TECHNICAL PAPERS

The Laboratory Growing of Quartz

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Synthetic or laboratory-grown quartz has been known in the form of microscopic crystals for over 100 years,[1] and 40 years ago several macro crystals were grown from seed, the largest increase having been about 3.1 gm. This was the achievement of Giorgio Spezia, mineralogist at the University of Turin, Italy, who used the hydrothermal method—sealing up quartz and dilute sodium silicate solution for 6 months at elevated temperature and pressure (*8*). His experiments demonstrated to the geological world that silica responded to its own crystallizing tendency many orders of magnitude faster at 150 atm and 320° C than at 6,000 atm and about 25° C.

Beginning in late 1943, Richard Nacken, in Germany, directed an attack on the problem of producing crystalline quartz in quantity, the use of quartz oscillator plates having become of enormous importance in military radio communication. He met with sufficient success so that a pilot plant seems to have been in operation at the end of the war, but to judge from information available through the Office of Technical Services, the work did not yield a formula for a commercial process (*11*).

TABLE 1

	Total quartz deposited (gm)	Growth rate ($mg/cm^2/day$)	Length of run (days)
Giorgio Spezia	3.1	38	200
Brush Development Co.	6.9	48	20

At a Symposium on the Synthesis of Single Crystals held during the Boston Meeting of the AAAS (December, 1946) it was announced that a number of projects for crystal growing were being sponsored by the U. S. Signal Corps in the interest of an improved position with respect to frequency control. Under this program the Brush Development Company has a contract to investigate the growing of quartz.

A method currently being explored by the Company consists of heating at the bottom a vertical tubular autoclave containing a dilute alkaline solution, a quantity of silica at the bottom to act as supply or feeder material, and one or more "seeds" cut from untwinned quartz crystals suspended near the top. The autoclave is made of chemically resistant steel capable of safely withstanding high internal pressure. Comparison of a fairly successful run with the estimated best results obtained by Spezia shows that progress toward higher rates of growth has been made (Table 1).

The supply in both experiments was crystalline quartz. Spezia's seed was cut normal to the optic axis, and the seed in the comparison experiment was cut parallel to a major rhombohedral face, a surface which normally grows at a much lower rate.

The number of millimeters of oriented quartz deposited on each face per day provides a comparison of growth rates if the seeds have the same area and are of the same "cut." Growth on different cuts or faces occurs at different rates. The rates on the R-cut, parallel to the major rhombohedral face, and the Z-cut, or artificial basal face (not existent in nature), are in the ratio of about 1 to 5. This is in accord with the "overlapping principle" that the largest natural face of a crystal is the one that grows most slowly (e.g. *5*). Growth on the Z-cut is usually so rapid that a porous structure results, except at the edges where the oblique rhombohedral faces begin to appear. These faces tend to grow as continuous planes, repairing and covering the open spaces beneath and making inclusions of them, after which the growth is normally unflawed.

This growth sequence on Z-cuts seems standard, and similar behavior has been observed in the growth of large crystals from water-soluble substances. In several experiments, however, a slow but dense growth of quartz in the Z-direction occurred. The pyramid was incomplete, due to insufficient time, with perhaps other conditions contributing, and a simulated basal face was formed. This surface is not plane, but is composed of many small rounded areas, and is said by C. S. Hurlbut, Jr., of Harvard University, to resemble the similar surface on the few natural specimens of quartz which lack the completed pyramid.

The growth rate in terms of milligrams of silica transferred in oriented condition onto 1 cm^2/day is another useful measure of success, although not free from complications due to changes in areas of different faces as the crystal grows.

The weight ratio of seed growth to supply loss × 100 may be called the per cent efficiency of the process and is a third useful yardstick. The silica leaving the supply has four possible destinations: (1) on the seed as desired, (2) on the walls of the chamber and on seed supports as a fine crystalline crust, (3) in chemical combination with the original solvent medium, and (4) in physical solution in the fluid phase.

