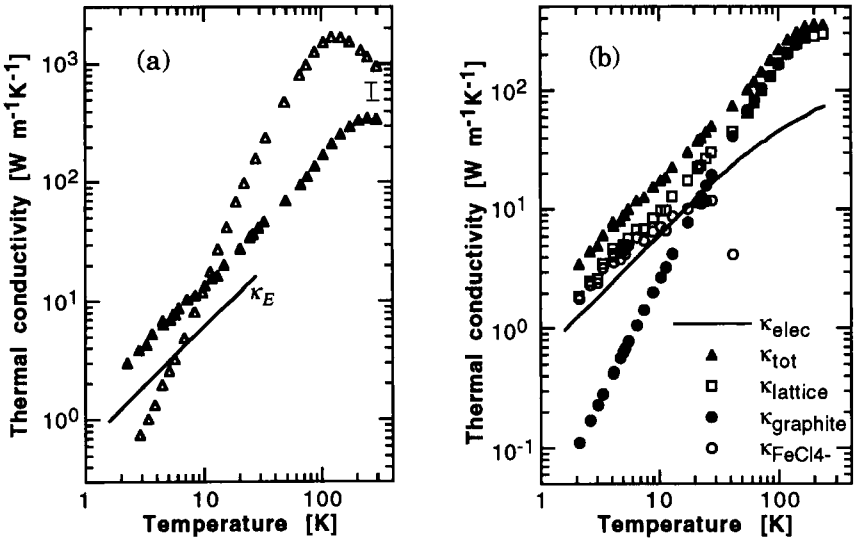

FIGURE 1 (a) Comparison between the temperature variation of the thermal conductivity of the pristine graphitized polyimide film (Δ) and of the intercalated film (▲). (b) Various contributions to the thermal conductivity of the intercalated film (see text).

At high temperature ($T > 40$ K), the intercalation reduces the thermal conductivity due to the increase of structural defects (Fig. 1(a)). Indeed, the fit of the lattice thermal conductivity above 40 K with a 2D model shows that the in-plane coherence length is reduced by one order of magnitude ($L_a = 0.32$ μm) and that the point defect concentration increases by more than an order of magnitude (Tabl. I).

At low temperature, the increase of the charge carrier density leads to an increase of the electronic thermal conductivity and thus of the total thermal conductivity. However, though the thermal conductivity follows a

T^1 dependence characteristic of electronic thermal conductivity, its values are about twice those of the electronic thermal conductivity computed from the electrical resistivity data using the Wiedmann-Franz law (plain line in Fig. 1(a)). This excess is attributed to a contribution of the intercalate phonons to the lattice thermal conductivity. The previous fit of the lattice thermal conductivity above 40 K with a 2D model enables the estimation of the contribution of the graphite layers to the thermal conductivity over the whole temperature range. By subtracting this contribution from the total lattice conductivity, one obtains an estimation of the temperature variation of the intercalate contribution to the thermal conductivity (Fig. 1(b)).

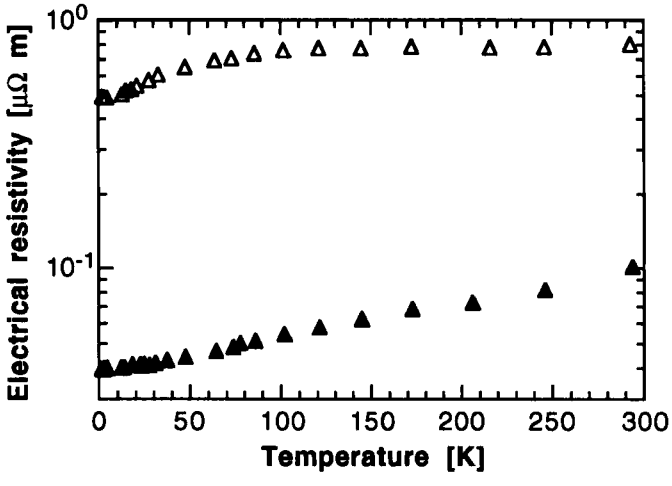

FIGURE 2 Comparison between the temperature variations of the electrical resistivity of the pristine graphitized film (Δ) and the stage-2 intercalated film (▲).

The electrical resistivity of both the pristine and the intercalated films are comparable to those of HOPG and stage-2 GICs (Fig. 2). However, the residual resistivity of the intercalated film (4.0 μΩ cm) is about three to four times higher than that observed on stage-2 metal chloride intercalation compounds obtained by classical methods of synthesis.[5] Since the thermal conductivity shows that the in-plane coherence lengths are comparable in both systems, we may infer that this difference is due to a lower hole density. This hypothesis will be confirmed by the analysis of the thermoelectric power.

