Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 29 Oct 2010

To cite this article: Noriyuki Yoshimoto, Takeshi Sato, Kaoru Ogawa, Kazuhiko Omote, Yoshio Saito & Masahito Yoshizawa (2002): In-Plane Structure Analysis of BEDT-TTF Thin Films by X-Ray Diffraction, Molecular Crystals and Liquid Crystals, 377:1, 381-384

To link to this article: http://dx.doi.org/10.1080/713738493

*Mol. Cryst. Liq. Cryst.*, Vol. 377, pp. 381-384

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290089338



# In-Plane Structure Analysis of BEDT-TTF Thin Films by X-Ray Diffraction

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Dibis(ethyleneditho)tetrathiafulvalene (BEDT-TTF) was vacuum-deposited onto KCl (001) and KBr (001). The in-plane crystal orientations of epitaxial thin films were investigated by X-ray diffractometry. The epitaxial relationship between BEDT-TTF and substrates was determined as $<211>_{\text{BEDT-TTF}}$ // $<110>_{\text{substrate}}$.

Keywords: BEDT-TTF; thin film; X-ray diffraction; in-plane orientation

## INTRODUCTION

There has been a great interest in organic thin films because of their notable functionalities. In order to apply the functional properties of organic molecules to electronics and optical devices, improvement of the molecular arrangement control and structural characterization of organic thin films is mandatory. Quite recently, Omote et al. developed a unique X-ray diffractometer, which can measure both of in-plane and out of plane diffractions by a laboratory source[1]. Using this equipment, we have successfully applied to investigate the epitaxial relations

between organic thin films and alkali halaid (001) substrates.

Dibis(ethyleneditho)tetrathiafulvalene (BEDT-TTF) is an organic donor molecule which constitutes principal organic superconductors such as $(BEDT\text{-}TTF)_2I_3$ and $(BEDT\text{-}TTF)_2Cu(NCS)_2$ [2,3]. To obtain the well-oriented organic conducting thin films, structural information of the constituent molecules in thin film state is necessary. In this study, the in-plane structure of BEDT-TTF thin films was analyzed with a fair degree of precision using a unique X-ray diffractometer.

## EXPERIMENTAL

BEDT-TTF powder was sublimated in a pressure of $5 \times 10^{-5}$ Pa from K-cell type crucible kept at 80 °C. The substrates used were air-cleaved (001) planes of KCl and KBr maintained at 20 °C after baked at 200 °C for 1 hour. The deposition rate and final film thickness were 3.3 nm/min and 100 nm, respectively. The as-deposited thin films were characterized using X-ray diffraction in air. Figure 1 shows a schematic setup of the employed X-ray diffractometer (Regaku Co., ATX-G). A parabolic multiplayer positioned next to the laboratory X-ray source produces high intensity parallel beam (Cu Kα). The goniometer has not only usual ω/2θ axes but also in-plane φ/2θχ axes for measuring both in-plane and out of plane diffraction.

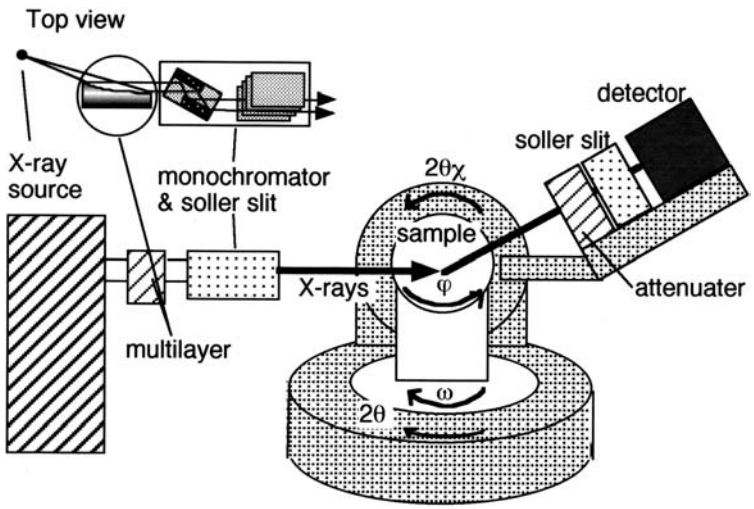


FIGURE 1 Schematic setup of in-plane X-ray diffractometer.

