



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Version of record first published: 24 Sep 2006

To cite this article: Seiji Isoda, Tomoyuki Haishi, Kaname Yoshida & Takashi Kobayashi (2001): Structures of Copper Phthalocyanine Crystals Grown in Inert Gases, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 370:1, 227-230

To link to this article: <http://dx.doi.org/10.1080/10587250108030076>

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Structures of Copper Phthalocyanine Crystals Grown in Inert Gases

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Crystallization process of copper phthalocyanine was studied in inert gases by sublimation. Near the sublimation source, crystalline particles of the α -form is grown, and they change into ribbon-like crystals as increasing the height from the sublimation source. The crystal structure of smaller ribbon-like crystals is the α -form, and transforms into the β -form with increasing the height. The same structural changes were also observed by increasing the gas pressure. The structure change from the α - to β -form happened at low height and low gas pressure, when the inert gas with large atomic number is used.

Key Words: Phthalocyanine; Sublimation; Inert gas; Polymorph

INTRODUCTION

Properties of molecular crystals depend on the state of aggregation as well as the molecular characteristic itself. It is, therefore, important to control the aggregation or crystallization of molecules so as to achieve an intended property as a practical material. In this report, we will present a method to control the polymorphic structures, α - and β -forms of copper phthalocyanine (CuPc), by using sublimation in inert gases. The β -form, stable form, exists as large needle-like crystal, and the α -form, metastable form, usually exists as very fine powder made by sublimation in inert gases or by grinding the β -form [1, 2]. We make clear the precise method to fabricate either of the forms.

EXPERIMENTAL

Powdery CuPc was heated in a small quartz crucible under various gas pressures of inert gases of He, Ne, Ar and N₂ (FIGURE 1). The changes in morphology and structures of formed crystals were examined as functions of the kind of gases, pressures and height of capturing plate from the sublimation source. The gas pressures were in the range of 0 to 40 Torr for each gas. The crystals were captured on electron microscopic grids at capturing plates which is set at 3, 6 and 9 cm from the source.

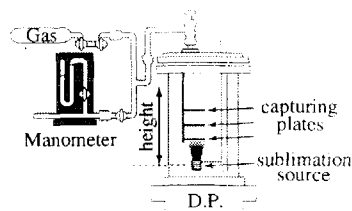


FIGURE 1 Crystal growth in inert gases.

RESULTS AND DISCUSSION

The morphological changes as functions of pressure and height in the case of He gas are shown in FIGURE 2. In the figure, the particle and ribbon-like crystals are observed. The particles are found to be formed at low pressure and small height, while the ribbon-like crystals at high pressure and large height. As for the height dependence, the CuPc crystals grow from vapor to particle, and finally to ribbon-like crystals in due course of growth. This tendency is also observed in other gases, but the values of pressure and height where the morphology changes are different for each kinds of inert gas. The observed morphology changes at the height of 3 cm are summarized in FIGURE 3. With increasing the atomic number of inert gas, the morphological change from particle to ribbon-like crystal happens at lower pressure, which indicates the importance of collision process of CuPc and gas atom in the present growth process.

FIGURE 4(a) shows a typical diffraction pattern from particles obtained at 2 Torr of He gas pressure, where strong reflections with 11.9 Å spacing correspond to 002-reflection of the α -form. The α -form is known to have the lattice dimensions of $a=23.180\text{ Å}$, $b=3.818\text{ Å}$.

$c=23.84\text{\AA}$ and $\beta=91.9^\circ$ [3]. At around 20Torr, the crystal grows as ribbon-like one which exhibits a diffraction pattern shown in FIGURE 4(b). The spacing of 3.79\AA agrees with the (020) spacing of the α -form. At higher pressure of 40Torr, the ribbon-like crystal grows further and gives a spacing of 4.79\AA which is the (020) spacing of the β -form as shown in FIGURE 4(c). With increasing the size of ribbon-like crystals, the structure changes into the β -form. The lattice dimensions of the β -form are $a=19.407\text{\AA}$, $b=4.790\text{\AA}$, $c=14.628\text{\AA}$ and $\beta=120.56^\circ$ [3]. Between 20 and 35Torr, the ribbon-like crystals of α - and β -forms coexist as shown in FIGURE 4(d). The structural changes are

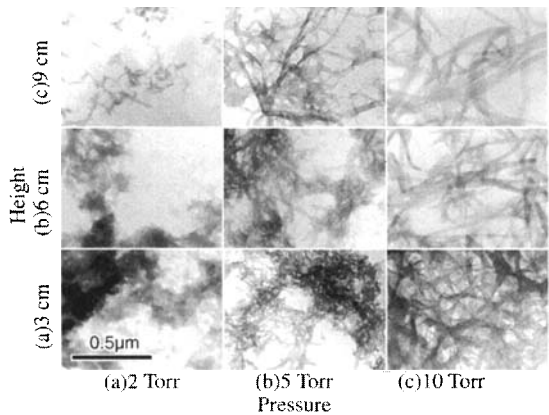


FIGURE 2 Morphological changes of captured crystals depending on gas pressure and height in the case of He gas.

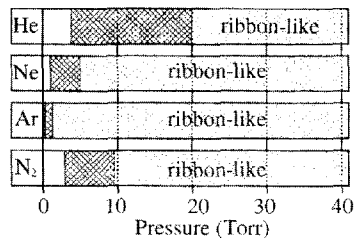


FIGURE 3 Pressure ranges of the morphological changes are indicated by cross-hatch for each inert gas. At lower pressures from the range, only particles were observed, and ribbon-like crystals were observed at higher pressures.

summarized in FIGURE 5, which indicates a possibility to control the polymorph of CuPc by choosing appropriate crystallization conditions in inert gases.

As for the change from the α -form to the β -form, it happens in the growing process of ribbon-like crystal, which suggests the size effect of energetic stability of both forms. Actually Iwatsu has reported that the α -form is stable at smaller crystal size and the β -form becomes stable with increasing the size from an energy calculation [4]. The threshold size has been concluded to be some hundreds Å, which agrees well with the present result.

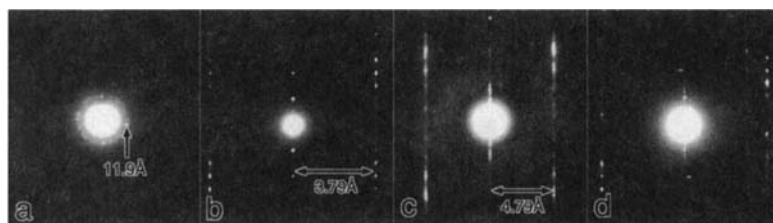


FIGURE 4 Electron diffraction patterns of α -form fine particles (a), α -form ribbon-like crystals at lower pressure (b), β -form ribbon-like ones at higher pressures (c) and mixture of α -form and β -form at intermediate pressures (d).

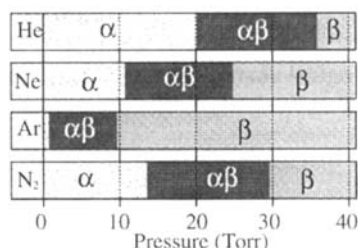


FIGURE 5 Structural changes of CuPc with gas pressures. α , $\alpha\beta$ and β indicate the existing ranges of α -form, mixture of both forms and β -form, respectively.

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