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ON THE GROWTH OF SINGLE CRYSTALS OF NAPHTHALENE

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ABSTRACT. A glass furnace for the growth of single crystals of naphthalene (m.p. 80°C) from the melt by Bridgman-Stockbarger method is described. Crystals upto 1 in. in diameter and 8 in. in length can be easily grown. Different parameters affecting the growth of single crystals and various laboratory procedures have been outlined. The furnace, with suitable alterations, can also be used to grow single crystals of anthracene (m.p. 217°C).

INTRODUCTION

The increasing amount of interest in the studies of semiconducting, optical and ultrasonic properties of naphthalene and anthracene have prompted various workers in growing single crystals of these materials. A large number of methods are available for growing crystals of various materials (Buckley, 1951; Lawson and Nielsen, 1958; Gilman, 1963; Reynolds, 1963). Many theories have been developed to account for the various phenomena observed in crystal growth, but these are of very little assistance in the actual crystal growth in laboratories. For convenient operation and handling, every material requires a particular method for crystal growth, the selection of which depends much upon the melting point, chemical properties and crystal structure of the material. A method suitable for one material may be totally unsuitable for the growth of another material because of differences in melting point or chemical properties.

Although it appears that Bridgman (1925)-Stockbarger (1936) method is more frequently used, it is not the only available and not necessarily even the best method. Vapour phase or sublimation method (Volmer and Schultze, 1931; Obreimov and Prikhotjko, 1932; Lipsett, 1957; Mark, 1961) has been successfully used for growing single crystals of naphthalene in the form of flat platelets. Stober's method (1925) in which the crystal container is kept stationary and the temperature gradient varied, has been used by Belyaev *et al* (1959) and in a modified form by Roussett and Lochet (1942) to obtain good crystals of naphthalene. Kyropoulos (1926) method has also been used for obtaining large single crystals of naphthalene (Lawson and Nielsen, 1958).

Hendricks and Jefferson (1933) were probably the first to grow naphthalene crystals from melt. They adopted the method of Obreimov and Shubnikov

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(1924) which is a modification of methods devised by Tamman (1923) and also very much identical to Bridgman's method for growing inorganic crystals from melt. Bridgman's method has been extended by many workers (Feazle and Smith, 1948; Pimentel and McClellan, 1952; Pick and Wissman, 1954; Riehl, 1955; Sangster and Irvine, 1956; Lipsett, 1957, 1958; Yun and Beyer, 1964) for the preparation of large naphthalene crystals and is now mostly used.

REQUIREMENTS FOR THE GROWTH OF LARGE SINGLE CRYSTALS OF NAPHTHALENE BY BRIDGMAN-STOCKBARGER METHOD

In this method the material is melted in an evacuated glass capsule and very slowly lowered through a furnace which should have a sharp vertical temperature gradient near the crystal solid-liquid interface. A good large single crystal can be obtained depending upon the following parameters.

(a) *Furnace design*

The two essential points in designing a furnace for Bridgman-Stockbarger method are, achievement of good temperature gradient and convenience in operating and handling the furnace. The best form of temperature gradient is shown schematically in Fig 1. The maximum temperature should be kept 25° to 40°C

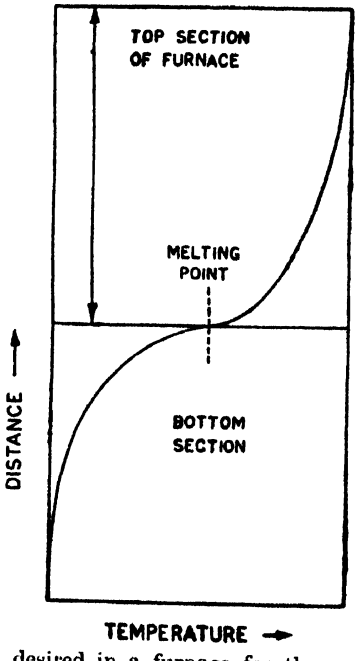

Fig. 1. Temperature gradient desired in a furnace for the growth of naphthalene single crystals.

above the melting point of naphthalene (80°C) to get rid of all traces of crystallinity in the melt. The temperature should fall gradually until the lowest part

of the top section is reached, and then it should drop abruptly, preferably to 65° or 70°C from 80°C.

