

JOEL E. AREM

Man-Made Crystals



MAN-MADE CRYSTALS

JOEL E. AREM

Man-Made Crystals

SMITHSONIAN INSTITUTION PRESS WASHINGTON, D.C. 1973

The author wishes to acknowledge the assistance of the following in the preparation of this book: Dr. Edwin Roedder, U.S. Geological Survey; Dr. Fedia Charvat and Dr. Herbert Moeller, Union Carbide Corp.; Dr. Kurt Nassau and Dr. Ed Spencer, Bell Telephone Laboratories; John S. White, Jr., Nancy Harris, and Hope Pantell, Smithsonian Institution; and Milton Arem, my father.

Photographs and diagrams are by the author, except for the following:

Arthur D. Little, Inc.: 32 (bottom)

A T & T Co.: pages 12 (bottom right), 60

Bell Telephone Laboratories: pages 32 (top), 35, 36, 40, 41, 80 (top), 89 (top left)

Fisher Radio Corp.: page 12 (center)

General Dynamics Corp.: page 63

General Electric Co.: pages 43, 44

Harshaw Chemical Co., Div. of Kewanee Oil Co.: page 62

Hewlett Packard Corp.: page 12 (top left)

Hughes Aircraft Co.: page 68

Isomet Corp.: page 91 (top)

Optovac, Inc.: page 82

Perkin Elmer Corp.: pages 55, 66

Pulsar Div., HMW Industries: page 12 (bottom left)

Sawyer Research Products, Inc.: page 38, 76, 77

Texas Instruments, Inc.: page 58 (top)

Tyco Laboratories, Inc.: page 84 (bottom)

Union Carbide Corp.: frontispiece, pages 46 (bottom), 83

(Photographs on pages 27, 28 (bottom), 47, 53, and 92 reprinted from Smithsonian magazine)

Cover: Magnesium crystals grown accidentally in a refinery.

Frontispiece: Crystals of various shapes, sizes, and colors are all useful to modern technology.

*Library of Congress Cataloging in Publication Data
Arem, Joel E. 1943-*

Man-made crystals.

1. Crystals—Growth. I. Title.

QD921.A76 548'.5 73-8695

ISBN 0-87474-139-4

ISBN 0-87474-141-6 (pbk)

Copyright © 1973 by Joel E. Arem. All rights reserved

Printed in U.S.A. by Lebanon Valley Offset

Designed by Elizabeth Sur

Smithsonian Institution Press

Publication Number 4830

Contents

PREFACE **7**

CRYSTALS: AN INTRODUCTION **9**

What Are Crystals? • Synthetic Is Not “Imitation” • The Importance of Crystals to Our Society

THE ROOTS OF THE CRYSTAL-GROWING ART **13**

Early Efforts to Make Ruby • The Quest for Diamond • Synthesis of Quartz • Gems and Exotic Crystals from the Laboratory

TECHNIQUES FOR GROWING CRYSTALS **20**

How Crystals Grow • Vapor Growth • Melt Growth • Growth from Solution

MAN-MADE GEMS **42**

Diamond • Ruby and Sapphire • Spinel • Quartz • Beryl • Other Gems

TRANSISTORS, LASERS, AND BUBBLES **54**

Transistors • Lasers and Masers • Bubbles

CASE HISTORIES **73**

Silicon Carbide • Quartz • Silicon and Germanium • Light-Emitting Diodes • Halides • Corundum • Spinel • Rochelle Salt, ADP, KDP, and EDT • Garnets and Ferrites • Molybdates, Niobates, Tantalates, Tungstates, and Bananas

THE FUTURE **93**

APPENDIXES **95**

GLOSSARY **97**

HOW TO GROW CRYSTALS AT HOME **104**

INDEX **110**

Preface

We live in an age of high-speed transportation and communication, an age of rapid social, environmental, and political changes. A key factor in the development of society as we know it is technology—one of the fastest growing of all human enterprises.

Knowledge in past centuries increased at a more or less linear rate. Each generation built on the information and achievements produced by its predecessors. This rate of progress is no longer linear, but exponential. Simply stated, each new idea, new device, or new technology gives rise to many other advances, sometimes in fields very different from the one in which the original work was done. The ability to convey ideas rapidly has been a key factor in this kind of progress. More has been learned in the past few decades than in all the previous centuries of recorded history.

Largely unseen and unacknowledged in today's society are crystals. They are manufactured by industry and used in industry, incorporated in products that the consumer ultimately buys. But the consumer is generally unaware of their very existence, although their existence is critical to the availability of the products themselves.

Crystal technology is almost entirely a 20th-century endeavor. Although much of the basic understanding of the nature of crystals had been developed before 1900, it remained for modern science to weld this knowledge into a useful and profitable industry. The crystal industry is now worth millions of dollars, and without it society as we know it would cease to exist.

Crystal growers are a special breed of technologists. The science of crystal growth is extremely complex and still basically in its infancy. But the technology of growth is a great art, one whose practitioners are few but well known among their peers.

The history of crystal-growth research extends far back into the past, yet most of the great advances have been made in the last fifty years. It is still possible to talk to many of the people who were actually involved in the development of materials that now have industrial significance. Many of the "first-grown" crystals of specific materials are in the hands of their creators. But time has a way of clouding events; details are lost because they were never recorded and exist only in the memories of participants. With the passing of such men goes knowledge of the whereabouts of many of the crystals they grew.

The need to preserve this historically significant material led to the creation by the author of the National Synthetics Collection in the Smithsonian Institution, Washington, D.C. This invaluable archive will not only document the early man-made crystals and their histories, but will also represent a cross section of the materials being pro-

duced in industry. In future years it will be possible to open a drawer in the National Museum of Natural History and find an array of crystals grown over a period of decades, representing a wide variety of techniques and a large number of laboratories.

Many of the photographs in this book illustrate material from the National Synthetics Collection. Others have been provided through the courtesy of numerous industrial firms and are individually acknowledged. The technical scientific literature of crystal growth is enormous, and no attempt has been made here to summarize it. Rather, the author has tried to pick key developments and materials, and explain why they are important and how they fit into the general picture of materials science.

Crystals:

An

Introduction

Crystals are objects of wonder. They have fascinated man since earliest times and their use almost certainly predates recorded history.

To primitive cultures, crystals inspired reverent awe. They served as ornaments, medicines, and tools. In more advanced societies, crystals have more sophisticated uses, such as for lenses, curios, and even windows. In our high-speed, technological civilization, crystals are more important than ever before.

We live in a world of crystalline materials. The colors of wall paint and gemstones, the texture of fudge and ice cream, the strength of bridge cables, the shapes of gallstones and hailstones, the hardness of diamond and the shiny appearance of metals are all determined by crystallographic properties.

A crystal is solid material, as opposed to liquid or gas. All solids are characterized by a definite arrangement of their atoms and molecules, the submicroscopic particles that make up all matter in the universe. In liquids and gases, these particles are moving about so rapidly that they cannot remain in any kind of fixed positions relative to one another. In solids, atomic motion is merely vibration about fixed points. Every atom in a solid has definite neighbor atoms, all at fixed distances and relative positions. This creates a kind of long-range order, like rows upon rows of soldiers standing at attention.

Long-range order is the primary feature of crystalline materials; therefore all solids are, by definition, crystalline. Crystals are frequently bounded by plane surfaces called *crystal faces*. The positions and arrangements of faces are a direct consequence of the

WHAT ARE CRYSTALS?



Natural crystals are minerals, such as these wulfenite crystals from the Rowley Mine, Theba, Arizona.

internally ordered structure. The study of such arrangements is called *morphology*.

The fixed pattern of atoms in a specific solid gives it recognizable and constant properties. For example, there may be distinct planes of weakness in the atomic structure. In the soldier analogy, we could imagine all the soldiers linked by holding hands with those on either side. The linkage along rows of held hands might be very strong, but there would be no connection between a soldier in a row and the soldier in front or behind. In crystals, the atoms are held together by *atomic bonds*, which are powerful electric forces. The bonds between certain rows or planes in a crystal structure might be weak; if so, it would be relatively easy to break the crystal through those bonds. Knowledge of the structure of a crystal leads to understanding of such properties. Scientists have made great advances in this specialized type of information since 1912, when the techniques of x-ray analysis were developed.

But structural information has further uses than understanding crystal geometry. It enables scientists to predict how changes in the crystal structure, chemical composition, and processing history of a material will affect its properties. Once this is understood, the next step is to try to make special types of crystals that have desired properties. The technology for doing this is, even today, as much an art as a science.

Crystal growers are a special breed of scientists, engineers, and technicians, with an “intuition” about how crystals form and how they can be enticed to grow larger and more perfectly.

Everyone grows crystals. Home refrigerator freezer compartments contain trays of a crystalline substance known as ice. These crystals are forced to fill special cube-shaped containers, and so ice cubes are not really a true indication of the natural form of ice crystals. Well-formed ice crystals are, nonetheless, known to everyone—as snowflakes. While snowflakes are not generally thought of as important industrial commodities, knowledge of how they form is essential in studies of weather and the Earth’s atmosphere. Thus, even the growth of snowflakes has been extensively studied in the laboratory. Knowledge of the growth of many other types of materials has fundamental importance in modern industrial processes. The technology for growing crystals of these materials is critical to the well-being of our society.

It is important to differentiate *natural*, *synthetic*, and *imitation* crystals. Natural crystals are those found in nature—in rock beds, loose sediments, and natural waters. These crystals are of minerals, which are naturally occurring chemical compounds with a characteristic crystal structure and a composition that varies within defined limits. Synthetic crystals are manufactured from simple or complex components. The word synthesis literally means “put together.” Thus, a synthetic gemstone can be chemically, physically, and structurally identical to its natural counterpart. The only difference is that the synthetic was made by man, rather than by nature. Identification of a synthetic is possible only because the growth method generally introduces characteristic defects, inclusions, or other visible features.

An imitation is a material with properties that mimic those of a different, more costly material. Thus, red glass is a widely used (though rather poor) imitation ruby. Synthetic ruby, however, is *not* an imitation. It *is* ruby—manufactured by man in the laboratory in a way that may or may not be the same process as that used by nature.

Household products that we take for granted would not be available without the existence of an industry devoted to growing crystals. Most watches contain a number of “jewels”; they are made of synthetic ruby. Portable radios and TV sets, miniaturized hearing aids, auto ignitions, telephone systems, and thousands of other devices contain “solid-state” components—small chips of single crystals with a complex fabrication history.

Crystals help to regulate the power supplies of our cities. They manage our bank accounts and credit card purchase records, help supervise our communications, direct

SYNTHETIC IS NOT “IMITATION”

THE IMPORTANCE OF CRYSTALS TO OUR SOCIETY



rail and airline traffic and reservations, help diagnose diseases, and may ultimately provide the key to the production of limitless energy on Earth.

There is no aspect of day-to-day existence in technologically advanced countries that is not influenced directly or indirectly by crystals.

Man-made crystals are so important that without them civilization as we know it would not be possible. Yet few people know of their usefulness or of the vast industry that creates them. This is understandable, since most of the material produced is consumed by other industries, incorporated into products that the public ultimately buys. Nonetheless, the world of man-made crystals is fascinating, educational, and ablaze with form and color. Such is the world explored in the pages of this book.

The Roots of the Crystal-Growing Art

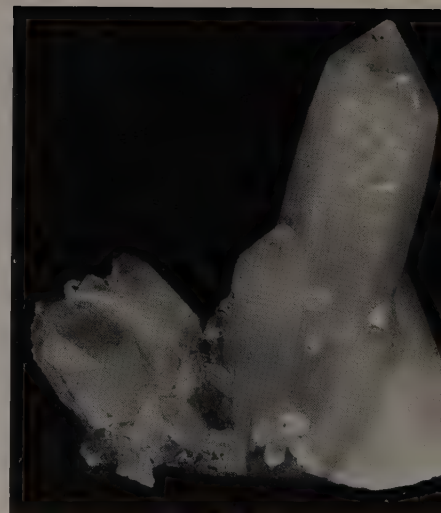
Records of the earliest attempts to grow crystals are lost in antiquity. But even those efforts must certainly have been predated by attempts to understand the growth process itself, the mechanisms whereby crystals form their glittering exteriors.