The temperature dependences of the thermoelectric power of the pristine and the intercalated films are compared in figure 3. Below 10 K, the thermoelectric power of the intercalated film follows a linear temperature dependence characteristic of hole diffusion (inset in Fig. 3).

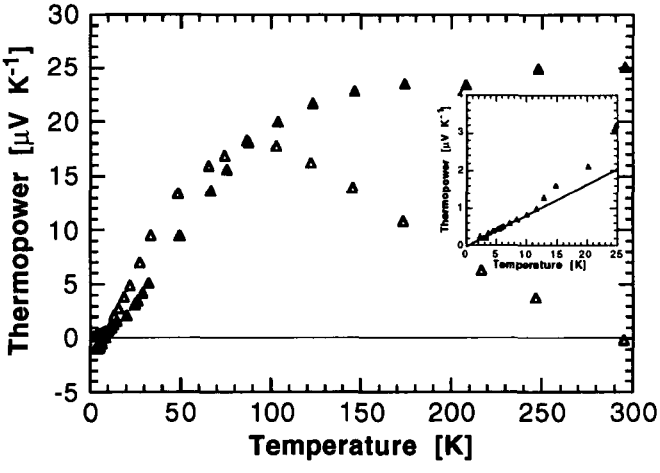

FIGURE 3 Temperature dependences of the thermoelectric power of the pristine graphitized film (Δ) and the intercalated one (▲). The inset reveals the details of the variation of the intercalated-film thermopower below 25 K.

Using the Blinowski-Rigaux band model, it is possible to evaluate the Fermi energy, ε_F, from the slope of the diffusion thermopower.[6,7] We found a value of 0.47 eV which is lower than that generally found in stage-2 metal chlorides intercalation compounds (0.8 eV). This Fermi level corresponds to a hole density equal to 0.54 10^{14} cm^{-2} which is approximately three times lower than that reported for stage-2 $FeCl_3$ compounds obtained by the classical method (1.55 10^{14} cm^{-2}). This result confirms that the higher residual resistivity of our intercalated film should be ascribed to a lower carrier density rather than to a more disordered structure.

However, the hole density determined from the thermopower is lower than that which may be expected from the compound stoichiometry if a complete charge transfer to the graphene layers is assumed (1.36 10^{14} cm^{-2}). This discrepancy suggests that less than fifty percent of the charges are actually transferred to the graphene layers. The remaining charges may be

transferred to the co-intercalated molecules solvating the $FeCl_4^-$ ions, possibly in the form of H_3O^+ ions.

CONCLUSIONS

This study confirms the high degree of graphitizability of polyimide films. It shows that the intercalation of $FeCl_4^-$ ions strongly decreases the structural perfection of the material. The contribution of the intercalate phonons to the lattice thermal conductivity has also been evaluated.

The analysis of the diffusion thermoelectric power allows the evaluation of the hole density. A value about three times lower than that observed in stage-2 $FeCl_3$ compounds obtained by classical synthesis methods was found. This leads to a higher electrical resistivity than in those compounds. The low value of the hole density compared to that expected from the sample stoichiometry also suggests that more than fifty percent of the charge is transferred to co-intercalated molecules.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Professor M. Inagaki for providing them with the graphitized Novax film. The work performed in Louvain-la-Neuve is part of the program "Action de Recherche Concertée" sponsored by "D.G.E.S.R. de la Communauté Française de Belgique".

REFERENCES

1. M. Inagaki, S. Harada, T. Sato, T. Nakajima, Y. Horino and K. Morita, Carbon, 27, 253 (1989)
2. Y. Hishiyama, S. Yasadu, A. Yoshida and M. Inagaki, J. Mater. Sci., 23, 3272 (1988)
3. H. Shioyama, M. Crespin, A. Seron, R. Setton, D. Bonnin and F. Béguin, Carbon, 31, 223 (1993)
4. B. Nysten, J.-P. Issi, R. Barton, D.R. Boyington and J.G. Lavin, Phys. Rev. B, 44, 2142 (1992); B. Nysten, Microstructure and Transport Properties : Carbon Fibres (Ph.D. Thesis, Unité PCPM, Université Catholique de Louvain, Louvain-la-Neuve, 1991)
5. N.E. Nadi, E. McRae, J.-F. Marêché, M. Lelaurain and A. Hérold, Carbon, 24, 695 (1986)
6. J. Blinowski, Nguyen Hy Han, C. Rigaux, J.-P. Vieren, R. Le Toullec, G. Furdin, A. Hérold and J. Mélin, J. Physique, 41, 47 (1980)
7. L. Piraux, M. Kinany-Alaoui, J.-P. Issi, A. Perignon, P. Pernot and R. Vangelisti, Phys. Rev. B, 38, 4329 (1988)