High pressure synthesis of organic charge-transfer complex (BEDT-TTF)(TCNQ)

Tomoyuki Tenkawa, Hiromi Taniguchi, and Kazuhiko Satoh
Graduate School of Science and Engineering, Saitama University, Japan
Email: s08mp114@mail.saitama-u.ac.jp

We are developing the novel method of synthesizing organic charge-transfer complexes by introducing the high-pressure technique into synthesis procedure. This study is motivated by that new materials are possibly harvested under unusual condition. At the beginning, we tried to synthesize (BEDT-TTF)(TCNQ) by applying the pressure. Usual method of the synthesis of (BEDT-TTF)(TCNQ) is the direct reaction (at ambient pressure): after making BEDT-TTF and TCNQ molecule dissolved in organic solvent, the solution is refrigerated or evaporated to saturate radicalized molecules. We have introduced a pressure into this synthesis. In general, solubility of solution decrease as the pressure increase. So, with increase of pressure, the solution(of radicalized molecules) become saturated and then crystals are produced.

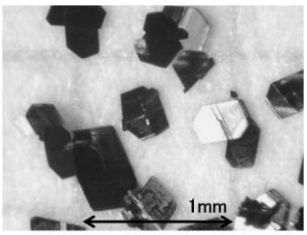

Fig.1 crystals obtained under 0.087GPa

The examined pressures are 0.087, 0.17, 0.35, 0.44, 0.52, and 0.61GPa, which are generated by large piston cylinder with inner diameter of 12mmϕ. In a typical experiment, 1.3×10^{-3}(mol/L) of BEDT-TTF and TCNQ molecules are dissolved in 1,1,2-trichloroethane. And crystals are obtained after several days at room temperature.

We found that the obtained crystals depend on three characteristic parameters; pressure, concentration of molecules, and synthesizing time. As the pressure increase, the number of crystal nucleus increases and size of crystals reduces. For example, in low pressure of 0.087GPa, the single crystals shown in Fig.1 are obtained. In contrast, a large amount of tiny crystals are obtained in high pressure of 0.52GPa. This is attributable to rapid growth in this condition. The difference in the obtained crystals between low and high pressures suggests that the pressure contributes to the crystal growth by decreasing solubility of solvent. Second is the dependence in concentration of molecules in solvent. We succeed in controlling the phase of the crystal: we obtained β"-phase[1] in lower concentration of 1.3×10^{-3}(mol/L) and β'-phase[2] in far higher concentration. Third is time dependence. As synthesizing time under pressure increase, crystals grow larger.

We succeeded in synthesizing (BEDT-TTF)(TCNQ) under pressure for the first time. Now, we are exploring suited conditions for getting new phase crystals by controlling parameters.

[1] H.M. Yamamoto *et al*., Synthetic Metals 133–134 (2003) 449
[2] Y. Iwasa *et al*., Phys. Rev. B. 49, 5 (1994) 3580