The ancient Greeks knew the mineral we call quartz, one of the commonest minerals on Earth. They believed that it could only be a form of ice, water frozen so hard (by some unnatural degree of coldness) that it could never thaw. Mineral crystals were believed to consist (prior to solidification) of earth and water. Both heat and water could be driven off in the process of crystallization. Aristotle, one of the greatest of the Greek philosophers, said:

And some of these solids cannot be melted or softened like amber and some kinds of stone, for example stalactites in caves; for these too are formed in the same way, being solidified not by fire but because their heat is driven out by the cold and their moisture accompanies it when it retires.

The writings of Aristotle and other ancient sages were held to be immutable for centuries. The concept of crystals as hardened water remained even into the 17th century. In his *De Magnete* (On The Magnet) William Gilbert wrote:

Lucid gems are made of water; just as Crystal which has been concreted from clear water, not always by a very great cold, as some used to judge, and by a very hard frost, but sometimes by a less severe one, the nature of the soil fashioning it, the



Quartz, a mineral, has been used by man for thousands of years. It was once supposed to have formed from water frozen by such an unnatural degree of coldness that it would never thaw.

humors or juices being shut up in definite cavities, in the way in which spars are produced in mines.

The very term crystal comes from the Greek word *krystallon*, meaning ice.

The sciences of metallurgy, ceramics, chemistry, and mineralogy developed rapidly through the 17th and 18th centuries. Progress in one area led to discoveries in other fields, and experimentation in crystal growth increased. Early theories of growth were inseparably linked to theories of crystal structure and the nature of matter. Considerable effort was expended in trying to understand what causes the external forms of crystals to be so regular. Alkaline and acid “principles” were suggested, as well as particles with special shapes, crystalline “essence” or juices, and geometric or “architectonic” principles.

Nicolaus Steno (1638–1686) made great strides in improving our understanding of crystal growth. Before Steno’s work, it was widely believed that minerals “grew” in much the same way as plants and animals. That is to say, if two rocks were shut up in a dark place and left alone for a while, many small (infant) rocks might be produced.

Steno’s writings eradicated this idea and replaced it with the concept of growth onto a kind of “crystal template.” He admitted ignorance as to how tiny “seed” crystals might form, but stated that after a seed did form, crystal growth continued, based on the pattern of the seed and expanding the same basic shape. The eventual shape of the crystal would depend on the rate of growth of different faces, and the rate of growth in any specific direction might vary with time. These views are remarkable in that they closely match ideas now held to be correct.

Theories of crystal structure and crystal growth progressed hand in hand through the Renaissance. Notable advances were made by such men as René-Just Haüy and Romé de l’Isle, and by the end of the 18th century essentially modern ideas about crystal growth began to emerge.

Nicolas Leblanc (d. 1806) believed that crystallography should include studies of the conditions of crystal growth. It might then be possible to explain the formation of specific crystals, and also to predict and even control the external form a growing crystal might take. Leblanc believed that many factors, including chemical composition, the nature of the growth medium, humidity, temperature, currents, and other external influences all affect the form of crystals.

Leblanc’s term for crystal growth research was “cristallotechnie”—a type of work that could be considered both a science and an art. Modern crystal growers do, in fact, consider their activities to be as much an art as a science.

Throughout the 19th century, scientists experimented with crystal growth, but this interest was not pursued to develop techniques for manufacturing crystals. Rather, these men were profoundly concerned with the internal structure of crystals and why they assume specific geometric forms. Growing crystals was just one line of investigation into these problems. A few men, however, did become interested in the commercial production of crystals. Not surprisingly, the materials involved were destined for use as gems.

As early as 1837 Marc Gaudin reported the results of his efforts to make ruby in the laboratory. After years of research, he concluded in 1870 that his technique was incapable of producing clear rubies in useful sizes. But work in progress elsewhere in France was leading to more encouraging results. Edmund Frémy, at the Museum of Natural History in Paris, had discovered a technique for crystallizing ruby from a flux (a material that causes a lowering of the melting temperature of a substance with which it is mixed). Frémy published his findings in 1877.

Unfortunately, Frémy's rubies were all thin, fragile plates with a maximum diameter of about $\frac{1}{2}$ inch—and thus were useless for gem purposes. In 1876 Frémy hired an assistant, Auguste Verneuil. Their collaboration led to the manufacture of the first ruby crystals suitable for use as watch bearings and as gemstones. These crystals were also grown from a flux, in ceramic crucibles that were heated to about 1,500°C. To make larger crystals it was necessary to use larger crucibles, and at one point Frémy and Verneuil were experimenting with vessels holding 3 gallons. They eventually planned to try crucibles more than four times that size!

Before these ambitious experiments could be performed, Frémy died and his procedures for making ruby were abandoned, not to be revived for more than sixty years. Verneuil, however, continued to work on a different line of approach and in 1902 published his results. There is good evidence that he actually had developed his technique about fifteen years earlier.

This technique, known as *flame fusion* or the Verneuil (*vur-noy'*) method, is capable of producing good quality gem ruby in prodigious quantities. In 1907 Verneuil reported an annual production of 5 million carats. (A carat is a gemmological unit of weight, equal to one-fifth of a gram.) Today, the Verneuil approach is used to make a wide variety of crystals, and some factories in Europe boast more than 1,000 Verneuil furnaces, all operating 24 hours a day. The annual output of such a factory is measured in tons, rather than in carats.

Another enticing goal of crystal synthesizers was diamond. Throughout the 19th century, reports appeared in the literature claiming successful diamond synthesis, but none of these experiments could be validated. Some of the best work was done by Henri Moissan who, in 1896, embedded carbon in molten steel and froze the melt by sudden cooling. Moissan believed that this procedure would create enormous internal pressures that would reform the carbon atoms into diamond.

Diamond and graphite are both pure carbon, though graphite is the softest and diamond the hardest natural substance. The difference in properties lies in the different arrangements and bonding of the carbon atoms within the structures of the two minerals. Natural diamonds are found in specialized types of rocks formed deep within the Earth at very high temperatures and pressures. Thus, experiments in

EARLY EFFORTS TO MAKE RUBY

THE QUEST FOR DIAMOND



diamond synthesis all involved methods for reproducing such conditions in the laboratory.

The actual temperatures and pressures in which diamonds form, however, proved beyond the capabilities of all growers until 1955. In that year the General Electric Company announced the successful production of synthetic diamond. The G.E. method is now well known, and is responsible for the manufacture of millions of carats of diamonds annually (see page 43).

SYNTHESIS OF QUARTZ

Quartz is one of the most abundant minerals on Earth, and has been known and used for millennia. There is some evidence that quartz was used as a primitive fire-making lens as early as 1500 B.C. The clarity of the finest natural quartz gave it mystical properties. Note the significance of the crystal ball in the operation of the fortune teller!

Experiments in quartz synthesis were recorded as early as 1848, by Schafhäütl, but crystals of only microscopic size were produced. Commercially applicable methods are

Rubies made by Edmund Frémy were thin, fragile plates. They were grown by a flux process.



Auguste Verneuil developed a method of producing large ruby crystals in commercial quantities. The early Verneuil crystals were less than half an inch long.

attributed to Richard Nacken, who first reported his work in 1908. Little success was attained prior to World War II, however. During the war, Allied blockage of German shipping stopped delivery of a critical wartime substance: Brazilian quartz. Because quartz was used in virtually every radio and transmitting device made, the war effort would have come to a halt without it. Thus, the Germans began a crash program to develop methods of making quartz in the laboratory. Nacken's early experiments were modified and his techniques were improved. Immediately after the war, American scientists found Nacken's laboratory and discovered that he was on the way to perfecting methods suitable for growing large quartz crystals.

Improvements were made upon Nacken's techniques in the United States. Experiments performed at Brush Laboratories in Cleveland, Antioch College, and Bell Telephone Laboratories (among others) led to practical commercial methods. The team that worked successfully at Brush Laboratories formed the Sawyer Research Products Company in 1956. This company is now a leading producer of what it terms "cultured quartz." The term "cultured" is used because the quartz process involves dissolution and redeposition of natural quartz, rather than actual synthesis from oxide components. This process is examined more fully on page 77.

Quartz was synthesized in commercial quantities in the years following World War II. It has been used for many years in making crystal oscillators for radio communications.



GEMS AND EXOTIC CRYSTALS FROM THE LABORATORY

Obvious candidates for crystal synthesis are gem materials, and most of the more popular gem minerals can now be made. A recent success involves the synthesis of precious opal. Diamond, ruby, sapphire, emerald, spinel, zircon, and even star sapphire and star ruby can all be produced in the laboratory in a quality that equals or surpasses nature's.

In the years since World War II, technological demands have caused a tremendous increase in the variety and perfection of many exotic crystals made by man. Many of these crystals do not have natural counterparts, and their uses are in technologies that were not even known several decades ago. By far the greatest interest in recent years has centered on silicon—as a basis for transistors—and on a host of exotic materials for lasers and electronic use. It was the expansion of crystal-growth technology that made possible such completely new devices as the transistor and the laser, both of which have altered the course of human history.

Crystal growth is a multimillion-dollar industry today, and a primary research and development effort of numerous giant corporations. New and exciting devices are continually being developed that require ever more sophisticated techniques for growing crystals.

Crystal growing is very much an art, as well as a science. It is well known in the

industry that certain men have a "touch" that enables them to grow crystals of a size or purity unattainable in other laboratories. This "craft" aspect is somewhat ironic in view of the tremendous influence crystal growth has had on many "precise" sciences, but the factors that affect crystal growth are so complex that they are only now becoming understood.

Natural crystals have been studied for centuries, and dozens of theories of their formation have been proposed. Only the concentrated efforts of this century have at last yielded accurate insights regarding what actually takes place in the vat or crucible where a crystal is slowly forming. Experimental tools for studying crystal growth are slowly becoming available and the coming years will undoubtedly see major advances in our knowledge of these processes. Such advances will spur significant breakthroughs in producing a wide variety of crystals.

Techniques

for

Growing

Crystals

Because crystals possess certain physical, chemical, and structural properties not found in other classes of substances, they have unique technological applications for which no substitutes are available.

In past centuries, natural specimens were the only source of large, well-formed crystals. But most of the largest and finest mineral specimens are now museum pieces and thus are not generally available for technological uses. Techniques therefore had to be developed for growing large crystals. Before discussing some of the most popular growth methods currently in use, it would be useful first to see just how crystals grow.

HOW CRYSTALS GROW

A crystal *is* a crystal because of long-range internal order; its atoms are arranged in periodic, regular arrays. The growth of such a crystal must therefore involve the addition of atoms in a systematic and regular fashion, each atom finding its proper place in the structural pattern. It is not necessary for the crystal to end its growth with flat, well-formed plane faces on its exterior. To be a crystal, it must simply meet the requirement of periodic, long-range ordering of its constituent atoms.

Crystal growth usually starts with a tiny "seed." The mechanism of formation of such a protocrystal is still not well understood. Once a seed forms, however, it acts as a substrate, or base, for the deposition of new material. Atoms travel through the

medium in which the crystal is growing and deposit on the seed. But the seed crystal (a solid) and the growth medium (generally a liquid or vapor) may offer equally suitable environments for any particular atom. To grow crystals it is therefore necessary somehow to force the atoms to leave the growth medium and attach themselves to the seed. This is done by causing the growth medium to contain more atoms of a crystal material than it can comfortably handle.

In human societies, when cities become too crowded there is an exodus to the suburbs. A similar thing happens in the case of crystal growth. If a growth medium is forced to accept, and atomically disperse within itself, a large quantity of material (generally a powder of the desired crystal substance), a point is reached where the medium cannot hold any more at a given temperature. If the temperature is then lowered, the solution's only recourse is to "dump" any excess, thus forcing atoms out of the medium and onto any seed crystal that might be present.

If the "dumping" tendency is strong enough the medium will actually force the creation of many tiny seed crystals on which to deposit excess solid. This "driving force" in crystal growth can be very strong. It is produced by changing the conditions within a growth medium in such a way that the previous condition of stability no longer exists. This can be accomplished by various means, usually by adding additional solid to a solution or by evaporating the solution. In the case of solidification from a melt, the driving force is created by lowering the temperature.

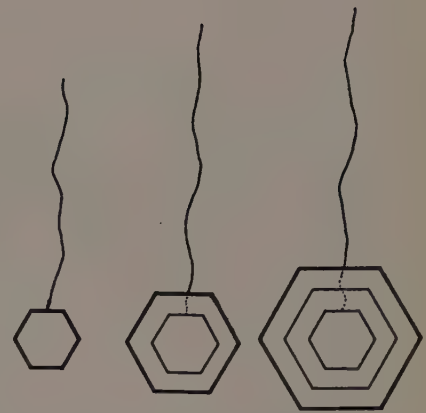
The theory of crystal growth is still quite young and many problems are unresolved. Early workers could not explain the discrepancy between the rates of crystal growth they actually observed and those predicted on the basis of driving-force calculations. This particular dilemma was solved by the suggestion that crystals are not really as "perfect" as people had always supposed. Instead, they may contain numerous defects and regions of misfit of layers of atoms, called *dislocations*.

