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PACS.61.66.Hq – Organic compounds
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Abstract. — Crystals of (BPE-DMB)IBr₂, where BPE-DMB denotes 1,4-bis[2-(pyrene-1-yl) vinyl]-2,5-dimethylbenzene, are found to be twisted along the growing axis. Their morphology was examined in detail by X-ray examination, scanning electron and optical microscopic observations. It was found that the twisted crystals are quasi-stable and that the twisting is not discrete but rather continuous in sub-micron scale. The relation between a twist pitch and the cross-section area was obtained and compared with the dislocation model proposed by Eshelby.

1. Introduction

In general, crystals show various morphology on growing under unequilibrium conditions, for example, dendritic growth of succinonitrile crystals [1], island formation of evaporated thin films [2] and twisting growth of metal whiskers [3]. Morphology is expected to give us a lot of important information both of constitutional materials and of crystal growth processes under unequilibrium conditions.

Visser and deBoer have reported that some needle-shaped crystals of substituted morpholinium TCNQ complexes [4] are twisted or curved. This is the first observation of unusual morphology of organic crystals, though such has been frequently found in whiskers of metals and inorganic compounds. Webb and coworkers reported that whiskers of α-Al₂O₃, silver, copper and palladium grown by chemical reaction are in the form of helices and twisted prisms [3,5,6].

We found that some crystals of (BPE-DMB)IBr₂ exhibit twisting along the growing axis over a macroscopic scale. (BPE-DMB)IBr₂ is a conducting charge transfer complex, where BPE-DMB is 1,4-bis[2-(pyrene-1-yl) vinyl]-2,5-dimethylbenzene [7]. The donor molecule consists of two pyrenes conjugated by divinyl-dimethylbenzene, as shown in Figure 1. It is expected that a large π-molecular orbit is extended over the molecule. (BPE-DMB)IBr₂ shows high conductivity of 100 S/cm at room temperature along the growing axis. Chemical compositional analysis revealed that ratio of (BPE-DMB):IBr₂ in single crystals is 1:1 [8]. Though its crystal

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1,4-bis[2-(pyrene-1-yl)vinyl]-2,5-dimethylbenzene

Fig. 1. — Molecular structure of BPE-DMB.

structure has not been determined yet, we estimated from X-ray oscillation photograph that the period along the growing axis is 1.08 nm.

In this work, we study morphology of the twisting crystals of (BPE-DMB)IBr₂ by scanning electron and optical microscopic observations and also by X-ray examination. The results are compared with the finding by Eshelby who proposed that the twist is stabilized by screw dislocations with giant Burger vector parallel to the growing axis [9]. The preliminary result of electrical conductivity measurement of the twisted crystal is compared with that of the non-twisted one.

2. Experimental

Molecule of BPE-DMB was synthesized as described in reference [7]. Crystals of (BPE-DMB)IBr₂ were grown by the standard electrochemical growth method from tetrabutyl-ammonium IBr₂ and BPE-DMB. CH₂Br₂ was used as a solvent. The obtained crystals are of needle shape with the typical size 3 × 0.01 × 0.003 mm³. Chemical compositional analysis for C and H and fluorescent X-ray analysis for Br were carried out. The results confirmed that the ratio of (BPE-DMB):IBr₂ in single crystal is 1:1 and solvent molecule of CH₂Br₂ was not detected within experimental sensitivity of 5 at. %.

Twisting morphology of the crystals was observed by scanning electron (SEM) and optical microscopes at room temperature. Especially, the twist pitch and the cross-section area were measured by SEM with an accuracy of 10%, where the twist pitch is defined as the length along the needle axis for 2π rotation of the crystal plane. X-ray oscillation and Weissenberg patterns were recorded using imaging plate. Data were processed with Rigaku Automated X-ray Imaging System at room temperature, with resolution of 50 × 50 μm² in area. Electrical conductivity of the crystal was measured by a dc four probe method. As electrodes, fine gold wires were attached with gold paste.

3. Results and Discussion

Many crystals of (BPE-DMB)IBr₂ were examined by optical microscope and about 5% of the crystals are twisted visibly. Some crystals are twisted clockwise while others counter-clockwise, with approximately equal proportions. The twist pitch is not uniform in a crystal; it is coarse in the tips and fine in the center. Figure 2 is a SEM image of a typical twisted (BPE-DMB)IBr₂
crystal which is twisted about 180° in 80 µm length in the center: its pitch is 0.16 mm. The non-uniform pitch is apparent in this figure. We measured the pitch in the crystals which were relatively large and capable of being handled. In most crystals the twist pitch near the center spreads from 0.1 to 8 mm. Because some twisted crystals were grown perpendicular to the electrode wire, it is not likely that the twist is a result of some electrostatic force applied by the electrode wire during growth.

We made an experiment in which external twist stress was applied to one tip while the other was fixed. After releasing the stress, the crystal recovered the original distribution of the pitch. In another experiment, the twisted crystals were heated up to the melting temperature of about 250 °C and quenched into liquid nitrogen. The distribution of the twist angle along the needle axis is not affected by both heating and cooling treatments. This result is in contrast with the finding by Visser et al. that morpholinum TCNQ complexes show a reversible development of twisted form on cooling. From the present results, thermally induced residual stress is not the origin of the twist; the twist morphology is quasi-stable.