(b) *Lowering rate*

The difficulties in growing large naphthalene crystals are mainly because of its great supercooling tendencies and low thermal conductivity. Almost all the heat of fusion of the growing crystal must be removed through the solid, which means that naphthalene due to poor thermal conductivity will take much time to solidify. Hence, lowering rate should be very slow, of the order of 0.1 in./hr or even less. The container is usually moved through the furnace by an electrically driven geared motor.

(b) *Shape of crystal container*

The super cooling tendencies of naphthalene and other organics required considerable care in the construction of crystal container. In designing the containers, the attempt is to initiate the growth of a singe crystal at a point or constriction. A number of crystal containers of various shapes, as shown in Fig. 2,

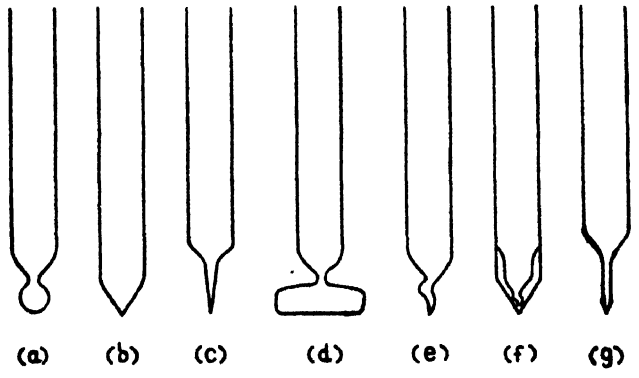

Fig. 2. Containers employed by various workers for the growth of single crystals : (a), Constricted bulb (Bridgman, 1925 and others) ; (b), Conical tip (Stockbarger (1936); (c), pointed capillary (Huber, et al., 1949 ; Loninger, 1952) ; (d), constructed bulb of large area (Lipsett, 1957) ; (e), Spiral tip (Spendiarov and Aleksandrov, 1959); (f), baffle tip (Sherwood and Thompson, 1960) ; and (g), ordinary thin capillary tip.

have been used by various workers. The authors have tried all these crystal containers and found type (d) and (e) the most suitable for naphthalene.

(d) *Purity of naphthalene*

When growing crystals by the Bridgman method, it is essential to use only material of the highest purity. Various methods are available for purification which include chromatography, multiple vacuum sublimation, vacuum sublimation with sulphuric acid treatment (Okamoto, *et al.*, 1962), normal freezing (Lipsett, 1957) and zone refining (Wolf and Deutsch, 1954; Herington *et al.*, 1956; Hayakawa, 1966; Inokuchi, 1966). In general, it has not been proved that any one of the

