QUARTZ CRYSTAL

By Gordon T. Austin

Electronic-grade quartz crystal is single-crystal silica that is free from all visible defects and has piezoelectric properties that permit its use in electronic circuits for accurate frequency control, timing, and filtration. These uses generate practically all the demand for electronic-grade quartz crystal. A smaller amount of optical-grade quartz crystal is used as windows and lenses in specialized devices including some lasers.

More natural quartz crystal was consumed in electronic and optical applications until 1971, when cultured quartz crystal took the lead. Since that time cultured (synthetic) quartz has replaced natural crystal in practically all these applications. The use of natural quartz crystals for carvings and other gemstone applications continued; quartz crystals for this application are discussed in the Gemstones Annual Report of the U.S. Bureau of Mines.

Legislation and Government Programs

At yearend the National Defense Stockpile contained about 109,000 kilograms of natural quartz crystal. The Fiscal Year (FY) 1994 Annual Material Plan established a goal of zero and also authorized the disposal of the entire quartz crystal inventory during FY 1994. The stockpile material, which primarily consists of large natural crystals, could be absorbed by the specimen and gem material industry. Very little, if any, of the material would be consumed in the same applications as synthetic quartz crystal.

Strategic Considerations

Natural electronic-grade quartz crystal was initially designated as a strategic and critical material after World War II. Cultured quartz crystal was not commercially available at the time of U.S. stockpile acquisition. With the changing patterns of quartz consumption, the Federal Emergency Management Agency asked the National Materials Advisory Board to assess the requirements and related trends for stockpiling quartz. The final report was published in early 1985 and recommended changes in stockpile goals to reflect the declining dependence on natural quartz crystal.[1]

The National Defense Stockpile contains natural quartz in several weight classes and grades, including about 13,000 kilograms of material consisting of individual crystals weighing more than 10,000 grams each. Some of the individual quartz pieces in this weight class are suitable for generating mother seeds for cultured quartz crystal production. These large pieces were acquired from Brazil because similar materials were not available from a domestic source.[2]

Production

Coleman Quartz Inc., Jessieville, AR, is the only domestic company known to supply the feed material for cultured quartz crystal, called lascas. Coleman mined only during the summer months, but processed lascas year-round. Lascas was mined, crushed, and sized. Crushed and sized material was transported to the processing plant where operators rinsed it in oxalic acid and then in deionized water to remove external contaminants. Finally, hand sorting, drying, and examination on a light table completed the necessary processing. The material was then shipped to cultured quartz crystal producers in 45-kilogram (100-pound) bags in 20,000-kilogram lots. *(See table 1.)*

Four companies produced cultured quartz crystals during 1994. The two largest producers, Sawyer Research Products Inc. of Eastlake, OH, and Thermo Dynamics Corp. of Merriam, KS, were independent growers that produced crystal bars for domestic and foreign consumers in the crystal device fabrication industry. Motorola Inc. of Chicago, IL, produced quartz crystal for both internal consumption and the domestic device fabrication industry. P. R. Hoffman Material Processing Co. of Carlisle, PA, also reported outside sales. Bliley Electric Co. of Erie, PA, used crystals from inventory for internal consumption and did not produce during the year.

These companies produced cultured quartz crystal using a hydrothermal process in large pressure vessels, known as autoclaves. Seed crystals, very thin crystals cut to exact dimensions, were mounted on racks and suspended in the upper growth region of the vessel. Lascas was loaded in an open-mesh wire basket that was placed in the bottom of the autoclave.

A solution of sodium hydroxide or sodium carbonate (the mineralizer), with additives such as lithium salts, and deionized or distilled water was used to fill the vessel to 75% to 85% of its volume. The bottom half of the growing vessel was heated to temperatures averaging between 350°C to 400°C; the temperature of the top portion was maintained at 10°C to 50°C less. At these temperatures, the solution expands and creates an internal pressure in the vessel between 10,000 and 30,000 psi. Under these conditions the lascas dissolves to create a solution saturated with silica.

Through convection, the saturated solution transports dissolved silica to the cooler upper half of the vessel where it becomes supersaturated, and the excess dissolved quartz deposits on the seed crystals in the top half of the autoclave. The process continues until the growing crystals reach their desired size. The process normally takes 30 to 60 days, but at least one producer is making runs that are about 180 days.

The processing of quartz crystals for various end uses is the same whether natural or cultured crystal is used. Crystals are examined for physical defects before cutting. They are then cut, usually with diamond or slurry saws, along a predetermined crystallographic plane to a thickness slightly larger than that desired. Each wafer is inspected and diced into blanks of the desired dimensions. The blanks then progress through a series of lapping stages until they reach the final thickness; electrodes are attached and the crystals are mounted in suitable holders. The final assembly, called a quartz crystal unit, is ready for insertion into an electronic circuit.

The U.S. Bureau of Mines collected domestic production and consumption data for quartz crystal through a voluntary survey of U.S. operations. Four of five companies responded to the canvass for the production of cultured quartz crystal, representing 100% of total production shown in table 1. Of the 28 operations canvassed concerning consumption of quartz crystal, 22 responded, 5 of which did not consume quartz crystal in 1994. These companies represented nearly 100% of total consumption, also shown in table 1. Consumption for the nonrespondent was estimated using reported prior-year consumption levels. *(See table 1.)*

Consumption

Consumption of lascas by the four domestic quartz crystal producers is shown in table 1. The 23 active device-fabricating companies in 9 States consumed quartz crystal in 1994. Of these companies, all but one consumed only cultured quartz crystal. The one company that used natural quartz used an extremely small amount.