Atoms in a growth medium find it easier to attach themselves to crystals at the surface of certain types of dislocations, called *screw dislocations*. Crystals containing such defects would therefore grow much faster than theory predicted. Screw dislocations were observed soon after this theory was proposed. A whole science of defects and dislocations now exists as part of the field known as *crystal physics*.

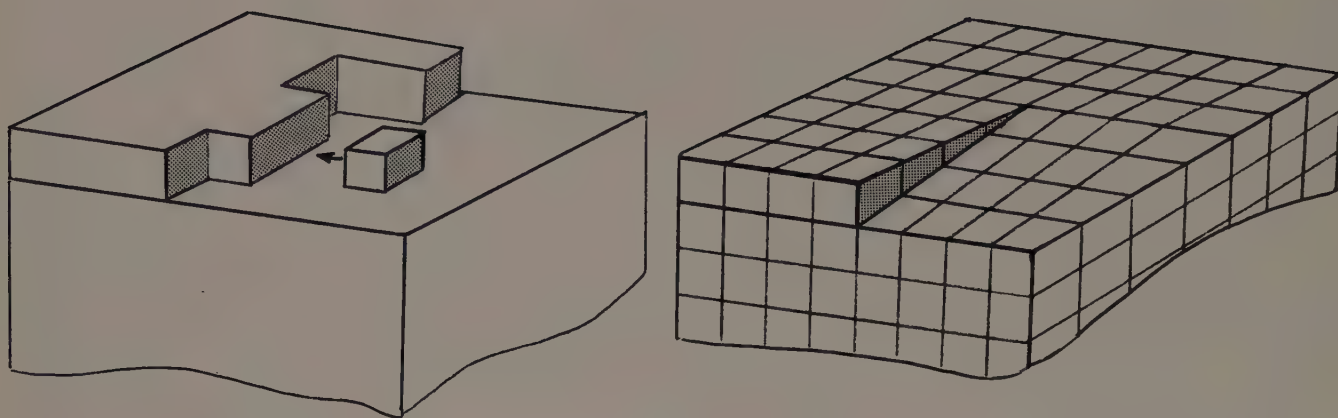
Certain materials grow well with several methods, but exhibit different properties depending on the particular technique used. Sometimes accidents occur in normally well-controlled growth environments, resulting in strange crystal forms or aggregates. These crystal "misfits" strongly resemble many types of natural crystals, which almost always grow randomly. Most man-made crystals, however, have distinct and predictable characteristics reflecting the growth technique that produced them.

The terminology of crystal growth is similar to that of agriculture. In every case, the desired material is "grown" from a "nutrient," which can be a liquid, a gas (vapor), or even a solid. The growth process usually starts with a "seed" of the desired material, and at the end of the procedure the newly formed crystals are "harvested."

Extreme care is generally required through all stages of the growth process. In some



Crystals grow by the addition of material, in layer after layer, to an initial seed crystal.



Atoms attaching themselves to a growing crystal find it easier to stick to edges and corners, such as along the edge of an incomplete layer (left). A dislocation is a region of slip in the structure of a crystal. The diagram at right shows a special type of slip, called a spiral dislocation, which perpetuates itself as the crystal grows, somewhat in the manner of a spiral staircase. The dislocation thus never disappears, and this allows very rapid crystal growth rates.

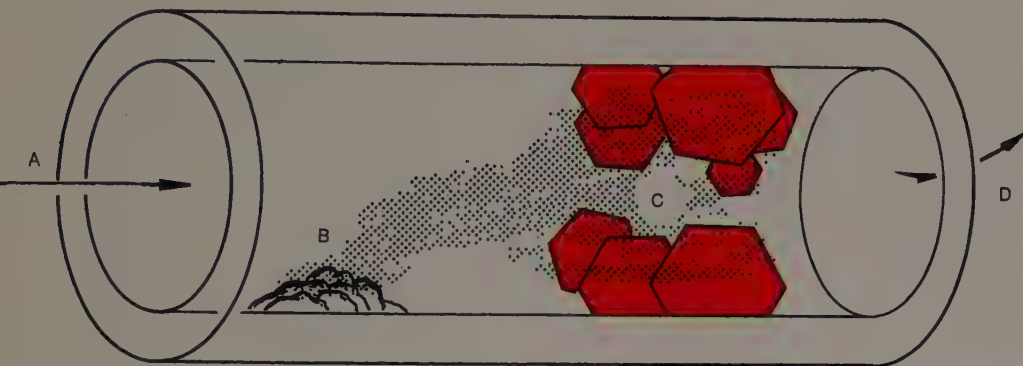
cases, temperatures have to be controlled with an accuracy of better than one one-hundredth of a degree, and dozens of factors conspire to prevent the growing crystal from attaining maturity and perfection. But if the art of the crystal grower prevails, the end product is a glittering masterpiece unrivaled even by nature.

Pioneer experimenters in crystal growth were delighted if their crystals had even the same outward appearance as those produced by nature. The requirements of industry now demand more stringent quality control. Crystal growers have been called on to prepare crystals containing less than one part per million of impurities (one impurity atom in one million atoms of crystal material). Even greater purity is now required to meet the exacting demands of current developments. In addition, the crystals must contain virtually no structural defects, such as displacement of adjacent atomic layers.

Some of the procedures used to achieve these conditions are truly exotic, though no more exotic than the materials themselves. A wide variety of crystal-growth methods are currently in vogue, with new ones being introduced continually. These methods can be conveniently divided into groups with certain fundamental similarities.

The most logical grouping is based on the nature of the growth medium. Crystal growth within the solid state is usually quite slow and therefore not of commercial importance. This leaves only two general procedures: growth from a vapor and growth from a liquid. The liquid can be either a solution or a melt. Some materials grow well with several techniques; others require elaborate and sophisticated equipment to produce exacting and highly specific growth environments. It might be added that nature seems to use all of the above methods in growing crystals, and perhaps even some that nobody has invented yet!

In vapor growth, a substance is heated and vaporized (B) in a furnace. The vapor is carried by an inert gas (enters at A) to a cooler part of the furnace where the vapor condenses as crystals (C). The inert gas is flushed out of the furnace (D) and recirculated.



VAPOR GROWTH

Vapor-growth techniques have limited applications because it is difficult or impossible to attain large crystal sizes with them. This very fact is an asset, however, if one wishes to grow very thin layers of one crystal material on top of another. Such layers are called *thin films* and form the basis of an enormous and important industry.

The substances that can best be grown from a vapor are those which pass directly from a solid to a vapor when heated, or whose components can be easily transported by a vapor. Materials that pass readily from a solid to a vapor are said to be *volatile*, and have a high *vapor pressure*. A good example is cadmium sulfide, which in nature is the mineral greenockite. Another is the element iodine, whose alcohol solution (tincture) is well known to generations of scraped and bruised children. Iodine crystals will vaporize in a match flame to form a purplish, poisonous gas which will immediately recrystallize on a cold surface.

In vapor-transport techniques the desired substance reacts (usually at a high temperature) with another material, and the products of the reaction are more volatile than the original ones. These new compounds are carried along as vapors and are allowed to react to reproduce the original substances. In doing so, at a controlled rate, they yield crystals of the desired material.

Vapor growth frequently produces crystals with the form of thin plates, as exemplified by the metals zinc and cadmium. A more striking characteristic of vapor growth is the formation of *dendrites*. These are delicate, lace-like crystals consisting of numerous thin branches that have grown into one another.

The formation of such crystals can be understood by considering the key factor in vapor growth (and also in solution growth in many cases): loss of heat. To produce a vapor of the desired material, it is necessary to heat it. Atoms of the solid then

Snowflakes are among the most familiar examples of dendritic crystals.



Sapphire (aluminum oxide) is rarely grown from a vapor. This crystal is less than an inch long.

leave it to fly about in the form of a dispersed gas. These atoms get their “flying power” from the energy they acquired during vaporization. To get the atoms back into a growing solid (the crystal), one must remove their excess energy. Unless this is done the crystal will simply not grow.

But gases are good environments in which to disperse heat energy because this energy can be carried away quickly by rapidly moving gas atoms. When a crystal grows from a vapor, therefore, it can grow at tremendous speed. Heat energy is carried away so quickly that the atoms joining the crystal don’t have time to migrate close to the main crystal mass. Instead, most of the atoms settle down where they can best give up excess energy, the so-called *heat of crystallization*.

Once a “finger” of crystal branches off the central body it may continue to grow out into the vapor. The crystal may develop side branches, which in turn grow out rapidly and develop branches of their own. Much later, the interior spaces between intersecting branches may fill in with crystal material. The final crystal might then not give any indication of its dendritic history.

Most snowflakes are dendrites. They form high in the atmosphere from vapor that hasn’t condensed into liquid droplets. Snowflakes have been studied by duplicating these same conditions in the laboratory.

Other types of dendrites, called *whiskers*, have proven important in the materials and electronics industries. They were first discovered when losses of current were noted in telephone and electric lines. Close investigation showed that such cables were being grounded by the growth of fine, hairlike crystals from the metallic cores of the wires. It soon became apparent that these crystals have phenomenal properties. They are unbelievably strong, approaching the theoretical strengths of pure metals. Research revealed that this strength results from the extremely high perfection of whiskers. That is, they contain very few defects and dislocations.

Once it was possible to grow such perfect crystals in the laboratory, a new branch of materials science was born: *composites*. Composite materials contain fibers of a material embedded in a matrix with different characteristics. Often, the embedded fibers are high-strength, defect-free whiskers; such composites as fiberglass and boron-in-epoxy are critically important to the future of technologies relating to transportation. Composites can be used in such diverse applications as turbine blades, aircraft wings, and auto bodies.

Crystals grown by vapor-growth techniques include the metals zinc, cadmium, aluminum, tantalum, beryllium, and copper (most of these in the form of thin films); cadmium sulfide; zinc sulfide; and oxides of silicon, tantalum, niobium, zirconium, and tin. In nature, vapor growth produces such oddities as “filiform” (hairlike) crystals of pyrite (iron sulfide, sometimes called “fool’s gold”). These grow in minute cavities in volcanic rocks, as a result of condensation of volcanic gases. Many other mineral crystals may start their existence as dendrites. Sometimes—as in the cases of copper, silver, gold, and some oxides—the dendrites never fill in, and remain for us to see as mineralogical curiosities.



Magnesium crystals, produced accidentally in smelters, sometimes grow as dendrites.



MELT GROWTH Most of the Earth's natural crystals grow from melts. Deep below the surface of our planet, below the thin upper layer we call the crust, rocks are mainly in a plastic, nonrigid state with interspersed areas of melted material. Occasionally, some of this molten material, or magma, works its way upward into cooler portions of the crust and begins to cool and harden. In that instance, the driving force for crystallization is lowering of temperature. During the cooling process, crystals form within the melt and eventually the magma is hardened into rock.

Sometimes rocks are fairly coarse grained, but magmatic crystals seldom reach dimensions of more than a few inches. The starting composition of the melt, and the total pressure on the melt during crystallization—combined with events that take place during crystallization—determine the compositions of the magmatic crystals that form.

Everyone grows crystals from a melt. Ice is a solid that melts at only 32 degrees F., and water is nothing more than molten ice. Ice cubes are not single crystals, however. Uncontrolled freezing of a melt generally results in the formation of many tiny crystallites that all grow at the same rate to fill up available space. An ice cube is thus termed a *polycrystalline aggregate*, consisting of a myriad of intergrown crystals. Poured ingots of molten metals crystallize in much the same way.

The general term for crystal growth from a melt is *solidification*. It is a very complex process, and not all materials can be grown this way. In some cases the melting point is too high for practical experiments. Frequently, the desired substance doesn't



crystallize from a melt of the same composition, or it may decompose before it can be melted. In principle, melt-growth techniques are the simplest. All one needs to know is the melting point of the desired substance. If a suitable nonreactive container can be found to hold the melt, crystals of high purity can be grown at remarkably high rates of speed.