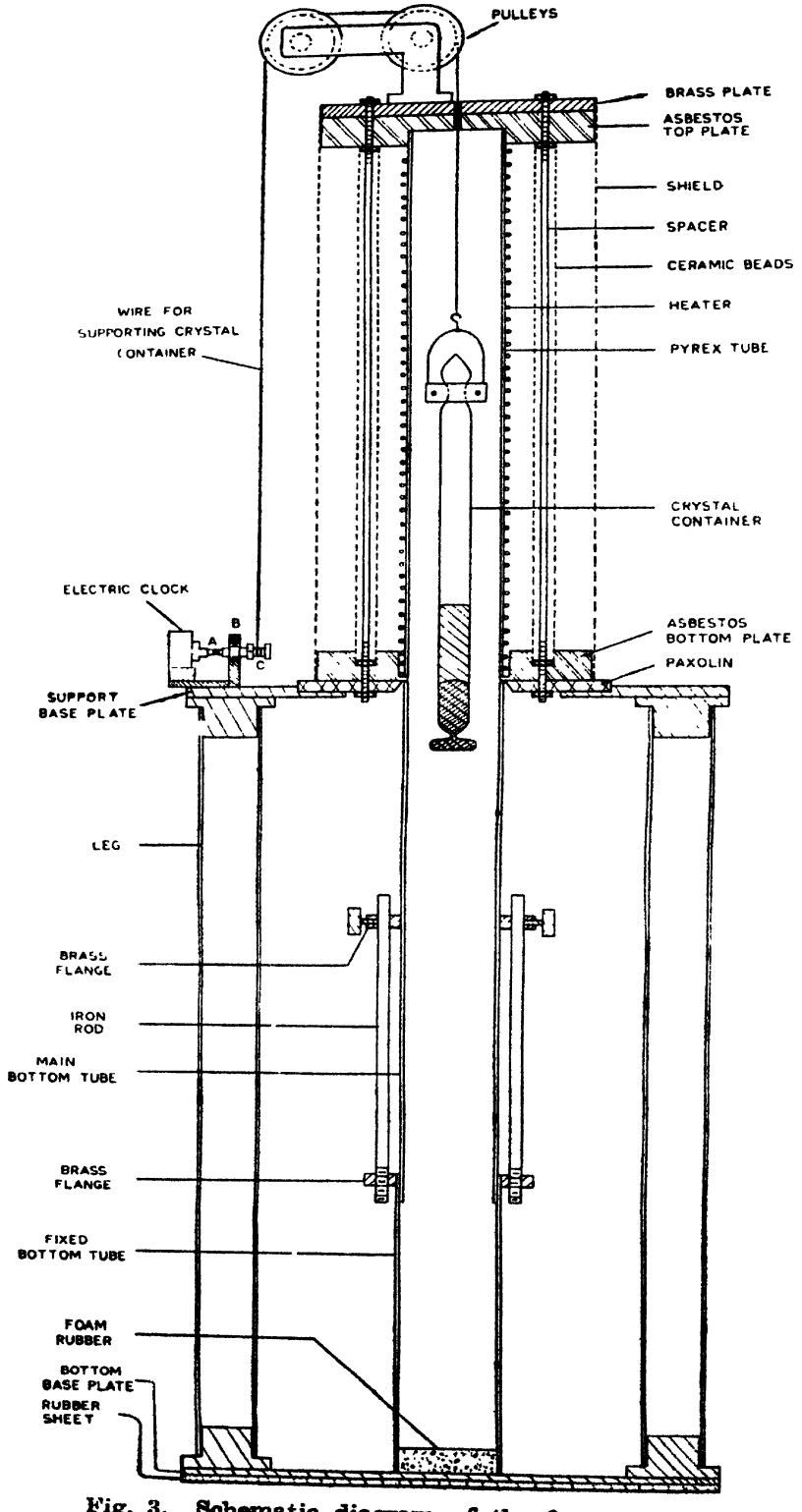

Fig. 3. Schematic diagram of the furnace.

above methods (excluding zone refining) possess advantages over others. Thus, one must carry out the purification by a combination of more than one of these methods. However, zone refining gives extremely pure naphthalene.

FURNACE FOR CRYSTAL GROWTH

A furnace incorporating the salient features discussed in the last section has been constructed in this laboratory. It is some what similar in design to that of Lipsett (1958).

The furnace, shown in Fig. 3, consists of two main sections—an upper Pyrex glass tube on which heater wire is wound and the lower brass tubes which are left at room temperature. The pyrex tube is 18 in. long and 60 mm in diameter. The tube rests on a thin (2 mm) asbestos projection which is supported by $\frac{1}{4}$ in. thick paxolin disc. The paxolin disc sits in a groove in support iron base plate, 14 in. square, and is fixed by three screws (not shown in the figure). The upper end of the pyrex tube fits tightly in a asbestos disc. A brass disc rests on the top of this asbestos disc. The top asbestos and the brass discs are secured in position by three iron spacers. This keeps the pyrex tube permanently in fixed position. The spacers are covered throughout their length by ceramic beads to prevent the heat being conducted to the top brass disc. This furnace is covered by galvanized iron sheet. The bottom section of the furnace consists of two tight fitting brass tubings. The lower tube is fitted to bottom iron base plate. This tube is 10 in. long and of $2\frac{3}{8}$ in. inner diameter and has a circular flange attached to it at the top. Two iron rods are firmly screwed in the top flange of the tube. The other tube which can slide up and down the iron rods is of $2\frac{3}{8}$ in. outer diameter and is 17 in. long. This tube can be fixed in any position on the rods by means of two set-screws. These brass tubes have been chromium plated. A piece of sponge rubber is placed inside the fixed bottom tube so that the crystal container is not broken due to some accidental release. The support base plate rests on four legs, made of $1\frac{1}{4}$ in. iron pipes. The complete unit is placed on a rubber sheet so as to reduce the effect of building and other vibrations to the furnace. The electric clock mechanism, etc., are mounted on the support base plate.

