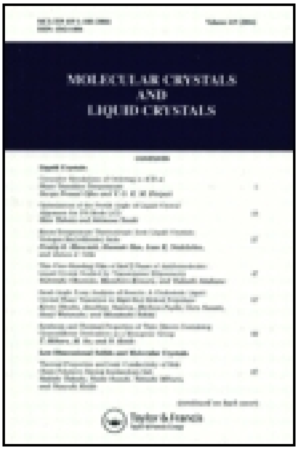

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Polymorphism and Crystal Growth of Organic Conductor $(BEDT\text{-}TTF)_2I_3$

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Polymorphism and Crystal Growth of Organic Conductor $(BEDT\text{-}TTF)_2I_3$

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The Polymorphism of $(BEDT\text{-}TTF)_2I_3$ was studied with X-ray diffractmetry. The observation of solution-mediated transformations clarified that the β-form is thermodynamically more stable than the α-form at least in the temperature range between 0 and 50 °C. The metastable α-form preferentially crystallized with increasing oxidation current or lowering the growth temperature. This polymorphic behavior was discussed in term of supersaturation using the classical equation of the nucleation. Using the information of the polymorphism, large single crystals of the α- and β-forms were selectively grown under the designed conditions.

Keywords: polymorphism; $(BEDT\text{-}TTF)_2I_3$; crystal growth; single crystal

INTRODUCTION

$(BEDT\text{-}TTF)_2I_3$ (dibis(ethylenedithio)tetrathiafulvalene triiodide) is an organic charge-transfer complex salt that shows quasi two-dimensional metallic conductivity. This salt has been of great interest due to low temperature physical properties such as superconductivity and metal insulator transitions [1,2]. However, it is very difficult to obtain the large, high-quality single crystals which is demanded to study the physical properties.

Generally, single crystals of BEDT-TTF salts were grown using an electrochemical oxidation method. Clarification of the crystal growth mechanism of BEDT-TTF salts using this method is necessary to control the growth and to obtain large, high-quality single crystals. We have so far investigated the crystal growth rates of β-(BEDT-TTF)$_2$I$_3$ and its equilibrium state with the solution [3,4]. In these works, we found that the β-(BEDT-TTF)$_2$I$_3$ crystals have a certain solubility against an organic solvent at a given temperature. This means that the supersaturation as the driving force of crystal growth can be defined also in this system, and that it can be dealt with as the normal solution growth. Therefore, it was predicted that the cmplex polymorphism of (BEDT-TTF)$_2$I$_3$ can be controlled in terms of the supersaturation.

(BEDT-TTF)$_2$I$_3$ has principal two polymorphic modifications, α- and β-forms. Generally, the two polymorphs appear at the same time in a crystal growth cell during the growth process using the electrochemical oxidation method. Hence, the control of the polymorphism has been demanded to obtain large and single phase single crystals. In the present study, we have investigated the polymorphism of (BEDT-TTF)$_2$I$_3$ and succeeded in selective growth of large single crystals of each polymorph.

EXPERIMENTAL

Thermodynamic stability between the α- and β-forms was determined by observing the solution-mediated transformation. The detailed studies of this kind of transformations and thermodynamic stability have been reported by Dabey *et al.* [5]. Mixture powder (α: β = 9:1) was dispersed into monochlorobenzene and stirred at given temperature between 0 and 50 °C. The powder dispersing in the solution was occasionally taken out and the α:β ratio was measured using X-ray diffraction.

Oxidation current dependence of polymorph to appear was investigated in crystallization process using the electrochemical oxidation method. THF was used as the solvent. The concentration of BEDT-TTF and TBA I$_3$ were 1×10^{-3} and 6×10^{-3} mol/l, respectively. The surface area of the Pt electrodes was 150 mm^2. Crystals were grown at 10, 20, 30 and 40 °C at the constant current (1, 10 or 100 μA) condition. The appeared polymorph in the powder crystals was identified using X-ray diffraction.