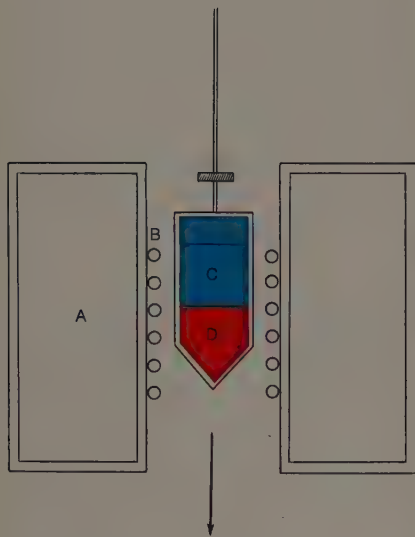
THE BRIDGMAN-STOCKBARGER METHOD

A useful technique for growing large single crystals was developed concurrently by P. W. Bridgman, an American; D. C. Stockbarger, a German; and the Russians Obreimov, G. Tammann, and A. V. Shubnikov in the period 1924 to 1936. This method, known in the United States as the Bridgman-Stockbarger method, involves cooling a molten mass in a specially shaped container, normally a cylindrical tube or cylinder that tapers to a point at one end. The entire mass is allowed to cool slowly until it is close to the freezing point. The temperature is then lowered at the pointed end until an initial "seed" crystal forms at the tip. This type of freezing is carefully controlled, as opposed to the random process that occurs in a tray of ice cubes.

The container shape makes it likely that only a single crystal will have a chance to form. Cooling then continues and the seed crystal grows out into the container, crowd-

Facing page: An igneous rock is one that forms from magma, molten material from deep within the Earth. The interlocking texture of crystals of various minerals in the rock—in this example a gabbro from Point Sal, California—gives evidence as to the way in which the rock was formed.

Above: Bismuth crystals have no industrial importance, but are extremely beautiful. The iridescence is caused by a thin oxide film. These crystals were made by slow cooling of molten bismuth.



In the Bridgman technique, a specially shaped crucible, filled with a powder of the desired crystal (C), is lowered through a furnace (B). The powder melts and a crystal starts to form in the pointed tip of the crucible as the crucible emerges into a cool part of the furnace. A single crystal grows (D) as the molten material solidifies. The entire assembly is surrounded by insulation (A).



Fluorite crystals of high optical quality are routinely grown by the Bridgman method.

Thallium bromo-iodide (KRS-5) is a material that is very transparent to infrared radiation. Crystals are readily grown by the Bridgman method, using glass crucibles. The unmelted powder is yellow; the finished crystals, deep cherry red. The colorless crystals are fluorite.

ing out any small competitors that might start to grow. Eventually, the entire melt is frozen, and the solid in the container is a single crystal.

Many variations of this technique have been devised, some for growing specific types of materials, such as metals. Crystals of exceptionally high purity and enormous size can be grown. The largest to date are crystals of sodium iodide and cesium iodide nearly a yard across and weighing more than half a ton.

Materials grown by the Bridgman-Stockbarger technique include metals; halides (fluoride, chlorides, iodides, bromides) of chromium, manganese, cobalt, nickel, zinc, calcium, and rare earths; sulfides, selenides, and tellurides of lead and cadmium; and various oxides.

THE VERNEUIL TECHNIQUE, OR FLAME FUSION

Historically, one of the most significant developments in crystal-growth technology was the introduction of the Verneuil technique. As mentioned earlier, Verneuil was looking for an improvement on the flux method of Frémy for growing large ruby crystals. Work dating as far back as 1886 led to a breakthrough that was announced in a 1902 publication. Verneuil had deposited several sealed documents with the Paris Academy of Sciences in 1891 and 1892. When opened in 1910, these papers revealed the details of Verneuil's early work on ruby synthesis.

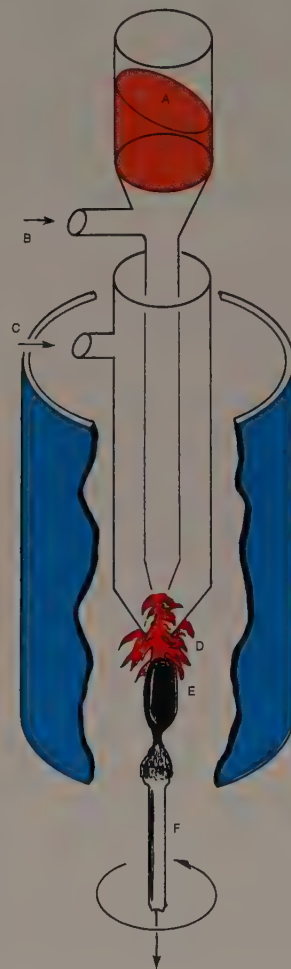
Soon after the publication of Verneuil's technique, manufacture of ruby commenced in many places. By 1907 total production had reached about 5 million carats annually. Modern Verneuil factories produce many times that quantity of fine corundum (ruby and sapphire), spinel, and other melt-grown crystals.

The Verneuil method employs an inverted hydrogen-oxygen blowtorch that maintains a small puddle of molten material at the end of a rod of solid substance. For this reason the technique is sometimes referred to as flame fusion.

The rod is slowly rotated and lowered, and the molten material freezes as it moves out of the hot flame. Additional solid in the form of a powder is added to the upper end of the rod. The powder falls from a hopper above the blowtorch and passes through the flame. By the time it has reached the rod, it has melted, forming a kind of "molten rain" consisting of tiny droplets. The rod continues to increase in length as it is lowered. Since the growth takes place at high temperatures, atoms in the melt have high mobility and can migrate to suitable attachment positions in the rod before freezing prevents further movement. A Verneuil rod is therefore a single crystal.

One great advantage to the Verneuil method is that the crystal grows in open space, rather than inside a container. Impurities that might be picked up from the container are thus avoided. The purity of the finished crystal depends solely on the composition of the feed powder and the atmosphere in which the crystal is grown. Flame fusion is a very tricky technique to master, however, since the particle size of the powder, flame temperature, purity of starting materials, and the rates of rotation

The Verneuil technique, developed before 1900, is still in use today in a manner closely resembling the original method. Feed powder in a hopper (A) falls through a screen and is mixed with oxygen (B) and hydrogen (C). These gases are burned (D) to create a very hot flame that melts the powder into fine droplets. The droplets fall in a kind of "rain" onto a ceramic rod below (F)—and eventually a crystal forms (E). The rod is rotated and lowered as the crystal grows.





Large disc boules of ruby are grown by allowing the molten droplets in a Verneuil furnace to fall onto the edge of a rotating disc. Large round "windows" of ruby can be obtained by slicing out the centers of such boules.



Spinel crystals for gem purposes are easily grown by the Verneuil method.

and lowering of the rod all affect the quality of the finished crystal. The popularity of the Verneuil method, despite these drawbacks, is indicated by the fact that about 100 different substances have been successfully grown with it.

Variations in flame fusion arise principally in the heating devices used. Some scientists have tried plasma torches, which provide an intensely hot flame. (A plasma is essentially a fourth state of matter, consisting of gaseous atoms whose electrons have been stripped off by extremely high temperatures.)

In one ingenious method of heating, a growing crystal is centered between two enormous parabolic mirrors. A very bright carbon arc (or other high-intensity lamp) is focused on the crystal. The entire energy output of the lamp is thus magnified greatly in a very small area, producing considerable heat. Since only light energy is involved, the method is extremely clean and growth can even be carried out in a vacuum. The method is called arc-imaging.

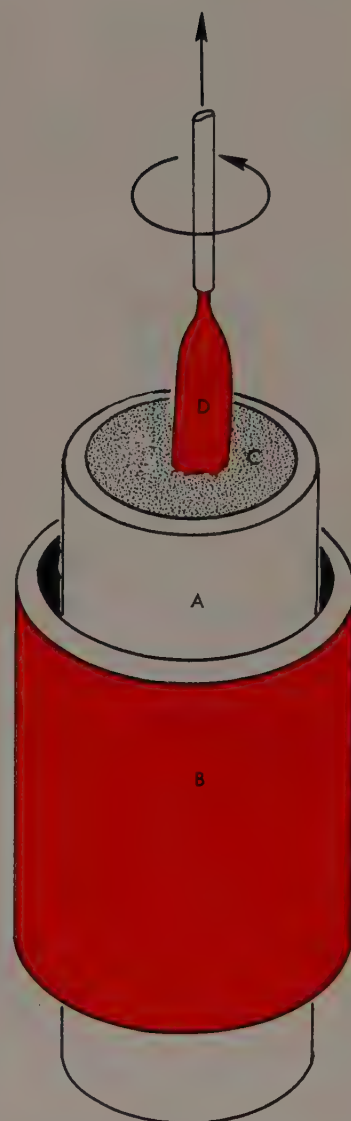
A major disadvantage of all flame-fusion methods is that the crystals, called *boules*, that are produced tend to crack upon cooling because of internal strain. This can be avoided by careful annealing of the crystals as soon as growth is completed. Annealing simply involves reheating the crystals to just below their melting point, thus allowing internal strains to work themselves out.

THE CZOCHRALSKI TECHNIQUE, OR CRYSTAL PULLING

One of the most important melt-growth methods currently in use is the Czochralski technique. J. Czochralski (chŭh-kral'-skee) originally developed his technique to measure the speed of crystallization of various metals. It soon proved useful as a way of growing large perfect crystals of many different compounds and elements. Molten material is contained in a crucible, which must not react with the melt. Typical crucible materials include platinum, iridium, quartz, ceramics, and graphite.

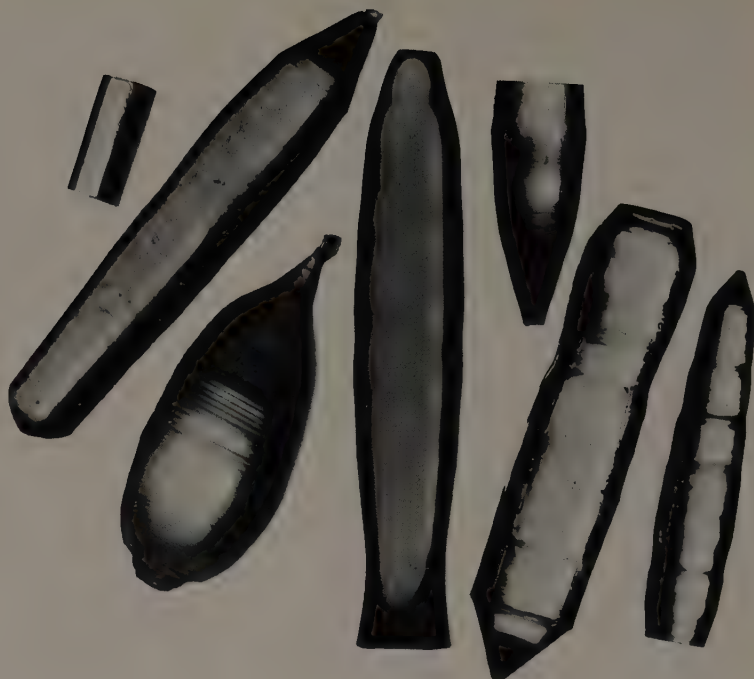
A rotating rod with a small seed crystal on the end is lowered into the crucible until it just touches the melt. After a brief pause, the rod is slowly withdrawn. At the melt-seed interface, crystallization occurs in two ways. Surface tension pulls some of the melt slightly out of the crucible and it then solidifies on the seed. In addition, heat conduction allows the solid to extend slightly into the melt. The removal of the rod from the melt allows material to be added continually to the end of the rod, and so a crystal grows. The growth arrangement has led to the term crystal pulling for the Czochralski method.

The pulling rate can be varied, and is normally in the range of about 1 millimeter to 10 centimeters per hour. Rotation of the rod is normally about 10 to 100 revolutions per minute. Melt temperature is very carefully measured, since thermal changes drastically affect the quality of the grown crystal. In many ways the Czochralski apparatus resembles a sophisticated drill press.