Two independent heaters have been used. The heater wires are insulated by small ceramic beads. The two heaters are connected together by means of a small ceramic connecting terminal strip so that they are arranged mechanicallly as a single wire, but are electrically insulated from each other. Stainless steel strips are used as anchors for the heater wire terminals. The wire is wound on the pyrex tube which is wrapped with asbestos paper to prevent slipping of the windings. The four heater leads are taken out through four small holes in the shield. Care is taken that no air leaks through these holes. All the leads are connected by means of screws and nuts, as hard soldering of the heater wires to the terminal leads in the furnace have a tendency to break after some heating

and cooling cycle. Power to both the top and bottom heater is supplied from two variable transformers fed from an A.C. line stabilizer. The temperature of the top portion of the furnace is nearly 110°C while it has been adjusted to 80°C at the bottom. A thermocouple has been permanently fitted to record the temperature of the furnace.

An electric clock mechanism has been used for lowering the crystals container. Care is taken to see that no undue strain is being exerted on the clock's gear train. A brass shaft of $\frac{1}{4}$ in. diameter passes through a ball bearing fitted in a brass hanger (B in Fig. 3) and projects on either side. One side of the shaft is coupled to the hour hand of the clock through a universal joint (A) which is bushed at one end to fit the clock. On the other end of the shaft, small wheel (C) with a groove of nearly 3/16 in. diameter is placed with the help of two setscrews. The wire supporting the crystal container is wound on this wheel. This wire passes from the wheel over two other ball-bearing pulleys through a small hole drilled in the top discs and is attached to a hanger which keeps the wire taut when no crystal container is suspended in the furnace. The crystal container is fastened to a collar at the bottom of this hanger. The usual rate of descent of the crystal container with 3/16 in. diameter wheel is about 0.049 in. in an hour. This could be made less by employing a wheel of smaller diameter.

LABORATORY PROCEDURES

The actual growth of a crystal is only a small part in the production of a final finished crystal. Many laboratory procedures have to be carried on before and after the growrh. The crystal container is throughly cleaned (Rosebury, 1956), then filled with naphthalene, evacuated upto a pressure of 10^{-5} torr and sealed.

After crystal is grown, it is carefully taken out by cutting the container (Lipsett, 1957). It is then examined for principal cleavage plane (Lipsett, 1957). Naphthalene crystallizes in the C_{2h}^5—$P2_1/a$ space group (monoclinic crystal structure) and the principal cleavage plane is the *ab*-plane (Bannerjee, 1930; Abrahams, *et al.*, 1949; Robertson, 1953; Winchell, 1954). Since solid naphthalene forms a biaxial crystal, it is possible to identify a single crystal and the location of *b*-axis by using a polarizing microscope (Winchell, 1947; Menzies and Skinner, 1949; Pimentel and McClellan, 1952; Lipsett, 1957; Bloss, 1961). The polishing of crystals is an important part in the production of crystals and standard techniques (Lipsett, 1957; Yun and Beyer, 1964) have been used. The polished surfaces of naphthalene crystals deteriorate by sublimation. To preserve the surfaces, one should keep naphthalene crystals either in an inert atmosphere or in a frigidare.

REMARKS

The furnace described above has proved very successful in growing naphthalene single crystals. Insertion or removal of a crystal container hardly takes a few minutes. Naphthalene single crystals upto 1 in. in diameter and 8 in. long have been grown in the furnace. Large diameter naphthalene single crystals upto 2 in. can be grown if the pyrex tube diameter is 5 in. or more. The rate of descent of the crystal container then should also be reduced to 0.01 in. per hour. Longer crystals can be obtained simply by using longer furnaces. The furnace described above can also be conveniently used for growing single crystals of anthracene (m.p. 217°C) by suitably altering the power input to the two heaters. Anthracene powder has, however, to be sealed in the container at a pressure of 10^{-8} torr to avoid degassing. Moreover, no light should fall during crystal growth, otherwise photochemical reactions will take place.

It should be mentioned that cutting and polishing of crystals occupies an important place in the production of single crystals. It is more difficult to cut and polish a crystal without fracturing it than to grow the crystal initially unfractured.

These crystals are being used for studying electrical properties of naphthalene. These results would be reported elsewhere.

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REFERENCES

Abrahams, S. C., Robertson, J. M. and White, J. G., 1949, *Acta Cryst.*, **2**, 233.

Bannerjee, K., 1930, *Nature*, **125**, 456.

———— 1930, *Indian J. Phys.*, **4**, 557.

Belyaev, L. M., Belikov, G. S. and Dobrzhanskii, G. F., 1959, *Rost Kristallov*, 2, 102; transl. in *Growth of crystals*, 2, 77, (1959).

