Trans. Mat. Res. Soc. Japan 38[4] 565-568 (2013)

Growth and X-ray topographic characterization of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals

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Crystalline perfection in organic charge-transfer complex single crystals, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, was characterized by means of synchrotron X-ray topography. Single crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br were grown electrochemically using a relatively large glass cell in order to scale up the synthesis. The quality of the crystals was examined using white and monochromatic X-ray topography. There was no asterism of each spot in the Laue photographs, though the defect image in the spot was not resolved because of low-resolution power of the white beam topography. We also obtained monochromatic X-ray topographs with 1.0 Å X-rays and were able to observe line images of dislocations. Dislocation density of the specimen was approximately 7 x 10^3 cm^{-2} on an average in the whole area of crystal. However, dislocation lines were annihilated in the topograph taken after annealing at room temperature for 5 months. Furthermore, new lattice defects were generated in the crystal after similar room temperature annealing for 15 months. The change of defect structure was caused by X-ray irradiation because dislocations in the un-irradiated crystal were observed by the monochromatic X-ray topography even after 2 years annealing at room temperature. Point defects formed by the X-ray irradiation probably interacted with grown-in dislocations and secondary defects were formed in the specimen crystal, though a long time was needed for this reaction at room temperature.

Keywords: synchrotron radiation, topography, organic compound

1. Introduction

Most organic charge-transfer complexes are synthesized by electrolytic deposition method. Considerable effort has been expended towards measuring physical properties, such as resistivity, magnetic susceptibility and specific heat, of the organic charge-transfer complex crystals. In general, these properties have been measured using small crystals because it is difficult to grow large organic crystals. However, it is important to experimentally compare the physical properties of crystals with different crystalline quality. Recently, Taniguchi *et al*. have reported that 50 mg-class single crystals of β'-(BEDT-TTF)$_2$ICl$_2$ were grown electrochemically using a large glass cell [1]. They established the preparation method for large single crystals of BEDT-TTF salts. The characterization of grown-in defects in crystals is important for obtaining large and high quality single crystals. However, reports on defects in organic crystals are very limited in number, since it is difficult to grow high quality crystals and to prevent radiation damage by X-rays during characterization. About 20 years ago, it has become possible to obtain X-ray topographs without crucial destruction of crystals using synchrotron X-ray because of very short exposure times [2]. A number of topographic investigations of organic crystals, such as low dimensional semiconducting salt; TEA(TCNQ)$_2$ (triethilanine tetracyanoquinodimethane), C_{60}, urea and lysozyme crystals, have been reported using this new method [3-6].

In this paper, we report the characteristics of defects in organic charge-transfer complexes, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals, using synchrotron X-ray topography with a white and a monochromatic beam. It is well known that the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystal shows a superconducting transition at 11 K [6]. Therefore, this material is of broad interest from the viewpoint of not only crystallography but also electronic properties. Many investigations on electric properties in the

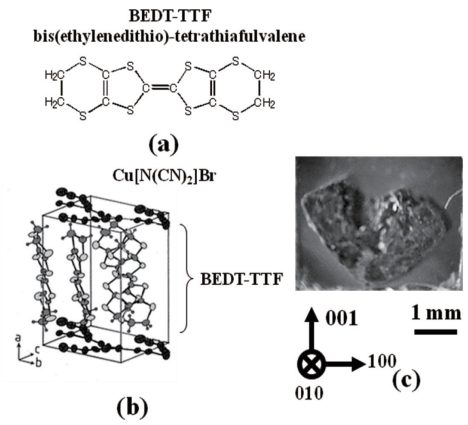

Fig.1 The chemical formula of BEDT-TTF (a), crystal structure (b) and photograph of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal specimen (c).

crystals were reported but topographic study on lattice defects was not carried out. The present work was a planed with the aim to characterize the grown-in defects using synchrotron X-ray topography.

2. Experimental procedure

Single crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (orthorhombic. space group *Pmma*, a=12.94Å, b=30.02 Å, c=8.54 Å) were grown by galvanostatic anodic oxidation of BEDT-TTF using φ_4P[N(CN)$_2$] and CuBr in 90% 1,1,2-trichloroethane and 10% ethanol [7]. For this growth, we used a relatively large glass cell, the inner volume of which was more than 200 ml, in order to scale up the synthesis. The reaction was carried out on platinum electrodes with a constant current of 0.5 μA, and the crystals were harvested after about 3 months. The chemical formula of BEDT-TTF, the crystal structure and a photograph of a κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal specimen are shown in Fig.1 (a), (b) and (c), respectively. The size of the specimen crystal was about 3x3x0.8 mm^3.