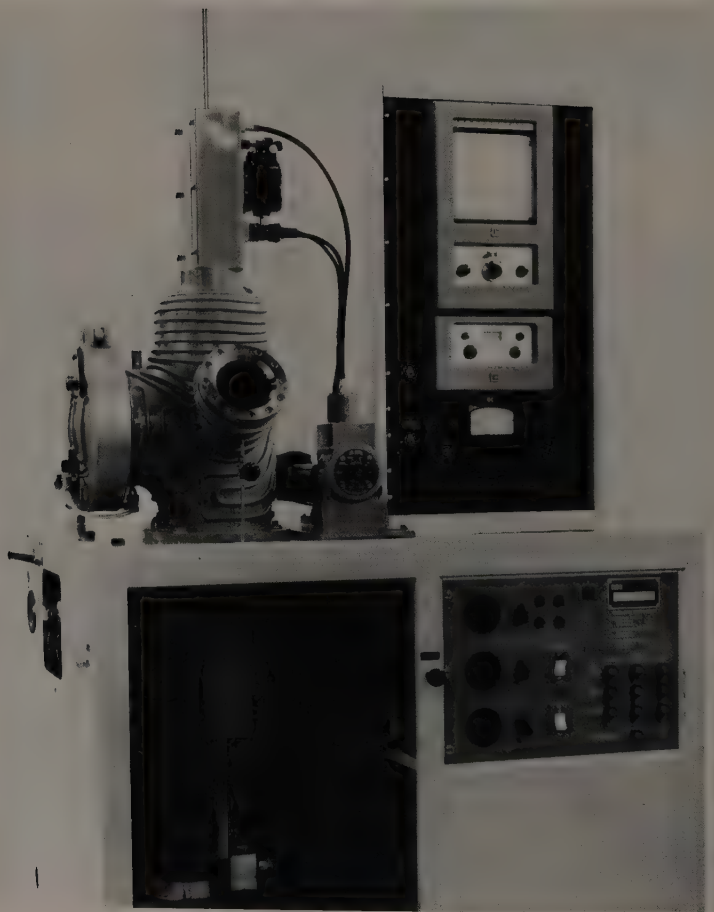


In the Czochralski method, a crucible (A) is filled with a powder of the crystal desired (C) and the powder is then melted in a furnace (B). A rod is lowered to the surface of the melt, allowed to touch it, and then is slowly rotated and withdrawn. A crystal (D) is thus "pulled" out of the melt. Very large crystals can be grown in this way.

Typical Czochralski crystals, left to right: two powellites (calcium molybdate), two wulfenites (lead molybdate), one sanmartinite (zinc tungstate), and two scheelites (calcium tungstate). The longest crystal is 3 inches.



The modern crystal puller is a versatile device, capable of handling many types of materials, atmospheres, and variations of techniques.



THE KYROPOULOS TECHNIQUE

A variation of crystal pulling, called the Kyropoulos technique, was developed by S. Kyropoulos between 1925 and 1935. The apparatus looks much the same as the Czochralski, but instead of the crystal being pulled out of the melt, the temperature of the melt is lowered from the seed crystal downward. This can be done by allowing heat to leak out through a seed holder, or by lowering the entire crucible through a temperature gradient (a zone with steadily decreasing temperatures). The crystal grows out from the seed as the material freezes. If carefully done, the technique produces good single crystals. The most suitable have a large diameter compared to height. In contrast, the Czochralski method is best suited for crystals much longer than they are wide.

The Kyropoulos apparatus is simple because pulling is not employed. However, the size and direction of growth are easier to control with the Czochralski method. In both processes, the main restriction is that the crystal to be grown must not decompose (break up into molecular components) at its melting point. Ideally, the grown crystal should have the same composition as the melt. Strange as it seems, this is not always the case!

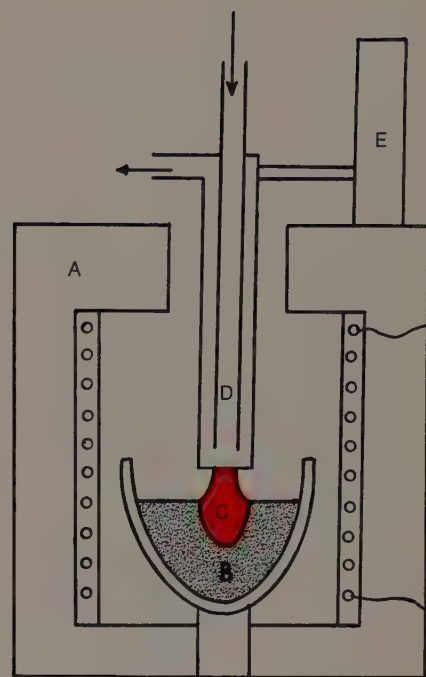
In addition, the material to be grown should not react with the crucible, and its melting point must be attainable within the usable range of some crucible material. In the early days of experimentation some rather spectacular failures resulted from unexpected reactions suddenly causing molten or perforated crucibles.

Crystal perfection is a function of pulling and rotation rates, temperature control, atmospheric purity, the purity of starting materials, and the properties of the crucible. When all goes well, remarkably perfect single crystals of enormous size can be grown. Examples include ruby crystals 2½ feet long grown for laser applications, colorless sapphire crystals weighing several pounds for use in making armor plate (sapphire is a very strong material capable of deflecting projectiles!), and the 2- and 3-foot-long silicon crystals grown by the transistor industry.

When Czochralski pull rates are increased to inches per minute, large and spectacular dendrites can be grown. The crystal size attainable is limited by the apparatus used. Crystals of more than 100 substances have been successfully pulled, and commercial Czochralski production is an established fact. Some laboratories have even computerized the pulling process so that all steps in the operation, including monitoring of the length and diameter of the growing crystal, are completely automated.

ZONE GROWTH

Zone growth is similar to the Kyropoulos technique in that a moving temperature gradient is used. The distinguishing feature of zone growth—and a modification called *zone refining*—is the use of a small molten region within a rod or slab of solid.



In the Kyropoulos technique, a furnace (A) contains a crucible of powdered material (B) that is melted. A seed rod (C) is cooled by a circulating liquid (D) and held motionless in the molten material. The exact position of the seed is adjustable (E). The furnace is then shut off and a crystal grows outward from the seed until the entire mass has frozen into a single crystal.

The molten zone is maintained by a local heater, which is allowed to move slowly along the length of the solid. Impurities in the material tend to remain in the liquid and the moving zone acts as a kind of "sweeper" that gradually accumulates these impurities, leaving behind a much purer crystalline solid.

Conditions are adjusted so that a single crystal results from the melting and re-freezing process. Many passes of the molten zone result in a very pure crystal. The technique can be carried out in a horizontal "boat," or by moving the heater down a vertical rod. The general nature of the technique has led to the name *float zoning*.

GROWTH FROM SOLUTION

Solutions are a part of everyday life. The coffee drinker may not realize it, but the simple act of preparing a hot cup of beverage is a study in solubilities. Lump sugar dissolves at a different rate than granulated sugar. Saccharine tablets have still a different solubility, and so does powdered coffee.

Several factors have an obvious effect on solubility: the temperature of the liquid, the relative amounts of liquid (generally termed the *solvent*) and solid (called the *solute*), the rate of stirring, and the particle size of the solute. Yet, in general, it can be said that most solids will dissolve more readily in hot liquids than in cold ones. This is strikingly demonstrated by sugar and water.

To anyone who has never made rock candy, the solubility of sugar in water can be astounding. Almost 5 pounds of granulated sugar can be dissolved in a quart of boiling water. Finally, after continued heating and stirring, some added sugar remains undissolved at the bottom of the pot. At this stage the solution is termed *saturated*—no more solute can be dissolved in it at that specific temperature. But what happens when the solution is allowed to cool?

If the water were never heated at all, it could be determined that much less sugar would dissolve in the same volume—in this case one quart. Obviously, raising the temperature (boiling the water) allowed additional solid to dissolve. In other words, saturated solutions contain different amounts of dissolved material at different temperatures. Saturation is always referred to a specific temperature. If a saturated solution is allowed to cool, it is capable of holding less solid, and the excess must precipitate out.

This is the mechanism of crystallization from solution. A solution that contains more dissolved solute than is permissible at a given temperature is termed *supersaturated*. Supersaturation is a driving force that promotes crystallization, even to the extent that it will force small *crystallites* (very tiny crystals) to form spontaneously in the solution. This effect, sometimes called *spurious nucleation*, must be avoided in the growth of large single crystals.

Growth from solution has several major advantages. Many substances will dissolve readily in appropriate liquids, and the mobilities of solute components can be very high. Growth temperatures can be controlled with great accuracy. Apparatus for solu-

tion growth is often very simple and inexpensive (e.g., a pot, some water, and a few mason jars). Very large crystals can be grown simply by increasing the time of growth and the size of the container.

The major object of solution growth is to supersaturate a solution and then cause the excess solute to deposit in the form of crystals. Supersaturation can be attained either by lowering the temperature or by evaporating the solution. Sugar crystals (rock candy), for example, are grown by slow cooling of a highly concentrated solution (syrup). When a person swims in the ocean and then lies in the warm sun, evaporation of the film of sea water on the skin produces a crust of fine, powdery salt crystals.

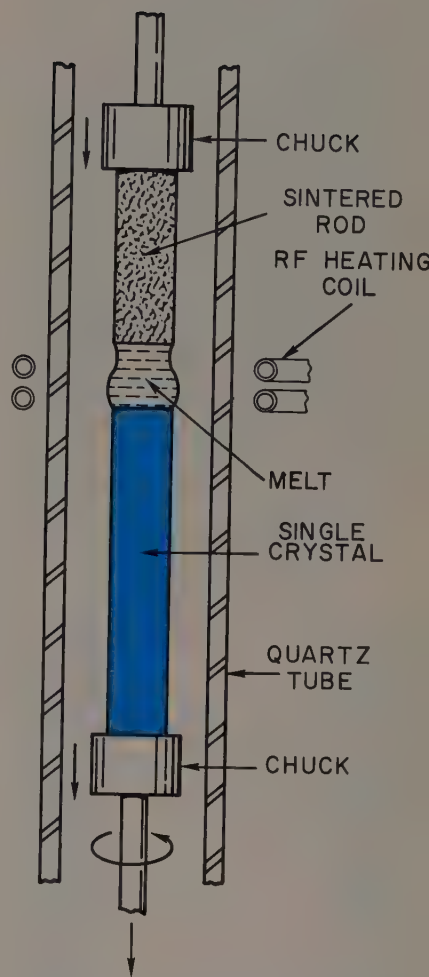
In a true solution, the solute particles are so small that they will never settle out, no matter how long the solution is allowed to stand. These particles are, in fact, atoms and molecules. Mixtures, on the other hand, contain larger particles that will separate. A good example is milk, which contains globules of butterfat as well as dissolved sugar. The fat can be physically separated and removed, but the sugar will remain in the residual liquid because it is dissolved.

Many compounds can be dissolved in water to make highly supersaturated solutions. A good example is sodium thiosulfate, a photographic chemical commonly known as "hypo," which dissolves readily in hot water. On cooling, this solution is unstable because it contains more dissolved material than would normally be possible at the lower temperature. The instability is due to a phenomenon called nucleation—the process of initial formation of a crystallite.

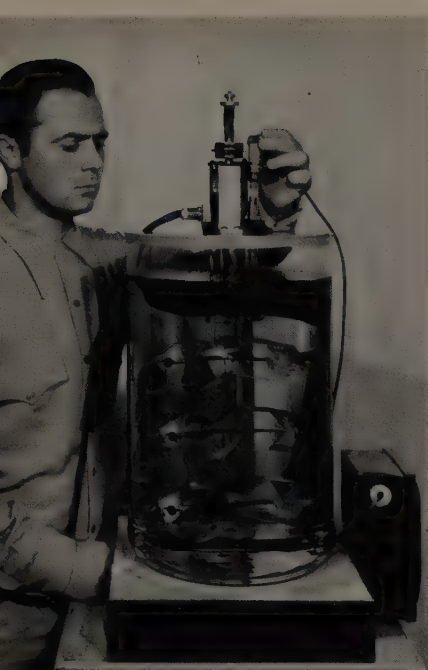
A small bit of energy is required to form a crystallite, and this energy may not always be available in a supersaturated solution. The cooled, supersaturated hypo solution will remain clear, if undisturbed, but even a slight vibration may provide the minute energy needed to form crystallites. Once a crystallite forms and grows beyond a certain critical size, continued growth may proceed at a very rapid rate. Thus, if a tiny speck of crystalline hypo is tossed into the jar of supersaturated solution, the entire jar instantly turns opaque as a crystallization chain reaction occurs. All the excess solute crystallizes out until the solution is once again just saturated.

Many ingenious techniques have been devised for growing large and perfect crystals from solution. Since crystal size is merely a matter of the scale of the equipment used, large commercial plants have grown crystals weighing several hundred pounds. To maintain crystal quality in such behemoths is a special art. It has been found that movement of the crystal, or the solution, or both, is essential to preserve adequate growth rates and perfection. Crystal scientists have experimented with rotating racks on which crystals are suspended in solution. The temperature of the solution is gradually lowered and the excess solute is deposited on the crystals. The best known of these inventions is the "rotary crystallizer" devised by Alan Holden of Bell Telephone Laboratories. Large and very perfect crystals are routinely produced in such an apparatus.

