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# Anthracene and Anthracene–Tetracene Crystals from Vapor†

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## Introduction

Molecular crystals in general are receiving increased attention and anthracene crystals in particular are in demand for use in various studies. Consequently, several techniques have been developed for growing anthracene crystals—most of which have involved growth from the melt.[1–3] In those instances where vapor growth has been used, the most common method is to use a cooled collector plate.[3, 4] The principal disadvantage of the latter method is the limited thickness of the crystal that can be obtained, owing to the low thermal conductivity of anthracene. In connection with our various studies of the interaction of energy with anthracene it is often necessary to be able to grow large and uniformly doped crystals. The techniques referred to above are not suited to the task. A procedure for growing relatively large anthracene crystals with tetracene uniformly distributed throughout is reported here.

## Methods

This system for growing large single-crystal anthracene from the vapor is simple and relatively inexpensive. Its principle is similar to that used by Pizarello for growing lead sulfide.[5] The apparatus consists of a bath of stirred GE Versilube F-50 with a tube-type immersion heater at the bottom and the temperature throughout the apparatus regulated by a single thermostat. The bath is

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covered by a thick sheet of Plexiglass which reduces temperature fluctuations resulting from air currents in the region immediately above the bath.

An important feature of the apparatus is a glass sheath through which the crystal-growing cell is withdrawn. This sheath extends to a depth of 3 to 5 mm below the liquid level of the bath. Without the sheath, the temperature fluctuation in this region becomes excessive.

The bath temperature is about 200°C (m.p. of anthracene is 217°) with fluctuations corresponding to the on–off cycle of the heater of about ±0.2°. This temperature variation apparently occurs simultaneously in the growth and nutrient regions and hence the growing crystal is essentially unaffected. The difference in temperature between the growth and nutrient regions is about 0.8° as measured by thermocouples in an unevacuated cell.

About five grams of anthracene (previously purified by chromatography, vacuum sublimation, and zone refining)[6] are placed in an evacuated precision-bore Pyrex cell (8 mm × 10 cm). The precision bore facilitates removal of the anthracene after the crystal is grown. A capillary ending in an expanded bulb in the crystal-growing tip of the cell is used to initiate crystal growth. Prior to placing the cell in the bath, the bulk of the anthracene is sublimed to the nutrient end of the cell and a small portion sublimed into the expanded bulb. The capillary is then gently heated with a torch to prevent spurious deposition of the anthracene in the capillary region. The cell is then immersed in the bath, and after thermal equilibration, it is raised sufficiently to allow growth to occur in the expanded bulb. Subsequently, the cell must be constantly rotated and raised at a rate no greater than the growth rate of the crystal (6 mm per day).

To prepare the small tetracene concentrations for the mixed anthracene-tetracene crystals, a dilution technique was employed in a Pyrex manifold containing a number of cells. A measured amount of tetracene was added to the anthracene for the first cell. After melting and thoroughly mixing, half of the mixture was added to an equal amount of anthracene at the next cell. The first cell was sealed off. The new mixture at the second cell was melted and the process repeated as before. In this manner, concentrations of tetracene of 1 to 500 ppm were prepared. At this point the same apparatus and technique described in the previous paragraph were employed to grow the mixed anthracene–tetracene crystals.

## Results

Two defects seem to characterize these vapor-grown anthracene crystals: short triplet lifetimes (2 msec) and poorly defined cleavage planes. The former probably comes from inclusion of impurities throughout the growing crystal. It could also be caused by the fact that the crystals were not grown under red light conditions. The cause of the latter defect is uncertain. Growth rates as low as 1 mm per day did not improve the cleavage planes. No apparent difference was observed in evacuated cells or in cells containing an inert gas. The crystals were examined in polarized light and had the appearance of single crystallinity.

The concentration of tetracene (1 to 500 ppm) in anthracene crystals was checked by comparing the ratio of the fluorescence emission spectra at 5620 Å and 4350 Å with known mixtures.[7, 8] The concentration was equal to the average concentration in the polycrystalline starting material. No difference in concentration from one end of the crystal to the other could be detected. This result is in sharp contrast with melt-grown mixed crystals where a distinct concentration gradient of the impurity is apparent.

Rejection of impurities is more pronounced in melt-grown crystals than in vapor-grown crystals. There are two phases in the melt process: the liquid nutrient and the solid growing crystal. In vapor process, on the other hand, there are three phases: the solid nutrient, the intermediate vapor phase, and the solid growing crystal. In the melt process the impurity distribution coefficient is such that generally the liquid becomes more concentrated with the impurity until the bulk of the impurity is deposited at the time the last remaining liquid is converted to solid. In the vapor process the solid nutrient and the solid growing crystal are at nearly the same temperature. If the growth process is sufficiently slow, the impurity is at equilibrium in the vapor phase between these two solid phases. Therefore, the concentrations of impurity in the two solid phases are essentially the same, and a uniform distribution of impurity in the growing crystal is the result.

Growing doped crystals from the vapor should be considered if a relatively large crystal with a uniform impurity concentration throughout is desired.

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