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D.C. CONDUCTIVITY OF POLYMER COMPOSITES WITH $(BEDT\text{-}TTF)_2I_3$ SUPERCONDUCTOR

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Electrical properties of conducting reticulate doped polymeric films containing BEDT-TTF iodide crystalline network were investigated. Conditions of preparation of this kind of films i.e. time of doping by iodine vapours and time and temperature of annealing and their influence on transformation of the BEDT-TTF iodide crystallites into superconducting phase are discussed.

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1. Introduction

It was shown recently that it is possible to prepare conducting reticulate doped polymer films containing low amount of organic superconductors [1]. This kind of materials is more interesting as compared with single crystals considering their potential applications. In this paper we report our works on optimization of conditions of producing of a network of organic superconductor in a polymer matrix. It is well known that BEDT-TTF polyiodides can form multiple phases with different iodine concentration and crystallographic structures. It was found that other (especially iodine-rich) phases can be converted to so called β_t-phase by proper thermal treatment [2]. This phase has the same arrangement of ET backbone as the β-phase but differs in position of ethylene groups. It is probably identical with β^*-phase (obtained from β-phase under pressure) and with α_t-phase (obtained from α-phase by heating). β_t-phase is particularly interesting because it exhibits the superconducting transition at $T_c \approx 7.5$ K. Our aim was to find conditions which assure the transition to β_t-phase of the BEDT-TTF iodide by adjusting the time of iodine vapours treatment and the BEDT-TTF iodide crystallization as well as the time and temperature of the annealing.

2. Experimental

Surface conducting polycarbonate films were obtained in a two-step process elaborated recently [3]. In the first step the nonconducting film with 2 wt% of molecularly dispersed donor (BEDT-TTF) was cast. In the second step the surface of the obtained film was exposed to solvent/iodine vapours, with CH_2Cl_2 used as the solvent. A reaction of iodine with BEDT-TTF in solvent-swollen layer results in crystallization of the charge-transfer (CT) complex in a form of fine network penetrating the surface layer of the polymer matrix.

For annealing the samples were tightly packed in thin teflon film in order to reduce an escape of iodine from the sample. Glass chamber filled with dry nitrogen was preheated and then the sample was put in and kept in the chamber for a definite time. In some cases the samples were annealed also in iodine vapours. D.C. conductivity measurements of the polymer films were performed in a helium exchange gas cryostat (KPO-729/A KRIOSYSTEM) or a closed cycle helium cryostat (APD CRYOGENICS INC) using four probe technique with pressure contacts made of graphite foil.

The contactless microwave measurements were performed in a cylindrical cavity, working in the TM_{010} mode at 10.2 GHz by usual cavity perturbation technique [4–6].

3. Results and discussion

In the as obtained reticulate doped films a mixture of the α- and β-phase of BEDT-TTF is present, as evidenced by X-ray diffractograms and microspectroscopy. There are also probably some admixtures of other polyiodide phases, like ε or ξ. D.C. conductivity exhibits semiconducting behaviour (Fig. 1b, curve I), however the 10.2 GHz microwave conductivity (Fig. 1a, curve I) is metallic down to about 150 K indicating a significant contribution of α-phase which has metal–insulator transition at 135 K [2]. Before annealing the amount of the metallic phases in the obtained films is below the percolation threshold. Enormous change in the conductivity behaviour follows upon annealing at high temperatures due to the conversion of both β- and α-phase into metallic (and superconducting) β_t-phase [2]. Both D.C. and microwave conductivities demonstrates metallic features over the entire temperature range (Fig. 1a and 1b, curves II). Moreover, these phase transitions yield also changes in the transmission spectra and in the colour of film, similar to those observed for the $(BEDT\text{-}TTF)_2I_3$ single crystals [7].

From our work it follows that the properties of annealed samples depend very strongly on the preparation conditions i.e. on time of exposition to solvent/iodine vapours, and on temperature and time of annealing. Influence of time of exposition to solvent iodine vapours on the D.C. conductivity is shown in Fig. 2 and we can notice that the time of the exposition affects both the conductivity value and its temperature dependence in the annealed films. For the studies of optimization of the annealing conditions we chose the samples obtained after 1 min of exposition to solvent/iodine vapours. We found that if the temperature of annealing is too high, the transition to the metallic phase occurs quickly, but for longer annealing