An intriguing technique involves the use of separate vessels, connected by a tube. One vessel contains a seed in a saturated solution, the other contains a "nutrient" material which is dissolved in a solution maintained at a higher temperature. The



In float zoning, a single crystal can be purified by means of a molten zone that acts as a "sweeper" for impurities. In the arrangement shown, a sintered rod or a single crystal is moved past a heating coil. In the zone of the coil, the rod melts and impurities are pushed into the liquid. Moving on, the molten material solidifies into a single crystal, leaving the impurities behind in the liquid.



The rotary crystallizer was developed by Alan Holden of Bell Telephone Laboratories. Its chief feature is the stirring of a nutrient solution by means of a rack containing the growing crystals. Because of this type of agitation, the crystals grow more uniformly.

nutrient solution migrates through the connecting tube where it cools and deposits the excess solute on the seed crystal. The cooled solution, now depleted of solute, returns to the nutrient vessel through a return pipe.

Water, of course, is not the only solvent one can use to grow crystals. Organic compounds grow well from such solvents as acetone, carbon tetrachloride, and alcohol. Large and perfect sulfur crystals can be grown by evaporating solutions of sulfur in carbon disulfide. Many pharmaceuticals are purified by crystallization from solutions.

Additional variations in solution techniques include growth by chemical reactions (the desired material is added to a seed crystal by forming it in a chemical reaction) and electrolysis (the formation of a solution species by an electric current).

Some of the crystals grown from water solutions include alum (potassium aluminum sulfate), Rochelle salt (sodium potassium tartrate), ADP (ammonium dihydrogen phosphate), KDP (potassium dihydrogen phosphate), EDT (ethylene diamine tartrate), salt, sugar, niter (sodium nitrate), and copper sulfate.

For decades, crystal growers have speculated that every substance, if left to itself in ideal growth conditions, would form crystals of characteristic shape, the so-called *equilibrium form*. Ideal conditions are seldom achieved, however, and even trace amounts of impurities will change the resulting crystal form, or *habit*.

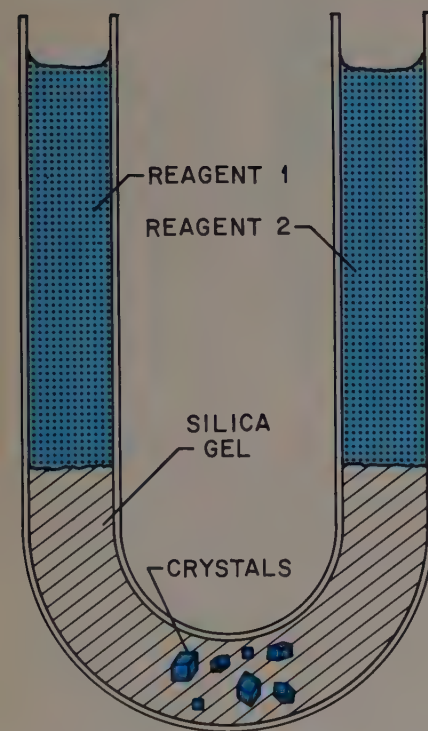
Once understood, the ability to alter crystal habits can be a useful tool. Sometimes problems arise in packaging industrial chemicals because the chemical grains are rounded and tend to pack tightly together and form lumps. These problems can be solved by adding very small amounts of certain other chemicals to the solutions from which the desired compounds are crystallized. These additives can change the habits of the desired material, producing elongated or fibrous crystals. Such crystals break easily and do not form cakes and lumps.

GEL GROWTH

An interesting variation of solution techniques is gel growth. A gel is a spongelike network of material, such as silica (silicon dioxide) or gelatine (a protein compound), which is made in various ways. It can be allowed to form in a solution of chemicals, so that when the gel sets, it is permeated with these chemicals. A second solution is then poured on top of the gel. This solution contains chemicals that react with those in the gel. When the upper solution diffuses (migrates slowly) into the gel, such a reaction takes place, and crystals grow as the reaction product.

An alternative method (see diagram) uses a U-shaped glass tube, which is partially filled with a gel containing no chemicals. The two reactive chemical solutions are placed on opposite ends of the gel. These solutions diffuse toward each other, and when they meet, a reaction occurs. The reaction products are crystals, which slowly form in the gel over a period of days to weeks.

The gel technique is very useful in growing relatively insoluble compounds that are difficult to grow by other methods. Crystal size is limited chiefly by the scale of the apparatus used.



In gel growth, chemicals in solution (reagents 1 and 2) diffuse (migrate) through an inert gel. Where the solutions meet, a reaction occurs and crystals grow as the reaction product.

HYDROTHERMAL GROWTH

The term hydrothermal means, literally, "hot water." But in the jargon of the crystal grower, hydrothermal also implies conditions of high pressure as well as high temperature. The pressure is created by sealing water, "seed crystals," and "feed material" of the desired substance inside a steel vessel called (rather ominously) a *bomb*. The bomb is placed in a furnace and heated to several hundred degrees centigrade, at which point the water expands to fill the vessel and the pressure within the bomb increases. Adjustment of the filling level and the final temperature determine the ultimate pressure attained.

The chief advantage of the hydrothermal method is the increase in the dissolving power of solvents in hydrothermal conditions. Their action is especially noticeable on substances that are reluctant to dissolve at room temperature and pressure. A chief disadvantage is the inconvenience of the equipment and the ever-present danger of explosions!

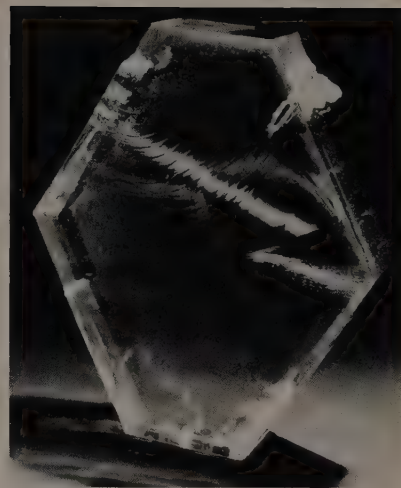
Nature employs the hydrothermal technique rather effectively in forming mineral veins. Nature also has the advantage of unconcern with preserving the growth "apparatus" used. She doesn't care about corrosion of the walls of the pressure vessel (the rocky walls of a vein or fissure deep within the Earth), or possible rupture of the vessel, or even the exact composition of the solution. Very high temperatures and pressures are created with impunity.

As a result, nature can grow mineral crystals such as spodumene, topaz, feldspar, and quartz whose dimensions are measured in feet and weigh hundreds of pounds or even tons. The Etta Mine in South Dakota boasted spodumene crystals 40 feet long. The largest feldspar crystal ever found reportedly weighed hundreds of tons and filled two railroad boxcars. In such cases it is possible to open a mine within a single crystal!

The earliest experiments in hydrothermal synthesis were done by mineralogists who wished to test theories of mineral genesis. Only small crystals were needed in these experiments, but the general techniques developed are still employed in growing large single crystals. The most familiar laboratory-grown hydrothermal crystals are quartz (silicon oxide), sapphire (aluminum oxide), and zincite (zinc oxide). Many other materials can be grown. However, much work still remains to be done in perfecting hydrothermal methods.

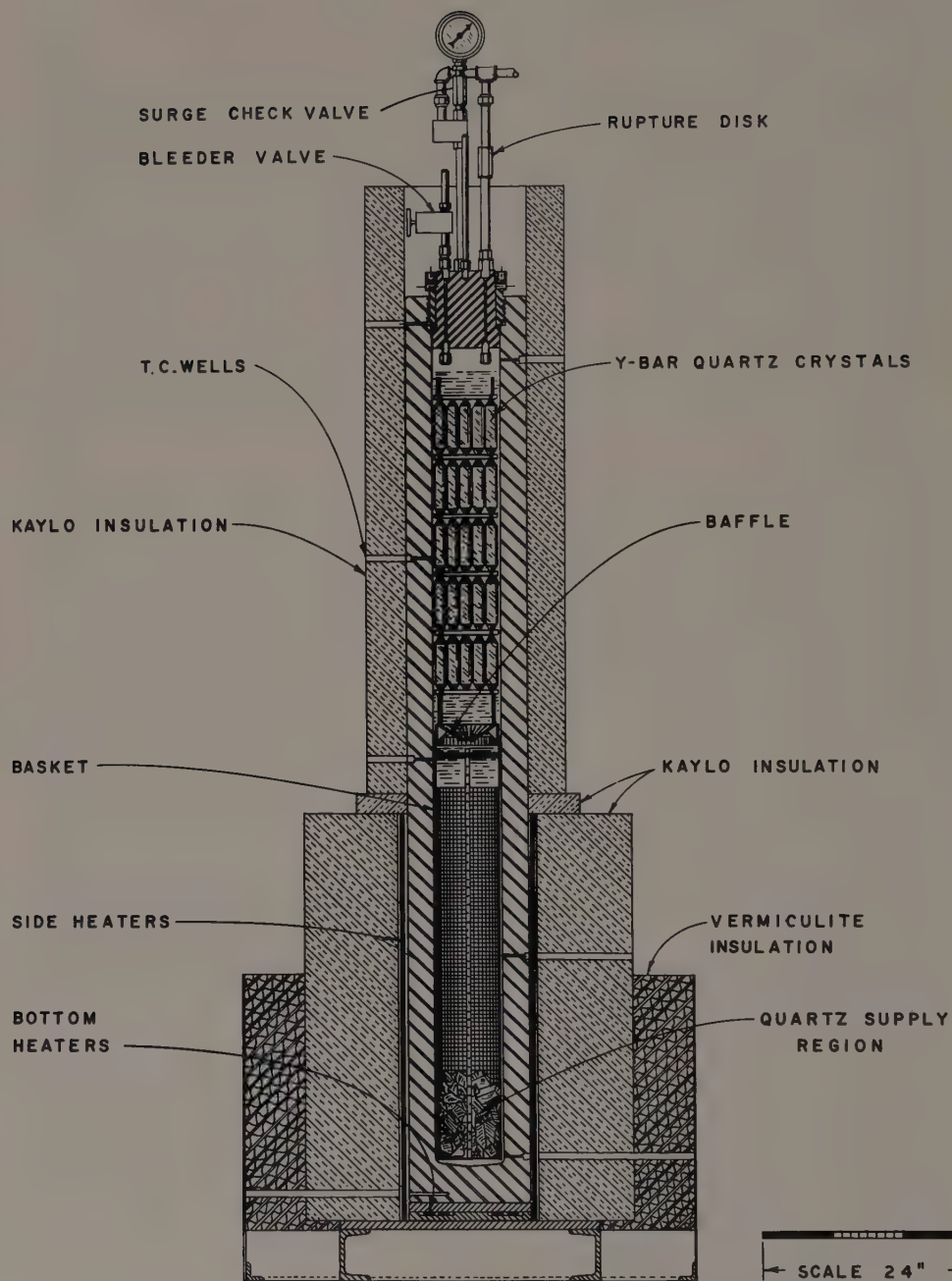
The most critical problems involve finding suitable solvents for specific materials, and determining the right temperatures and pressures for maximum growth rates. The chief difficulty in choosing equipment for hydrothermal growth is in finding an inert, leakproof container. Also, the growth times in hydrothermal runs are normally quite long, further complicating the selection of a container material. Since the growth of hydrothermal crystals generally takes place in steel containers, it is not possible to visually observe the progress of the growing crystals unless special experimental arrangements are made, using x-rays.

Purity in hydrothermal growth presents special difficulties. Impurities are less likely to be absorbed by the crystal at lower growth temperatures, but growth rates are then



Zincite crystals (zinc oxide) of exceptionally high quality are grown hydrothermally.

A hydrothermal autoclave is, in effect, a pressure cooker. In growing quartz, feed material (crushed natural quartz) is placed at the bottom of the autoclave and bathed in a caustic solution. When the solution is heated, the quartz dissolves and migrates upward into a cooler portion of the autoclave. Here, the dissolved quartz deposits on seed crystals hung on racks. Growth takes approximately 50 to 70 days.



79-LITER, SINGLE CHAMBER, VERTICAL, STATIONARY AUTOCLAVE

correspondingly slower. Water is frequently observed as an impurity in hydrothermal crystals. In many cases the solutions dissolve the steel walls of the bomb, so liners made of inert precious metals have to be used.