RESULTS AND DISCUSSION

Figure 1 shows the time dependence of the X-ray diffraction patterns of the powder dispersed in the solution at 20 °C. The ratio of β to α in the powder clearly increased with time. Finally, all the *α-form disappeared, and only the* β-form remained. The same phenomena were also observed between 0 and 50 °C. This fact suggests that the solubility of the β-form is less than that of α-form. Therefore, the β-form is thermodynamically more stable than the α-form in this temperature region.

As to the oxidation current dependence of polymorph to appear, the results are summarized in Fig. 2. With increasing oxidation current or lowering the growth temperature, the metastable α-form preferentially crystallized. This suggests that the increase of current gives rise to the increase of supersaturation. The anomalous behavior that the α-form crystallized in the metastable temperature region may be explained using the classical equation of the nucleation. The activation free energy for the formation of a critical crystal nucleus is expressed as

$$\Delta G^* = f \gamma^3 v^2 / \Delta\mu^2 , \qquad (1)$$

where, f is a geometrical factor of the

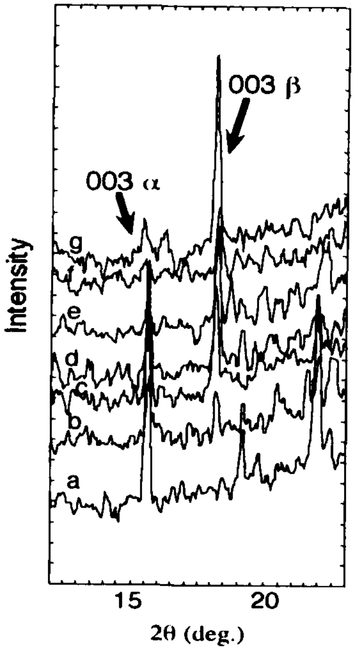
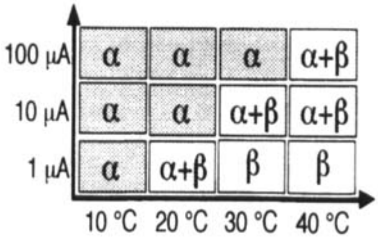


FIGURE 1 Time dependence of the X-ray diffraction patterns of the powder dispersed in the solution at 20 °C. (a) -(g) denotes passage of time ; (a) from 1 day after the start, (g) 7 day s after the start. X-ray: CuKα.



	10 °C	20 °C	30 °C	40 °C
100 μA	α	α	α	α+β
10 μA	α	α	α+β	α+β
1 μA	α	α+β	β	β

FIGURE 2 Identified polymorphs of (BEDT-TTF)2I3 crystals in terms of crystallization temperature and oxidation currents.

crystal nucleus, and v and γ are the molecular volume and crystal-solution interfacial energy, respectively [6]. $\Delta\mu$ is the difference in chemical potential between the crystal and solute, which is in proportion to the supersaturation. $\Delta\mu$ is always favorable to the stable polymorph. Hence, the fact that the metastable polymorph preferentially nucleates suggests the remaining terms must contribute to the nucleation of the metastable polymorph. With increasing supersaturation or lowering the temperature, the difference in $\Delta\mu$ between the two polymorphs should decrease relatively. Consequently, the metastable α-form can preferentially crystallize at sufficiently high supersaturation. In the case of electrochemical oxidation, it should be reasonable that the increase in current gives rise to the increase of supersaturation. From these, we can conclude that increase in current and lower temperature are effective to obtain the α-form.

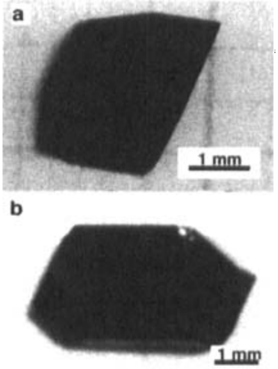


FIGURE 3 Photograph of obtained lage single crystals. (a) α- $(BEDT\text{-}TTF)_2I_3$ and (b) β-$(BEDT\text{-}TTF)_2I_3$.

Using this information, large single crystals of α and β polymorphs were successfully grown under the designed conditions at 10°C and 30 °C respectively. The typical photographs of the single crystals are shown in Fig.3. The solute concentration of the employed THF solution and the anode were the same as thoes descried in the experimental section.

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