Crystal structure determination of $(H_2pc)_3 PF_{6-x}Cl_x$ by synchrotron powder diffractometry

Takashi IDA*[1], Fumiharu SATO[1], Hiroyuki OKUNO[2], Hideo YAMAKADO[2] and Hideo TORAYA[1]
[1]CRL, Nagoya Inst. Tech., Tajimi, Gifu 507-0071, Japan
[2]Wakayama Univ., Wakayama 640-8510, Japan

A new partially oxidized metal-free phthalocyanine (H_2pc) salt was electrochemically synthesized from neutral H_2pc in 1-chloronaphthalene solution with $(n\text{-}Bu)_4N\ PF_6$ as the electrolyte. The electric conductivity along the growth axis of a needle-like crystal was about 9 S cm^{-1} at room temperature. The results of chemical analysis have implied that the composition is nominally $H_2pc\ (PF_{5.28}Cl_{0.72})_{0.28}$. It has been suggested that the fluorine atoms in the PF_6 ions were partly substituted by chlorine atoms during the electrochemical process.

Powder X-ray diffraction data have been collected with a high-resolution powder diffractometer MDS [1] on beamline BL4B2 at the Phothon Factory. The incident beam wavelength was 1.2072(4) Å. A Lindemann glass capillary of 1.0 mm ϕ in diameter filled with 9 mg of the grinded powder sample was used as the specimen for the powder diffraction measurement. The collected diffraction data range was 1 to 150º in 2θ at a step size of 0.004º using a counting time of 8 s per point.

All the detectable diffraction peaks were indexed by assuming a rhombohedral (*R*3) unit cell with the refined lattice parameters of a = 21.3427(4) Å and α = 119.42784(2)º. The cell volume of 1909.5(1) $Å^3$ indicates the existence of three H_2pc molecules in the unit cell. The periodicity of 4.8687(2) Å along the [111] direction coincides with the observed periodicity along the growth axis in the oscillation photograph taken for a bundle of thin needle-like crystals in our laboratory.

The chemical composition of $(H_2pc)_3\ PF_{6-x}\ Cl_x$ was assumed to satisfy the requirement of the symmetry. The powder diffraction pattern was simulated for further simplified composition, $(H_2pc)_3\ PF_6$ (x = 0). The position and orientation of the H_2pc and PF_6 molecules were optimized by a least-squares method to fit the observed diffraction intensity data, treating H_2pc and PF_6 molecules as rigid bodies. The common isotropic atomic displacement parameter of 0.01 $Å^2$ was assumed for all the atoms.

Figure 1 shows the experimental powder diffraction data, calculated curve for the optimized structure of $(H_2pc)_3 PF_6$, and the difference plot. The reliability factor for the profile fitting was 11.89 %.

The projection of the refined crystal structure along the [111] direction is shown in Fig. 2. H_2pc molecules are uniformly stacked along the [111] direction. The optimized angle between the [111] and the normal direction of the H_2pc molecular plane was 46.88(1)º, which gives the interplanar distance between the neighboring H_2pc molecules to be 3.33 Å. The orientation of each H_2pc molecule relative to the stacking axis is very similar to that of the X-polymorph of neutral H_2pc [2].

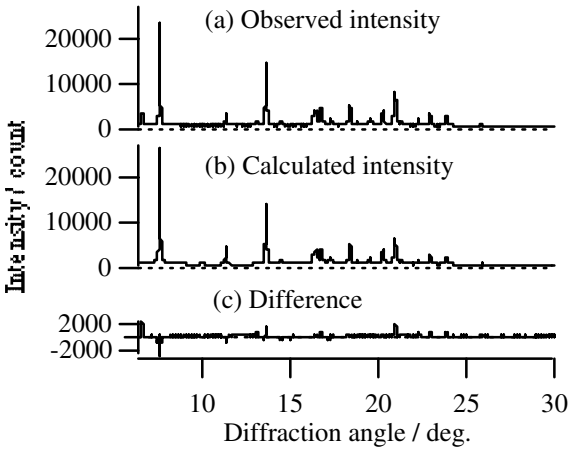

Fig. 1 (a) Synchrotron powder diffraction pattern of $(H_2pc)_3\ PF_{6-x}\ Cl_x$, (b) calculated curve for the optimized $(H_2pc)_3\ PF_6$, and (c) the difference.

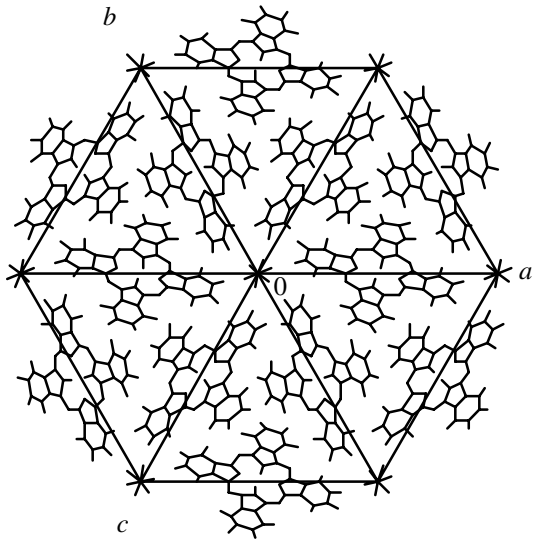

Fig. 2 Projection of the optimized crystal structure of $(H_2pc)_3\ PF_6$.

References

[1] H. Toraya et al., J. Synchrotron Rad. 3, 75 (1996).
[2] R. B. Hammond et al., J. Chem. Soc. Perkin Trans. 2, 1527 (1996).

* ida@crl.nitech.ac.jp