We first obtained Laue photographs of the specimen crystals using a highly parallel white X-ray

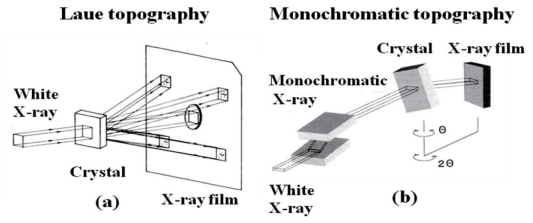

Fig.2 Schematic illustration of the experimental setup for Laue (a) and monochromatic (b) X-ray topography.

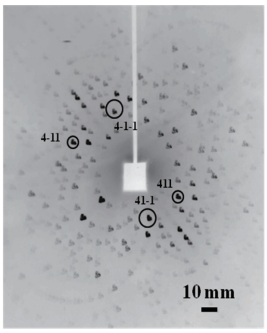

Fig.3 Laue photograph of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br for determination of crystal orientation of the specimen and observation of white beam topographs.

beam (0.4 Å < λ <2.5 Å) from a synchrotron source (Laue topography). Next, we obtained topographs using monochromatic X-rays with 0.6, 1.0 and 1.5 Å wavelengths, and the optimum wavelength for the present experiments was determined. The diffraction plane used for the present observations was {411}. Figure 2 shows the experimental setup for Laue and monochromatic topography. The topographic observations were carried out at the high speed X-ray topographic station (BL-15B1) at the Photon Factory in Tsukuba, Japan. With the synchrotron operating at 2.5 GeV and approximately 300 mA, typical exposure times were 0.5 s and 4 min. for the white and monochromatic topographs, respectively. Images were stored on an Ilford L-4 Nuclear Plate (25μm-thick emulsion) with a spatial resolution of a few μm. The distance between the specimen and the film was 265 mm for both the monochromatic and white beam topography. After the above observations, our experiments were interrupted by the completion of the allocated time from the synchrotron facility. Approximately five months later, we resumed obtaining monochromatic topographs with the same conditions as before. Finally, we also obtained monochromatic topographs after 20 months from the first observations. The specimen crystals were kept at room temperature with low humidity (40%) for 20 months.

3. Experimental results and discussion

Figure 3 shows the Laue photograph obtained using the synchrotron X-rays. There is no asterism of each of the Laue spots in the white beam X-ray topographs. Therefore, this crystal seems to be a good quality crystal at first viewing. Since each spot recorded on the X-ray film possesses a fine structure, the spots were stored on nuclear plates and enlarged using an optical microscope. Figure 4 shows a series

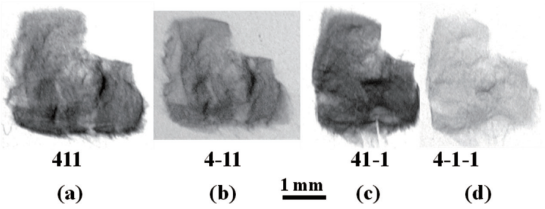

Fig.4 A series of enlarged white X-ray topographic images of the {411} spots obtained from κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal. The contour of the crystal and the diffracted area originated from lattice defects with high density were observed. However, individual defects were not resolved.

of enlarged white X-ray images of four {411} spots shown in Fig. 3. The dark areas in the topographs satisfy the Bragg condition. The diffracted area originating from lattice defects with high density varied with the diffraction plane. However, individual lattice defects such as dislocation lines were not observed in the topographs recorded on the nuclear plate because of low resolution of the white X-ray topographs and high defect density. Resolution power of the white beam topography was lower than 10 μ m at least. Thus, characterization of the lattice defects in organic conducting crystals by Laue topography with white X-rays is not suitable because of low-resolution power and high density of defects in the crystal.

We then obtained monochromatic X-ray topographs with 3 different wavelengths (0.06, 0.10 and 0.15 nm) in order to determine the optimum wavelength. Figure 5 shows the monochromatic (-41-1) topographs with different wavelengths. X-rays with short wavelengths are too sensitive to the strains of defects as shown in Fig. 5 (a). The weak image shown in Fig. 5 (c) indicates that absorption of long wavelength X-rays by matter is greater than that of short wavelength X-rays. The optimized wavelength for the observation of lattice defects in the present crystals thus was 0.1 nm.

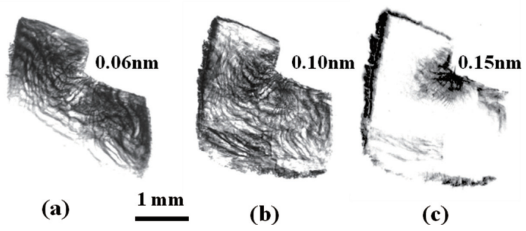

Fig.5 Magnified image of monochromatic X-ray topographs of the 4-11 spot with different wave length of X-ray. Topographs were taken by (a) 0.06 nm, (b) 0.10 nm and (c) 0.15 nm monochromatic X-ray, respectively. The optimized wavelength for observation of defects was 0.10 nm X-ray.