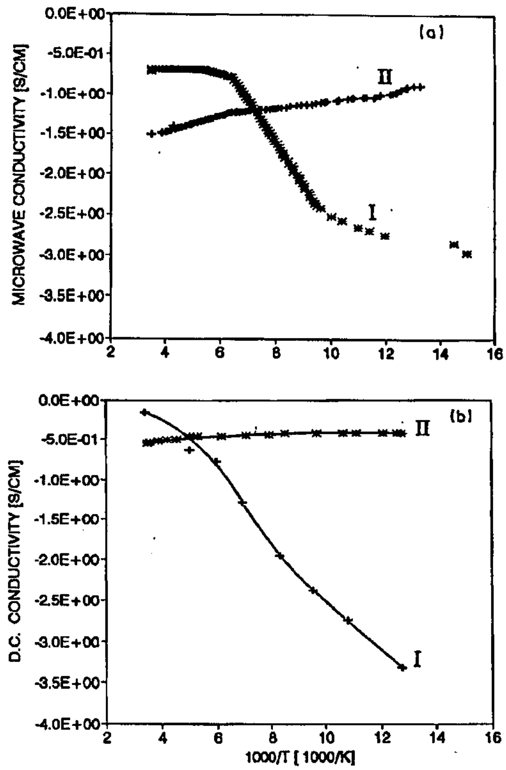

Fig. 1. Arrhenius plots of (a) microwave (10.2 GHz) and (b) D.C. conductivities of the PC+BEDT-TTF iodide films before annealing (curve I) and after 5 min annealing at 400 K (curve II).

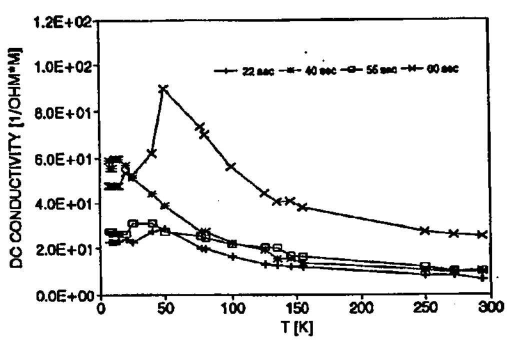

Fig. 2. Temperature dependences of the D.C. conductivity of the PC+BEDT-TTF iodide films obtained after various times of exposition to solvent/iodine vapours. Films annealed 150 min at 390 K in all the cases.

times the conductivity decreases and it loses its metallic temperature dependence (Fig. 3a) becoming thermally activated. On the contrary, results shown in Fig. 3b

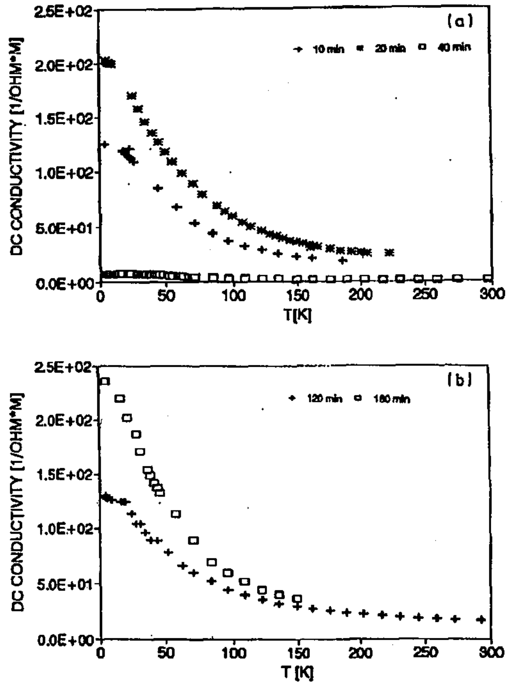

Fig. 3. Changes in the D.C. conductivity behaviour of the PC+BEDT-TTF iodide film after annealing at (a) 410 K and (b) 390 K. Annealing times indicated in the figures.

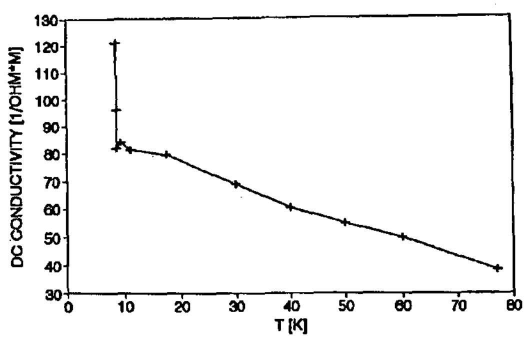

Fig. 4. Low temperature conductivity behaviour of PC+BEDT-TTF iodide film annealed 23 min at 400 K in iodine vapours.

imply that prolonged annealing at lower temperatures results in more pronounced metallic behaviour of the conductivity.

Considering the above mentioned results we can suppose that the observed effects of the annealing result from two phenomena: (i) conversion of the microcrystals into β_t-phase, yielding transition from thermally activated to metallic conductivity; (ii) loss of the iodine, which leads to deterioration of the conducting network.

We have performed also preliminary studies for the samples annealed in iodine/nitrogen atmosphere. In some cases the obtained materials exhibit a precursor of the superconductivity transition, as illustrated in Fig. 4. Similar results were obtained independently in other laboratory [8].

4. Conclusions

From the results shown above it follows that it is possible to obtain a continuous network of BEDT-TTF iodide salt in polymer matrix and to transform it into metallic phase by annealing. Preliminary experiments show that by the choice of proper preparation and annealing conditions continuous superconducting β_t-phase can be formed in the network, therefore flexible and transparent polymer films of superconducting properties could be produced.

Acknowledgments

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