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Publication Date

1951-01-26

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UNIVERSITY OF CALIFORNIA
Radiation Laboratory

Contract No. W-7405-eng-48

On the Preparation of Stilbene Crystals

R. F. Leininger

January 26, 1951

Berkeley, California

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ABSTRACT

A method of preparing large stilbene crystals suitable for use in scintillation counters is presented.

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On the Preparation of Stilbene Crystals

R. F. Leininger

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Introduction

In the past several years considerable interest has been aroused in the growing of crystals for use as fluorescers in quantum counters.^{1,2} The methods³ described herein have been used successfully during the past year to produce stilbene crystals for general use at the Radiation Laboratory. The procedure will be given in considerable detail so that persons unfamiliar with the techniques involved may duplicate the results.

Preparation of Materials

Trans-stilbene obtained from the Eastman Kodak Co. was further purified to remove trace impurities by passing it through the column shown in Fig. 1. The 20-in. section of 1-in. diameter tubing was filled with grade F-1 Alcoa activated alumina mesh 48-100. The 1½-in. section of glass tubing above the bed of alumina is then filled with trans-stilbene and the liter bulb filled with approximately 600 ml of N-pentane. Heating is achieved by a gas-coil heating mantle with power input reduced to a value that gives a moderate rate of pentane refluxing. The apparatus as described will handle about 150 grams of stilbene at a time and two charges of stilbene may be run through it before the alumina bed need be replaced.

After all of the stilbene has been transferred to the distillation flask,

^{1,2} Review articles on scintillation counters

(1) Robert Hofstadter, *Nucleonics* **4**, No. 5, 29 (1949).

(2) Jordan and Bell, *Nucleonics* **5**, No. 4, 30 (1949).

³ P. W. Bridgman, *Proc. Am. Acad. Arts and Sci.* **60**, 305 (1925).

the flask is cooled and removed from the reflux column, a condenser attached to it and the pentane distilled off using a hot water bath as a heat source (not over 60°C). Finally the stilbene is dried under vacuum, first by water aspirator and then by a mechanical pump.

Filling of Sample Tubes

Rectangular cross section bulbs were blown into a mold having the appearance and dimensions shown in Fig. 2. These bulbs were filled by distilling the stilbene into them under a low pressure of argon.

The detailed procedure is as follows. The apparatus used is shown in Fig. 3. The filled sample tubes hold approximately 120 grams of stilbene, and therefore 130-140 grams of stilbene are introduced through the large stem on the still pot, after which the tube is sealed off. The system is then evacuated by a mechanical pump and heat applied to the still pot by means of a gas-coil heating mantle at reduced voltage (~ 65 volts). The top of the still pot and the reflux column is insulated by wrapping them with several layers of cheesecloth.

As the stilbene melts gases and excess solvent are given off and when it is completely melted it will be found to distill rather irrationally under a good vacuum. For this reason argon at a pressure of about 3 mm is introduced into the system and the system isolated. Under these conditions stilbene vaporizes quite smoothly. As the material comes over from the distillation column it tends to solidify in the cold glassware. A soft flame from a glass blowing torch will melt it, and it may be kept molten in the sample bulb by an infrared heating lamp placed close to a flat side of the sample bulb.

When sufficient liquid stilbene to fill the sample bulb almost to the top has come over, the heat to the still is turned off, the heat lamp removed, and system evacuated to limit of a good mechanical pump. Under these conditions the stilbene slowly crystallizes and any dissolved gases are removed. When the

sample bulb is cold the tube is sealed off and a hook bent in the end to support it in the furnace. Since some purification is achieved by this distillation the excess material in the still pot, etc. is removed by distillation into a waste bulb.

Description of the Crystal Oven

The oven used maintained a definite, precisely controlled temperature gradient by the expedient of maintaining the two ends of an insulated, massive, copper tube at controlled temperatures. A complete drawing of the oven is shown in Fig. 4. Liquids boiling at constant pressure are used to control the temperature. The two alcohols used were chosen so that the melting point of stilbene (124°C) would lie exactly between their boiling points, 117°C and 130°C . The spacing between the two boilers is such that a temperature gradient of 1° per inch is set up in it.

To prevent oxidation of the alcohols an atmosphere of argon is maintained in the boilers. A mercury manometer having tungsten electrodes sealed into it is used to control the pressure in the system through solenoid valves. Sensitive relays are inserted in the circuit between the valves and the manometer to prevent arcing at the mercury-tungsten contacts. The system is double acting and will compensate from either side of the neutral position. It is necessary to make the rate of adjustment of the pressure small and to include a large reservoir (45 liters) in the system to prevent over shoot in the compensation.