## RESULTS AND DISCUSSION

Figure 2 shows conventional θ/2θ scan pattern of a deposited BEDT-TTF film on a KCl {001} substrate. The lattice parameters of a bulk single crystal of BEDT-TTF is monoclinic, space group is P21/c, a=0.6614 nm, b=1.3985 nm, c=1.6646 nm and b=109.55° [4]. On comparison of the observed lattice spacings and the calculated ones, the diffraction peaks in Fig.2 can be indexed by (10-2) and (20-4). From this facts, it was determine d that the (10-2) face of BEDT-TTF is located in parallel with the (001) face of KCl. Using this information, (03-2) asymmetry reflections that include the information of the in-plane orientations were measured as a function of rotation angle (φ) of the normal vector to the substrate surface. Figure 3 and 4 show the scattering geometries for the φ scans of (03-2) diffractions and an obtained diffraction pattern, respectively. In Fig.4, eight pairs of (03-2) diffractions are seen. Because there are two measurable (03-2) and the equivalent planes in each single crystal of BEDT-TTF, the results shown in Fig.4 demonstrates that the eight kinds of the degree of freedom in the in-plane orientations exists in the thin films on KCl (001) substrates. As for the BEDT-TTF thin films on KBr (001) substrates, the X-ray diffraction patterns were

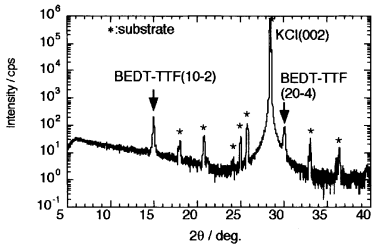


FIGURE 2 Conventional θ/2θ scan pattern of BEDT-TTF film.

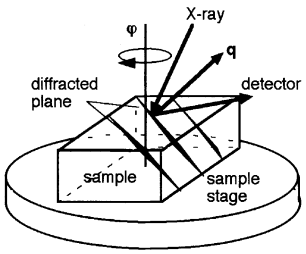


FIGURE 3 Schematic representation of scattering geom.-etries.

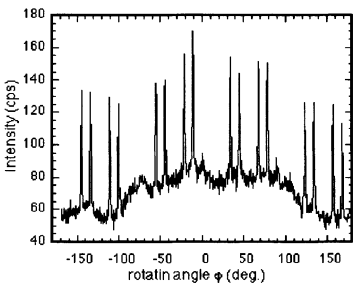


FIGURE 4 In-plane φ scan pattern for BEDT-TTF (03-2) diffraction.

completely same as that of on KCl substrates for both θ/2θ and (03-2) φ scans.

From the measured directions of the diffraction vectors and the crystal data, in-plane crystal orientations could be calculated. In comparison with the in-plane diffraction data for KCl (020), the epitaxial relationship between BEDT-TTF and KCl was determined as $<211>_{\text{BEDT-TTF}}$ // $<110>_{\text{substrate}}$. Using in-plane X-ray diffraction, the determination process of the relationships became easier and more accurate than that by using electron diffraction as we have reported elsewhere [5]. Figure 5 shows the schematic representation of the determined epitaxial relationship between BEDT-TTF and KCl. The ball-like objects in the background and string-like ones denote $K^+$ and $Cl^-$ ions of the substrate and molecular shape of EBDT-TTF, respectively. Alignment of the molecular axis paralleling with <110> of KCl seems to determine the epitaxy. The lattice mismatch was calculated as 1.9 % for KCl and 6.6% for KBr. The relatively small mismatch may contribute the determination of the orientation the in nucleation process. An adsorption energy calculation will lead an explanation for this phenomenon.

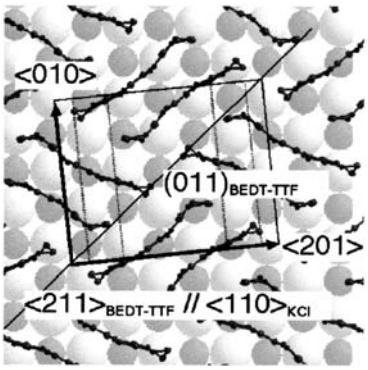


FIGURE 5 Schematic representation of epitaxial relationship between BEDT-TTF and KCl.

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