Detailed experiments must often be performed to determine the best conditions in which to grow a specific crystal. These so-called *phase equilibria studies* reveal the various compounds that form from the same starting components at different temperatures and pressures. Once this is known, the pressure-temperature region for growing a desired material can be effectively isolated. Crystals are then grown without interference by the formation of other, unwanted compounds. Also, it has been found that crystals tend to grow better inside their own stability fields.

Because of the dangers associated with hydrothermal equipment, bombs and furnaces are usually built into pits dug in the ground. The entire assembly is lined with steel plates. Bombs are fitted with "rupture discs" that are designed to break at pressures below the bursting point of the steel vessels. As with other techniques, the restriction on crystal size is limited by the scale of the equipment used.

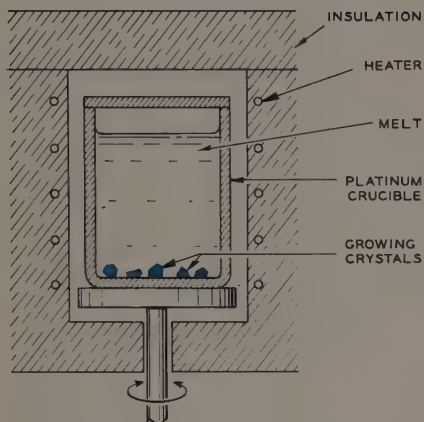
FLUX GROWTH

A flux is a material that lowers the melting point of a substance with which it is mixed. In crystal growing, typical fluxes are lead fluoride and boron oxide. Since water itself can be considered a flux (water is molten ice), flux-growth principles are almost identical with those of solution growth. A general rule of thumb among crystal growers is that, given enough time and a large enough chemical stockroom, it should always be possible to find a suitable molten-salt solvent to grow a particular crystal. The only difficulty in this approach is the time and number of experiments that might be required to find the right one!

Water is not the best solvent for many types of compounds, especially oxides. When a material dissolves, the molecules of the solvent actually break apart the compound and isolate the fragments from each other. Evaporation of the solvent allows the pieces to rejoin and reform the original material. Chemicals such as lead oxide, lead fluoride, and potassium fluoride are solids at normal temperatures, but become powerful solvents in a molten state. Unfortunately, such solvents are often unselective in what they dissolve. Thus, a particular solvent may seem to be the answer to a prayer for a flux to handle an especially insoluble material—until the flux starts dissolving the walls of the container as well! In addition, since fumes of many of the most widely used fluxes are toxic, special precautions must be taken to insure the safety of the crystal growers.

Flux growth (also called *molten-salt growth* and *fluxed-melt growth*) is usually carried out in crucibles made of platinum. In fact, the availability of platinum labware makes flux growth feasible on a practical, day-to-day basis.

Some fluxes even attack platinum, and so iridium and graphite are sometimes called for in special situations. The noble-metal pots used in industry are often very



In flux growth, a powder of the desired crystal material (or a mixture of components in the correct ratio) is mixed with a substance known as a flux. When the mixture is heated, the flux melts and becomes a powerful solvent for the other components. Crystal growth then proceeds by either evaporation or cooling of the molten mixture.

large, holding several quarts, and can cost over \$10,000 each. Platinum crucibles can withstand temperatures up to about 1,300°C.; above this temperature, rhodium and iridium must be used.

Flux growth is most advantageously applied to crystals with high melting points (too high for available Verneuil or Czochralski equipment), or which decompose at or below their melting points and must therefore be grown from a solution. Flux-grown crystals tend to be somewhat smaller than those attainable from water solution or from the melt. This is partly because of the costs and partly because of the difficulty of controlling large-scale flux equipment.

A key advantage in flux techniques is relatively rapid growth rates for most materials, combined with the simplicity of the procedure. A powder of the desired crystalline material, or a mixture of components in correct proportions, is weighed and mixed with a specific quantity of powdered flux. This mixture is melted (in a platinum crucible, for example) at a temperature known through experimentation to be in the stability range of the desired crystal. The molten mass is then allowed to cool very slowly.

This procedure is analogous to the cooling of a supersaturated solution. After a period of slow cooling, the crucible is rapidly chilled and the flux is dissolved in water or acids. The residual material in the crucible consists of the desired crystals.

Sometimes a crystal is stable only over a narrow range of temperatures. Cooling might then result in possible decomposition and precipitation of unwanted material. In such cases a variation of the flux technique is employed, an approach called *solvent evaporation*, which is similar to water solution growth methods. It has the advantage of constant temperature, and the driving force for crystallization comes from removal of the solvent (flux). Probably some evaporation occurs in any flux experiment, and this contributes to crystal growth, though in an unmeasured way.

Most flux experiments allow spontaneous nucleation of crystals as cooling or evaporation progresses. It is possible to maintain better control over the growth rate, perfection, and orientation of grown crystals by seeding; that is, a carefully chosen, tiny crystal of the desired material may be added to the powder mixture before melting. Of course, as with any seeding approach, care must be taken to stop melting and start cooling before the seed has completely dissolved! The seeding method is useful but not widely employed because it requires more elaborate experimental arrangements.

Many different materials have been grown by flux methods. Among these are yttrium iron garnet (YIG) and yttrium aluminum garnet (YAG), both of which are complex oxides; barium titanate; sapphire; beryl (beryllium aluminum silicate); nickel oxide; bromellite (beryllium oxide); sodium niobate; periclase (magnesium oxide); yttrium vanadate; magnesium aluminate; lead zirconate; and a whole series of oxides of transition and rare-earth elements.

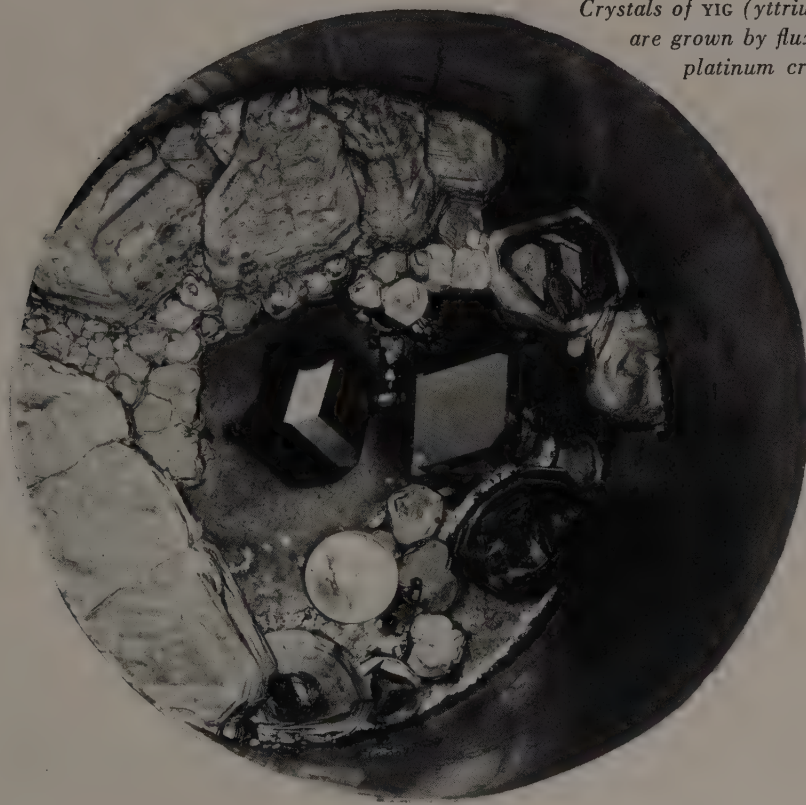
An unusual but important variation of the flux technique is growth from molten metals. Metals are familiar enough materials, but one does not ordinarily think of them as solvents for such esoteric crystals as gallium phosphide. Gallium arsenide and gallium phosphide are both grown from molten gallium. In the crystallization

of diamond (see page 43), graphite—the feed material—is dissolved in molten metal. The diamond is then precipitated from this melt under controlled conditions.

All of the techniques that have been discussed in these few pages are merely basic procedures. Every laboratory concerned with crystal growth adopts one or more of them and adds modifications to suit particular problems. It can be stated with remarkable certainty that no two materials grow in exactly the same way. Each offers its own brand of difficulties.

Once equipment has been modified, the first stage of crystal growth—the predictable, scientific part—is over. Any success now attained lies in the hands of the individual who operates the machinery, prepares the starting chemicals, adjusts the temperature and insulation, and generally mothers the apparatus. This is where wins or losses are scored in the field of crystal growth, and some people are better at it than others. They have a knack, a touch, a “feel” for the way crystals seem to grow best. They are irreplaceable, sought after by the crystal-growing companies as top professionals in their league. Their successes are responsible for much of the real progress in modern technology.

*Crystals of γIG (yttrium iron garnet)
are grown by flux methods in large
platinum crucibles.*



Man-Made

Gems

Gems have been prized for millennia. Their clarity, depth of color, hardness, and sense of permanence have fascinated man since earliest times. Jewelry or some form of personal adornment is found in the remains of the earliest human civilizations. Not surprisingly, the scarcity of natural gemstones has led to imitation. Historically, the most durable and popular simulations were made of glass.

Glass has been used for more than 4,000 years. The Egyptians used it, and Greek and Roman gold jewelry, studded with glass replicas of gemstones, can be found in any major art museum. Glass continues to be used to simulate gems, and in some cases it is an effective and attractive substitute. But glass lacks the hardness and brilliance of many natural gemstones, and man has long sought better substitute materials.

The laboratory creation of gems has been a major goal of crystal growers for about 100 years. Today, nearly all of the desirable gem minerals can be synthesized; that is, *duplicated* (not imitated) in laboratory experiments. It is likely that all gem varieties could be manufactured if sufficient demand existed to warrant the effort.

A sizable industry devoted to the manufacture of gem materials now exists. In addition, many of the crystals used for technological purposes have been found to possess attributes that are considered satisfactory for gem use. These will be discussed in a later section.

As noted earlier, it is important to distinguish between synthetic and imitation materials. A synthetic is a man-made equivalent of a naturally occurring substance. For example, synthetic ruby *is* ruby, made in the laboratory rather than by nature. In almost all of its chemical and physical properties it is virtually identical with the natural mineral. The subtle differences result from impurities in natural crystals not found in laboratory products, as well as certain characteristics inherent in laboratory-grown gems. These differences often require expert investigation to reveal. The diamonds made by the General Electric Company *are* diamonds, just as hard as the natural ones they are replacing in many industrial uses.

An imitation, on the other hand, is a material that fortuitously possesses some of the properties of a different, more costly material. Thus, glass is an imitation substitute for ruby, zircon, sapphire, and other gems. Recent diamond substitutes, such as YAC and Titania (see page 52), are unlike diamond in all but superficial appearance.



Small diamonds of high industrial quality are manufactured in large quantities today. These diamonds, the "lead" in the pencil, and the pile of graphite are all composed of the same material—carbon.

Diamond and graphite are both pure carbon. The hardness and optical properties of diamond result from the compact arrangement of the carbon atoms in its rigid, tightly bonded structure. Carbon is so insoluble that a graphite crucible can be used to melt almost anything within its temperature range (carbon volatilizes—becomes a vapor—at about $2,000^{\circ}\text{C}$.). Carbon does, however, dissolve to a small extent in molten iron. The occurrence of diamond suggests that it forms in nature under conditions of extremely high temperature and pressure. Early experiments at diamond synthesis, therefore, concentrated on crystallization from an iron solution.

Success in using this technique was reported by J. B. Hannay, a Glasgow chemist, as early as 1880; but the identity of the material produced by Hannay has been seriously questioned in recent years. Success was also reported in 1896 by Henri Moissan, a French chemist, who dissolved sugar carbon in molten iron and quickly solidified the metal by chilling. Moissan's products have been lost, so modern verification is impossible.

In the following years many tried to duplicate the early experiments, all without success, despite claims, counterclaims, and fierce arguments. By 1954 there was still no conclusive evidence that diamond had ever been produced in the laboratory. But then, in 1955, the General Electric Company announced successful diamond synthesis. Although their products were of industrial—rather than gem—quality, there was no longer any doubt that diamond could be produced in the laboratory. (Gem diamonds, extremely rare in nature as in the laboratory, must be of the finest color and degree of flawlessness.)