Bloos, F. D., 1961, "*An Introduction to the Methods of Optical Crystallography*" Holt, Rinehart, and Winston, New York.

Bridgman, P. W., 1925, *Proc. Am. Acad. Arts Sci.*, **60**, 305.

Buckley, H. E., 1951, "*Crystal Growth*", John Willey & Sons., Inc., New York.

Feazel, C. E. and Smith, C. D., 1948, *Rev. Sci. Instr.*, **19**, 817.

Gilman, J. J., 1963, "*The Art and Science of Growing Crystals*", John Wiley and Sons, Inc., New York.

Hayakawa, S., 1966, *Private communication.*

Hendricks, S. B. and Jefferson, M. E., 1933, *J. Opt. Soc. Am.*, **23**, 299.

Herington, E. F. G., Handley, R. and Cook, A. J., 1956, *Chem. & Ind. (London)*, 292.

Huber, O., Humble, F., Schneider, H. and Steffen, R., 1949, *Helv. Phys. Acta*, **22**, 418.

Inokuchi, H., 1966, *Private communication.*

Kyropoulos, S., 1926, *Z. anorg. Chem.*, **154**, 308.

Lawson, W. D. and Nielsen, S., 1958, "*Preparation of single crystals*", Butterworths, London, 11.

Leninger, R. F., 1952, *Rev. Sci. Instr.*, **23**, 127.

Lipsett, F. R., 1957, *Can. J. Phys.*, **35**, 284.

———— 1958, *Rev. Sci. Instr.*, **29**, 423.

Mark, P., 1961, *Z. Naturforschg.*, **16a**, 950.

Menzies, A. C. and Skinner, J., 1949, *Discussions Faraday Soc.*, **5**, 306.

Obreimov, I. W. and Shubnikov, L., 1924, *Zeits. f. Physik*, **25**, 31.

Obreimov, I. W. and Prikhotjko, A., 1932, *Phys. Z. Sowjetunion*, **1**, 203.

Okamoto, Y., Huang, F. T., Gordon, A., Brenner, W. and Rubin, B., 1962, "*Organic Semiconductors*", Proceedings of an Inter Industry Conference, Chicago, April 1961, Eds., J. J. Brophy and J. W. Buttroy, The MacMillan Co., New York.

Pick, H. and Wissman, G., 1954, *Z. Physik*, **138**, 436.

Pimentel, G. C. and McClellan, A. L., 1952, *J. Chem. Phys.*, **20**, 270.

Reynolds, G. F., 1963, "*Physics and Chemistry of the Organic Solid State*", *Vol. I*, Eds., D. Fox, M. M. Labes and A. Weissberger, Interscience, New York, London.

Riehl, N., 1955, *J. Phys. Chem.* (*U.S.S.R.*), **29**, 959.

Robertson, J. M., 1953, "*Organic crystals and Molecules*", Cornell University Press, Ithaca, New York.

Rosebury, F., 1956, "*Tube Laboratory Manual*", Second Edition, Research Laboratory of Electronics, M.I.T., Cambridge, Mass.

Roussett, A. and Lochet, M. R., 1942, *J. Physique*, **C3**, 146.

Sangster, R. C. and Irwine, J. W., Jr., 1956, *J. Chem. Phys.* **24**, 670.

Sherwood, J. N. and Thomson, S. J., 1960, *J. Sci. Instr.*, **37**, 242.

Spendiarov, N. N. and Aleksandrov, B. S., 1959, *Rost Kristallov*, 2, 78; transl. in *Growth of Crystals*, 2, 61, (1959).

Stober, F., 1925, *Z. Krist.* **61**, 299.

Stockbarger, D. C., 1936, *Rev. Sci. Instr.*, **7**, 133.

Tammann, G., 1923, „*Lehrbuch der Mettallographie*" Leipzig.

Volmer, M. and Schultze, W., 1931, *Z. Physik. Chem.*, **A156**, 1.

Winchell, A. N., 1947, "*Elements of Optical Mineralogy, Part I, Principles and methods*", 5th ed., John Wiley & Sons, Inc., New York.

———— ———— 1954, "*The Optical Properties of Organic Compounds*", 2nd ed. The Academic Press, Inc., New York.

Wolf, H. C. and Deutsch, H. P., 1954, *Naturwiss*, **41**, 425.

Yun, S. S. and Beyer, R. T., 1964, *J. Chem. Phys.*, **40**, 2538.