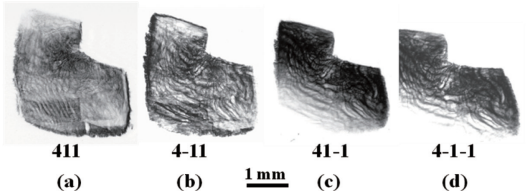

Fig.6 Monochromatic X-ray topographs of the {411} spots. The image of dislocation and its band were clearly observed in the topographs in contrast with white beam topographs shown in Fig.4.

Figure 6 shows four {411} monochromatic topographs obtained using the same diffraction conditions for the Laue topographs as shown in Fig. 4. The topographs clearly show images of defects, such as grown-in dislocations and dislocation bands, and the dislocation images varied with different diffraction planes. Dislocation density of the specimen was approximately 7 x 10^3 cm^{-2} on an average in the whole area of crystal. Unfortunately, we could not determine the Burgers vector of the dislocations because of lack of other topographs with different diffraction planes.

After obtaining the topographs shown in Fig. 6, the specimen crystal was kept at room temperature for 5 months. When machine time on the high speed X-ray topographic station again became available, we obtained monochromatic topographs in order to determine the Burgers vector. However, the topography images were vastly different from those obtained previously. Figure 7 shows the topographs taken under the same diffraction conditions as the topographs shown in Fig. 6 after annealing at room temperature for 5 months. Dislocation images were not observed in all the topographs in spite of the same conditions used for obtaining the topographs as before. We kept the specimen in room temperature again for 15 months for additional annealing after the observations shown in Fig. 7. Figure 8 shows the monochromatic

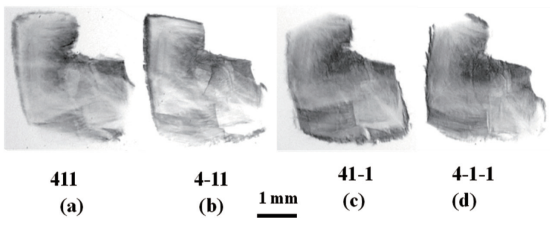

Fig.7 X-ray topographs taken by the same diffraction condition in Fig. 6 after annealing at room temperature for 5 month. Almost the whole images shown in Fig.6 were annihilated. Point defects generated by previous X-ray observation were interacting with the grow-in dislocation or themselves.

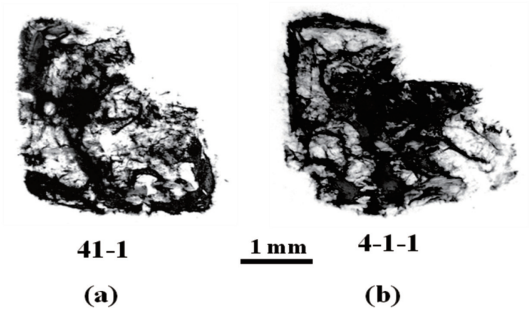

Fig.8 Magnified image of monochromatic X-ray topographs taken by the same diffraction condition in Fig. 6 after the annealing at room temperature for 20 months from first observation. There are new defects that have no relation to the grown-in dislocations shown in Fig. 6.

topographs obtained after the 15 months annealing. There are new defects that have no relation to the grown-in dislocations shown in Fig. 6. We also took monochromatic X-ray topographs shown in Fig. 9 of another un-irradiation crystal after about 2 years annealing at room temperature. Although the crystalline perfectibility was less than that of the large crystal in Fig.6, the topograph showed the dislocation images similar to those in Fig. 6.

At the topographic observation, new point defects such as vacancies were generated in the specimen by the synchrotron X-ray irradiation. A number of excess vacancies diffused to grown-in dislocation and were annihilated by absorption during the long time annealing. The dislocations were rearranged to tangled new dislocation network as shown in Fig. 8.

These results suggest that irradiation damage from the X-rays and formation of secondary defects occurred in the specimen crystal. Chemical bonding of organic molecules in the crystal is very weak. Therefore, the irradiated X-ray photons break bonds and form many point defects. These point defects interacted with grown-in dislocations or themselves and finally, new dislocation distribution was generated in the crystal.

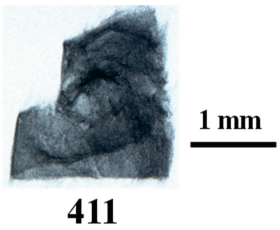

Fig.9 Magnified image of monochromatic X-ray topographs of another un-irradiation crystal after about 2 years annealing at room temperature.

In conclusion, defects such as grown-in dislocations in organic conducting crystals could be clearly observed using monochromatic X-ray topography. However, during characterization by synchrotron X-ray, radiation damage arises. This leads to the generation of point defects. It is necessary to develop a device such as the water filter for lysozyme crystals to deduce the irradiation damages [6, 8].

Acknowledgement

This work has been performed under the approval of the Photon Factory Advisory Committee (Proposal No. 2011G675).

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(Received June 8, 2013; Accepted August 3, 2013)