The chemical and physical solution obtaining at elevated temperature yields at room temperature, when the contents of the autoclave are examined, a true solution of more or less complexity, a colloidal suspension which

[1] K. F. E. von Schafhäutl, 1845; for a complete account and bibliography of the subject see reference *4*.

may also contain an amorphous precipitate, or one of these with a glass. If a glass be present, it must have been fluid at the temperature of the run, for the glass conforms to the bottom of the chamber and has a flat surface which is substantially horizontal. Such a condition, which implies two liquid phases co-existing at elevated temperature, was observed at the Naval Research Laboratory (*2*). In many of the runs made at the Brush Development Company the presence of a solid glass around chunks of undissolved silica implies that a dynamic condition has been arrested: the silica is on its way into solution, and a heavy concentration of alkaline and silicic components on the bottom results from the slowness of the diffusion.

Several kinds of silica are available from which to choose a supply to nourish the growing crystal. Quartz and vitreous silica are of particular interest, since quartz is the stable crystalline form at room temperature, whereas vitreous silica is the undercooled fluid. From the relative latent heats of fusion of quartz and cristobalite (3.1 and 1.0 kcal/mol, respectively) (*7*) a modification of Clapeyron's equation[2] demonstrates that the relative solubility at the same temperature should be of the order of magnitude of 1: 22, and vitreous silica, having a higher degree of instability at room temperature than cristobalite, should show a still higher solubility. Nacken, as reported in documents referred to previously, found the solubility of the vitreous form to be about 10-fold that of quartz, the solvent being water under its own vapor pressure at about 360° C.

This difference in solubility makes the isothermal technique attractive, and Nacken and others (e.g. *1, 10*) have experimented with it. The vitreous silica goes into solution at its own surface; oriented silica molecules deposit on the surface of the crystal. The difficulties of arranging special thermal conditions or slow evaporation do not have to be considered.

Vitreous silica in hot alkaline solution has the bad habit—from the experimenter's point of view—of devitrifying unless it can go completely into solution. This long-known phenomenon (*6*) has been especially puzzling, since the end-product has been reported at different times as cristobalite and as quartz (*10*). The alteration of form, and therefore of solubility, adds complexity to the isothermal growing system, and the high solubility carries with it the danger that the solution may become so supersaturated with respect to the crystalline quartz that it lies in the "labile state" (*5, 9*), in which event microscopic bits of solid impurities or microscopic sharp edges on the walls of the vessel and elsewhere act as nuclei upon which quartz will begin to deposit.

The controlled growing of quartz may be expected to yield economies of time and material in the process of converting crystals into oscillator-plate blanks. Grade I quartz crystals are always a small percentage of the weight taken from the mines because of the prevalence of flaws and inclusions. A large cutting loss occurs because the clear stones are usually more or less twinned, optically or electrically or both, and the oscillator plates must be cut from an untwinning region. The use of untwinned seeds of specially chosen size and orientation is expected to yield synthetic crystals which can be cut into blanks with a reduction of the usual loss by about one-fifth.

[2] This is essentially the freezing-point relationship, rigorously true only for dilute solutions obeying Raoult's Law; for example, see reference *3*.

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Effect of Diethylstilbestrol on the Thyroid Glands of Chicks Receiving Thiouracil

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Thiourea, thiouracil, and related compounds are known to inhibit the secretion of thyroxin. Then, in response to the thyrotropic hormone of the anterior pituitary gland, the thyroid gland becomes hypertrophied and hyperplastic (*1, 3, 4*). Studies with radioactive iodine have shown that thiouracil prevents the thyroid gland from utilizing iodine to form thyroxin (*2*). The lighter-weight breeds of chickens, such as the Leghorns, give a greater thyroid response to thiouracil than do the heavier breeds, and the females of several varieties (Buff Minorcas, White Leghorns, New Hampshire Reds, and Buff Orpingtons) develop much larger thyroids than do the males (*4*).

This sex difference in the response of the male and female thyroid gland to thiouracil suggested the possibility that a gonadotropic hormone might influence the effects of the drug. For this purpose the synthetic estrogen-like hormone, diethylstilbestrol, was used.

Sixty one-week-old New Hampshire Red chicks were divided into four groups of 15 chicks each: Group C was the control group; Group S received stilbestrol; Group T received thiouracil; and Group TS received both thiouracil and stilbestrol. The chicks were kept in the same brooder and fed a 16% protein growing mash. The