While satisfactory temperature regulation may be attained by operating the heaters from the unregulated electric mains, much greater stability was observed when the heaters were operated through a voltage regulator. The usual degree of control was within the limits of $\pm 0.03^{\circ}\text{C}$ over a one-hour interval and $\pm 0.10^{\circ}\text{C}$ over a period of 24 hours. It might be pointed out that slow temperature shifts are of little importance, but that relatively small temperature shifts at high

rates of change are very important in the growth of a crystal. Crystals are grown in this furnace at the rate of $1 \frac{5}{8}$ in. per day.

Operating Procedure

After assembling the apparatus, it tested for leaks, precision of pressure control, etc. The pressure on the system is set at 80 cm so that excess argon may be vented to the atmosphere. The pressure regulator should maintain the pressure constant to $\pm 1/4$ mm of mercury. Two centimeters of mercury pressure change at 80 cm pressure will cause a shift in boiling point of the alcohols of about 1°C . A twelve-in. piece of 10-mm glass tubing filled with stilbene and sealed is a convenience in determining the level in the oven at which stilbene crystallizes.

Crystal bulbs are first held at the top of the oven to melt them (6-8 hrs.). When melted the bulbs are lowered out of bottom of the oven for inspection. If the stilbene is completely melted the tip of the capillary is cooled to form a seed and the crystal bulb raised to that height in the oven that will place the center of the capillary at the melting point of stilbene. The crystal bulb is then lowered by a rebuilt electric clock at $1 \frac{5}{8}$ in. per day until the contained stilbene is completely solidified. The oven is then cooled gradually over a period of 24 hours to room temperature and the crystal bulb removed.

It must be emphasized that a seed must be present in the capillary when growth is started. If the stilbene is completely melted, on cooling it supercools and then later when it finally starts to crystallize it does so abruptly. This tendency to supercool will be observed if melting points are measured for the stilbene. It will melt sharply at 124°C but may cool to as low as 106°C before crystallizing.

Some precautions in handling stilbene might be noted. There is some question as to whether stilbene is carcinogenic; it is certainly an irritant and

should be handled with care. The crystals are very fragile. Having a relatively large coefficient of thermal expansion, they are very susceptible to thermal shock.

Cutting and Polishing Stilbene

Crystals may be cut by a hack saw blade if extreme care is used. Better control may be had if the blade is used without the saw frame. Any twist of the blade in the saw cut is certain to fracture the crystal. As a more refined technique a band saw was set up using laboratory equipment. The blade was multi-stranded (~ 4) 0.005-in. stainless steel wire using 400 mesh carborundum as a cutting agent. Gum arabic in the abrasive mud aids in carrying it into the saw cut. By using a light weight wire as a blade, torsional stresses are avoided while cutting the crystal.

The rough crystals are surface finished using Minnesota Mining and Manufacturing Company's Wetordry sand paper. The 200 grit paper will remove material rapidly and the 320 grit paper yields a finely sanded surface. Finally the surfaces are polished using 600 mesh carborundum on cheesecloth on a flat surface. All sanding and polishing operations are done wet. A very fine final polish may be had by rubbing moist 600 mesh carborundum on the crystal with a finger while wearing rubber gloves. In washing the crystal the water used should always be within $\pm 2^\circ\text{C}$ of the crystal temperature. Very fine crystals have been cracked by attempting to wash them in water 5°C cooler than the crystal itself. A basin of water standing in the room is most useful as a safe washing medium.

Conclusion

By using the methods described herein crystals have been grown that were $3/4$ in. x $1\ 3/4$ in. x $3\frac{1}{2}$ in. in size and free of fractures. More often however one or more fractures will appear along the length of the crystal. It is more

difficult to cut and polish a crystal without fracturing it than to grow the crystal initially unfractured.

The crystals we have grown are not single crystals but a number of crystals grown side by side with little or no discontinuity at the interface between crystals. The evidence of such multiple growth is drawn from the appearance of faces of crystals before cutting and the great tendency of crystals to fracture along the direction of growth.

From the experience obtained to date we feel that some of the precautions used here were necessary during development of the method, but should not be necessary in duplicating the equipment. If we were to set up the apparatus on a limited budget the micromax could easily be dispensed with as could also the voltage regulator for the heaters. The rest of the equipment is relatively simple and easy to fabricate.

I am indebted to Prof. E. Segre for his advice and interest in the development of this procedure. This work was done under the auspices of the Atomic Energy Commission.

FIG. 1

MU1294

6" LONG 1-2 M.M.
CAPILLARY TUBE

FIG. 2

MU 1295

FIG. 3

MU 1296

FIG. 4

MU 1297