Figure 3 shows a X-ray 0-th layer Weissenberg image of the typical twisted crystal, which was rotated around the growing axis during exposure. From optical and SEM observations the twist pitch of the examined crystal was 8 mm (1).

All diffraction spots are found to elongate along the rotating axis; the diffraction condition is satisfied at any angle of the crystal rotation. The X-ray film, whose diameter is 58.1 mm, is displaced synchronously by 1 mm while the crystal is rotated by 2°, and the length of the elongated spots is approximately 8 mm irrespective of the indices. From these values, the twist angle is 16° within the sample volume irradiated by X-ray beam (collimator diameter 0.7 mm). In Figure 4, the X-ray intensity profiles of an elongated spot along and perpendicular to the growing axis are plotted. Intensity of the reflection spot along the growing axis shows a continuous variation without any break or any step within experimental accuracy. Though its functional form depends on the experimental arrangement, asymmetry of the intensity

(1) In crystals of smaller twist pitch, X-ray diffraction spots are so broadened that intensity profile could not be separated from the background.
Fig. 3. — X-ray Weissenberg pattern of the twisting crystal.

Fig. 4. — X-ray diffraction intensity profiles of an elongated spot along (closed circle) and perpendicular to the growing axis (open circle).

Fig. 5. — Twist pitches plotted against crystal cross-section area.
distribution is explained by the non-uniform pitch along the growing axis and by the edge-like shape of this sample within the X-ray beam. If the crystal is twisted in discrete manner, X-ray intensity should show a discrete variation in the profile. We simulated if a discrete rotation of the crystal axes can be detected from Figure 4, assuming that the instrumental width of diffraction spot is given by that perpendicular to the elongated direction. We found that a stepwise and periodic rotation of the crystal axes by an angle larger than 0.2° could be resolved in Figure 4 as an oscillatory variation of the intensity. Careful studies were repeated and therefore we can conclude that the crystal is twisted rather continuously.

In whiskers of inorganic materials such as ZnS [10] and Pd [3], twisted ones have been frequently observed. Most of them are in a shape of spiral. Eshelby proposed that the twist is induced by the stress field by an agglomerate of screw dislocations parallel to the needle axis [9]. Webb and Forging found, in many crystals, a cavity of micron size inside the whisker [6]. Existence of such a cavity can reduce the core energy of the giant screw dislocation.

According to Eshelby [9], the twist pitch \( p \) is expressed by the relation

\[
p = 2\pi k(S/b)
\]

where \( b \) is the Burgers vector and \( S \) is the cross-section area. The constant \( k \) depends on the shape of a whisker but is not much different from 1. The above relation has been derived for isotropic medium but Frank has proved that it is usually applicable to crystals having anisotropic elastic constants [11].

In Figure 5, the pitches of the relatively large crystals are plotted against their cross-section area \( S \). In most crystals the pitch is not uniform, hence the averaged pitch in center part of the crystals is plotted in the figure. Though some other crystals show larger pitch of the twist, they are clearly separated from those plotted in the figure. The data show a rather large scatter, mainly because of limited accuracy of \( S \). Nevertheless, it is found that the pitch is proportional to \( S \). This result means that the giant Burgers vector \( b \) is independent of the samples and is as large as 240 nm. Since the real space period of the lattice along the growing axis is determined as 1.08 nm by the X-ray oscillation photographic image, each crystal contains approximately 230 screw dislocations, which are distributed near the center of the cross-section. It is quite unexpected that every crystal contains the same number of dislocations. According to Frank, screw dislocations have been introduced during growth, some in pairs, and those of the like-handed were self-trapped while others were expelled from the crystal. However there is no mechanism to keep a constant number of dislocations with the same sign in the crystal in spite of the crystal growth under different conditions of the electrochemical method. Furthermore the observed pitch is not uniform and changes gradually from one tip and another in all crystals of \((\text{BPE-DMB})\text{IBr}_2\); the pitch is fine in the central part of the crystal and coarse in both ends, as illustrated in Figure 2. This means that screw dislocations were introduced and then expelled as the crystal grows in spite that the cross-section area is uniform.

The electrical conductivity of the twisted crystal was also measured and compared with that of the non-twisted one. The former is one order of magnitude smaller than the latter. The difference is dependent on temperature and just outside the uncertainty limit of the sample size. The conductivity increases with increasing temperature. Assuming that \((\text{BPE-DMB})\text{IBr}_2\) is a semiconductor, the energy gap is about 400 K. Both temperature dependences of the twisted and the non-twisted crystals are approximately the same. This means that the twisting is correlated with many scattering centers for carriers in the crystal without significant influence on the electronic structure. This result may imply that there is considerable amount of imperfection or impurity in the crystal. It is not likely in metals that scattering is associated with screw dislocations; highly strained region localized near dislocations does not contribute
to such reduction of the conductance since they are parallel to the current path and small in volume. Further investigation is needed for clarifying the relation.

In conclusion, we found that some crystals of (BPE-DMB)IBr₂ are twisted. The twisting is quasi-stable against external twisting force and thermal treatments and is rather continuous in sub-micron scale. The observed twist is explained qualitatively by the Eshelby’s screw dislocation model. However, assuming this model, an unusual result should be derived that all twisted crystals have the same number of dislocations in it. Therefore, while the dislocation model for the twist is plausible in general, it should be more carefully examined the present system if the twist morphology in the organic crystals can be explained.

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