Quartz crystal was used in piezoelectric and optical applications. The piezoelectric effect is achieved when a suitable electrical signal is applied to a quartz wafer or blank with appropriate electroding, and the wafer then vibrates mechanically throughout the bulk of the material at a characteristic natural resonance frequency. The quartz resonators are uniquely suitable for military-aerospace and commercial bandpass filter applications that require very high selectivity or in oscillator applications that require very high stability. In addition, for many applications requiring only moderate stability, a quartz resonator offers a unique combination of high performance, small size, and low cost. Quartz resonators were used for many less demanding applications such as providing timing signals for watches, clocks, and microprocessors in industrial, automotive, and consumer products.

The quartz wafer becomes too thin for practical use for very high frequencies (above 100 megahertz). Quartz crystal structures that use surface vibrations, in which the frequency is determined by electrode dimensions rather than wafer thickness, have become more important at these higher frequencies. These structures are called surface acoustical wave (SAW) devices. Most optical applications used quartz in the fused form as silica glass. Relatively small quantities of cultured quartz crystal were used directly for special optical considerations. Quartz's crystal properties are responsible for its uses that deal with normally polarized laser beams. Quartz retardation plates (especially quartz wave plates), Brewster windows and prisms, birefringent filters, and tuning elements are used in laser optics.

Historically, quartz crystal has been a material of strategic importance. During World War II, quartz was used principally in analog communications (e.g., in telephone multiplexing and in mobile military radios). Today, because of military emphasis on command, control, and communications surveillance and the growth of more sophisticated electronic systems, the importance of quartz crystal devices has grown. Many of the military applications are at the leading edge of technology. It has been U.S. Department of Defense policy to require that all military systems be hardened to nuclear radiation. To meet this special requirement, cultured quartz crystal must be radiation hardened by sweeping, a technique to remove certain impurities from the quartz.

Cultured quartz was used almost exclusively by the crystal device industry because of cost advantages. For resonator applications, raw quartz must be cut into thin wafers oriented precisely with the raw material crystal axes. The uniformity and convenience of cultured quartz have made its use almost universal. Unlike cultured quartz, natural electronic-grade quartz requires special orientation, cutting, grading, and sizing to produce a quartz wafer. As a result, most device manufacturers that cut natural quartz in the past have discontinued its use. One of the remaining uses of natural electronic-grade material was in pressure transducers used in deep wells.

Prices

The average value of as-grown cultured quartz was $60 per kilogram. The average value of lumbered quartz, as-grown quartz that has been processed by sawing and grinding, was about $300 per kilogram.

Foreign Trade

The Bureau of the Census began using the Harmonized Tariff Schedule in 1989 to identify material passing through U.S. customs. This system makes classification codes for imports and exports consistent internationally. With the adoption of the new codes, imports and export codes for quartz crystal changed, and some formerly listed details are no longer available. The import code for Brazilian crude pebble, which represented nearly all lascas imports recorded, was eliminated. Although this material probably continued to enter the United States, the new code system aggregated several categories making information about specific materials unavailable. Likewise, the export data for natural electronic-grade quartz crystal were no longer available.

World Review

Synthetic quartz crystal production is concentrated in the United States, Japan, and Russia with several companies producing crystal in each country. Smaller production capacity exists in Belgium, Brazil, Bulgaria, China, France, Germany, the Republic of South Africa, and the United Kingdom. Details concerning quartz operations in China, the Newly Independent States (formerly the U.S.S.R.), and other Eastern European countries are unavailable. However, it is known that the Newly Independent States have significant capacity to produce synthetic quartz.

Outlook

Domestic production of cultured quartz crystal has grown or remained relatively stable since 1986. Demand for crystal devices for electronic consumer products and microprocessor controlled devices should continue to grow and quartz crystal production should remain strong well into the future. Because crystal devices continued to be used in an increasing variety of applications from kitchen appliances to military hardware in addition to the traditional items such as watches, demand should continue to increase and additional production capacity may be required worldwide.

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[1]National Materials Advisory Board. Quartz for the National Defense Stockpile. Natl. Acad. Sci., Washington, DC, NMAB-424, Jan. 1985, 99 pp.

[2]Work cited in footnote 1.

OTHER SOURCES OF INFORMATION

U.S. Bureau of Mines Publications

Quartz Crystal. Ch. in Mineral Commodity Summaries, annual.

Other Sources

Electronic News, weekly.
Electronics, biweekly.
Electronic Component News, monthly.
Industrial Minerals (London), monthly.
Mining Engineering, monthly.

TABLE 1
SALIENT U.S. ELECTRONIC-AND OPTICAL-GRADE QUARTZ CRYSTAL STATISTICS

(Thousand kilograms and thousand dollars)

	1990	1991	1992	1993	1994
Production:					
Mine 1/	423	454	778	454	544
Cultured	441	441	407	394	294
Exports:					
Cultured 2/					
Quantity	39	53	15	24	38
Value 3/	$1,750	$2,620	$1,280	$2,260	$6,110
Consumption:					
Natural (electronic-and optical-grade)	(4/)	1	(4/)	(4/)	(4/)
Cultured (lumbered)	14	12	10	31	48
Cultured (as grown)	326	353	276	275	312
Total	340	366	386	306	360

1/ Excludes lascas produced for specimen and jewelry material uses.
2/ Bureau of the Census as adjusted by the U.S. Bureau of Mines.
3/ Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits.
4/ Less than 1/2 unit.