The key in the G.E. process was the attainment of both high temperature and high pressure ($5,000^{\circ}\text{F}$. and 1.5 million pounds per square inch). This was achieved in special heat and pressure-resistant chambers placed in a 1,000-ton press. The method produces only small crystals, but the carat yield is very high. The G.E. method now

DIAMOND



Diamonds are made in huge machines that generate high temperatures and pressures simultaneously.

supplies industrial-grade diamond for abrasive uses in prodigious quantities. Almost any source of carbon can be used to make diamonds, if the correct temperature and pressure regime can be reached.

Many laboratories have reported successful production of diamond, including companies in Sweden, the Netherlands, and Japan. Industrial-grade diamond is also manufactured by De Beers Consolidated Mines Ltd., the company that controls mining of South African diamonds. Fearing that political disturbances might cut off the natural-diamond supply, De Beers constructed a plant for diamond synthesis in Ireland. This factory has reported an annual output of 750,000 carats.

Gem diamonds are still extremely costly to produce, but a few gem crystals have been made and cut by General Electric. These are all less than one carat in weight, however, and their cost of manufacture is so high that synthetic diamond will offer no competition to the natural stones on the gem market, at least for the present.

Ruby is the most precious of gems. In large sizes it is worth more, carat for carat, than any other popular gemstone. This situation is entirely due to the scarcity of large, fine rubies. Sapphire is not nearly as valuable as ruby, but is nonetheless a desirable gem. Its mysterious deep blue color has inspired tales of romance, greed, and adventure.

RUBY AND SAPPHIRE

Both ruby and sapphire are color varieties of the mineral corundum. An inherently colorless material, corundum is composed of aluminum oxide. Red corundum has a special name: ruby. It owes its color to the presence of a minute amount of the element chromium. The blue of sapphire results from traces of titanium and iron. Actually, sapphire refers to corundum of any color except red, and sapphires can be green, yellow, brown, colorless, pink, orange, and a subtle pink-orange shade called "padparadscha," as well as blue.

Ruby is sufficiently valuable to have been worth considering as a laboratory synthesis goal. The earliest experiments reported were those of Marc Gaudin in France in the mid-19th century. Gaudin was not able to make clear, gem-quality corundum, and he stated that neither his technique nor that of anyone known to him was capable of producing gem ruby of adequate size. This was, however, the beginning of the modern history of ruby synthesis.

In the mid-1880s, rubies appeared on the gem market that were initially considered natural, but which investigation showed to be manufactured products. The original source of this material was a mystery. Some people attributed the gems to a priest in a village near Geneva, Switzerland, giving rise to the name "Geneva rubies."

These rubies were frequently sold as genuine, a situation that caused French authorities to order the return of large amounts of purchase money to customers. Throughout the last part of the 19th century, rubies appeared on the market that had apparently originated in various laboratories, though details of their manufacture are obscured by time.

Red corundum is called ruby. Man-made ruby is more transparent and free from flaws and inclusions than natural crystals.



Just after the turn of the century a type of ruby called “reconstructed” or “reconstituted” began to appear. These were claimed to have been made by fusing together bits of fine gem ruby that were too small for individual use. Reconstructed rubies were supposed to be different from Geneva rubies, since the latter were clearly manufactured products.

Recent work by Kurt Nassau (Bell Telephone Laboratories) and Robert Crowningshield (Gemological Institute of America) proves conclusively that “reconstructed” ruby was never made in the way claimed. Rather, all such material was made by an early form of flame fusion, developed before Verneuil announced his process. Laboratory investigations show clearly that fusing bits of ruby together could not have produced the gems sold as “reconstructed.” It is likely that all manufactured rubies sold before 1905 were made in this way.

The development of commercial ruby manufacturing processes by Frémy and Verneuil was discussed earlier. Frémy ruby, grown by a flux technique in large crucibles, was not of sufficient thickness and size for cutting large gems. A few small stones were cut from the material, but its chief application was in watch bearings. Occasional crystals were mounted in jewelry without cutting, but Frémy’s technique could not fill the need for a gem manufacturing method.

After Frémy’s death, Verneuil continued working on ruby synthesis, but using a different approach. His experiments involved a high-temperature torch to melt powdered aluminum oxide, giving rise to the name flame fusion for the technique. It is remarkable that modern flame-fusion furnaces do not differ substantially in design from the model described in detail by Verneuil in 1904.

Verneuil’s apparatus made commercial production of synthetic corundum practical. The technique was quickly adopted by other growers, and by 1907 millions of carats of ruby were being produced.

Although ruby is now made using other growth methods, such as flux (a revival of Frémy’s work, with substantial improvements), hydrothermal, and Czochralski techniques, gem corundum is produced almost exclusively by the Verneuil method be-



Crystals of colorless corundum (sapphire) of enormous size are routinely grown by the Czochralski method.



These boules (ruby) were grown by the Verneuil method. Crystals up to 9 inches in length can be produced routinely.

cause of the low costs involved. One laboratory makes hydrothermal ruby of fine color, but the costs of manufacture elevate the price of cut gems substantially above Verneuil-grown gemstones.

In Verneuil work, the gases burned to create the high temperature torch flame, as well as the feed powder, must be of exceptionally high purity. The feed powder is snow-white aluminum oxide (alumina). To make ruby, about 8 percent chromic oxide is added, the mixture is heated, and the powder is then sprinkled through the torch flame (the melting point of alumina is about 2,050°C.) by tapping the feed-powder hopper at regular intervals. The powder melts in the flame and falls on a ceramic rod located in a cooler part of the furnace.

If nothing is added to the alumina powder, the boule grown is clear and colorless—synthetic “white” sapphire. Crystals of this type are made in huge quantities for colorless gemstones and for the bearings in electric meters.

Many colors of sapphire can be produced, however, by adding suitable oxides to the alumina feed powder. The initial experiments in making blue sapphire in 1907 failed because the true cause of the color in natural sapphire was still in doubt. Addition of cobalt produced a patchy blue color that did not really resemble the fine “corn-flower” blue of top quality sapphire. Addition of magnesium oxide eliminated the patchiness, but the resulting color did not match any color of natural sapphire. Careful study of these boules, however, showed that they had the characteristics of spinel, a happy accident that led to commercial spinel production more than twenty years later.

Investigations finally revealed that iron and titanium were the coloring elements of natural blue sapphire, and synthetics bearing the right hue finally appeared in 1910. A table listing the colors of transparent synthetic corundum and manufacturers’ trade names for these colors is reproduced here from Webster.*

* Webster, Robert. *Gems—Their Sources, Description, Identification*. London: Butterworths, 1970.



Hydrothermally grown ruby (Kashan Laboratories) has excellent color and optical properties, suitable for gem use.

COLORS OF TRANSPARENT SYNTHETIC CORUNDUM

<i>Color</i>	<i>Trade name</i>	<i>Color</i>	<i>Trade name</i>
Colorless	White sapphire	Yellow-brown	Madeira topaz
Red	Ruby	Brown	Palmeira topaz
Dark Red	Garnet color	Green	Green sapphire
Deep Pink	Pink sapphire	Pale green	Amaryl
Lilac-pink	Rose de France	Blue	Burma sapphire
Orange	Padparadscha	Purple	Amethyst
Deep yellow	Danburite	Purple-green	Alexandrite
Yellow	Topaz		

It is now possible to grow sapphires and rubies that exhibit stars of exceptional brilliance. This is done by adding 0.1 to 0.3 percent of titanium oxide to the alumina feed powder in a Verneuil furnace. Heating the resultant boules at 1,100°C. causes precipitation within the corundum of fine needles of the mineral rutile. The rutile

crystals are oriented along the crystallographic axes of corundum (directions within the crystal that define the internal symmetry of the crystal structure). Since corundum is a hexagonal mineral (displays six-fold symmetry), the rutile needles also display six-fold orientation and produce a six-rayed star.

The color of synthetic ruby and sapphire matches that of the finest natural stones. In addition, the evenness of color and transparency of the synthetic material are superior to all but the finest and rarest natural corundum. Happily, it is possible to differentiate the synthetics on the basis of characteristic growth features and inclusions, or imperfections.

All Verneuil boules contain curved growth lines, visible under the microscope when correctly illuminated. These lines are formed by the buildup of layers in boule growth. Natural corundums never show curved growth lines, nor do any other natural gems, so these lines are a sure indication of the synthetic origin of a stone. The lines frequently resemble the grooves on a phonograph record.

In addition to these curved striae, synthetic gems contain characteristic round or tadpole-shaped bubbles; such bubbles are positive diagnostics of synthetic origin. Other tests normally used to identify gems are not helpful, since synthetic corundum is identical, in most optical and chemical respects, to the natural material.

A synthetic corundum showing a color change (reddish in incandescent light, bluish-purple in sunlight) has been marketed as synthetic alexandrite. True alexandrite is a completely different gemstone, however, with a distinctly stronger color change.

The first synthetic spinel was produced accidentally by the addition of magnesium oxide to the alumina feed powder in Verneuil corundum manufacture. Spinel, however (except for the red variety), is not a valuable gemstone, and the new synthetic did not enjoy commercial success until more than twenty years after its discovery. Red spinel, known as "ruby spinel," does indeed often display the fine "pigeon's-blood" color of fine ruby. A classic case of mistaken identity is the large red stone in the Black Prince's Crown (British Crown Jewels), long thought to be a superb ruby. Modern gemological analysis revealed it to be a large, fine ruby spinel!

Although it is not very desirable as a gemstone on its own merits, spinel has found wide acceptance as an imitation of other important gems, such as zircon, emerald, aquamarine, and tourmaline. Spinel can be made in a wide range of colors, depending on the impurity added: manganese (yellow and green), chromium (dark green), iron (pink), and cobalt (blue shades). Red spinels are also made, as well as a type showing a color change designed to imitate alexandrite, one of the rarest of all gems. Spinel powder mixed with cobalt oxide and fused in an electric furnace produces a dense, deep blue material that strongly resembles lapis lazuli, a biblical stone of moderate to high value.

SPINEL



Gem-quality spinel crystals of many hues are grown by the Verneuil method.

COLORS OF SYNTHETIC SPINEL (Webster, 1970)

<i>Color</i>	<i>Trade name</i>	<i>Color</i>	<i>Trade Name</i>
Colorless	Synthetic white spinel	Dark green	Tourmaline green
Blue	Hope sapphire	Yellow green	Peridot
Bright blue	Azurite	Pink	Synthetic pink spinel
Green-blue	Blue zircon	Red	Synthetic red spinel
Pale blue	Aquamarine	Green-red	Alexandrite
Yellowish-green	Brazilian emerald		

QUARTZ Natural quartz is common and very inexpensive, so it is surprising to find that synthetic quartz could have value as a gem material. Nonetheless, the value of the finest citrine (yellow to amber-colored quartz, sometimes called “Madeira topaz”) and amethyst is high enough, and the cost of manufacture low enough, for commercial synthesis of colored quartz to be worthwhile.

Citrine is made by the addition of iron as an impurity, combined with careful control of the growth process. Such additives are called *dopants*; the process is known as doping.

Man-made quartz can be colored by adding suitable impurities. Several colored varieties are popular gem materials.



Amethyst is made by specially doping quartz crystals with specific impurities that do not produce a visible color.

But irradiation of such specially doped quartz brings out the amethystine color, and some very dark and fine gem material has been made in this way. The process of amethyst manufacture is significant because the cause of coloration in natural amethyst has long been a question in the minds of geologists. It is likely that natural amethyst obtains its color through natural irradiation (exposure to radioactive minerals), by analogy with the laboratory process. This observation is a good example of how laboratory experiments can shed light on otherwise mysterious natural events.

Quartz grown in hydrothermal autoclaves (essentially, high-temperature pressure cookers) is as good as the finest natural quartz. In addition, the growth process is similar to that which occurs in nature. Synthetic quartz, therefore, displays color zoning and inclusions similar to those of the natural material.

The mineral beryl (beryllium aluminum silicate) occurs in many colors in nature. Five of these have been given special gem names: morganite (pink), goshenite (colorless), heliodor (yellow or golden beryl), aquamarine (blue), and emerald (green). Of these, only emerald has sufficient value to warrant serious efforts at laboratory growth.

BERYL

Such experiments began as early as 1848, but not until 1912 was synthesis of carat-sized emerald reported. Nacken, who was responsible for the prototype quartz synthesis process, grew tiny emeralds up to about two-fifths of an inch long and one-tenth of an inch wide, using a process similar to the hydrothermal technique followed for quartz.

Experimentation continued in Germany, and in 1934 emerald crystals were successfully produced by the I. G. Farbenindustrie conglomerate. These emeralds, called Igmerald, were true synthetic emerald of fine color and clarity.

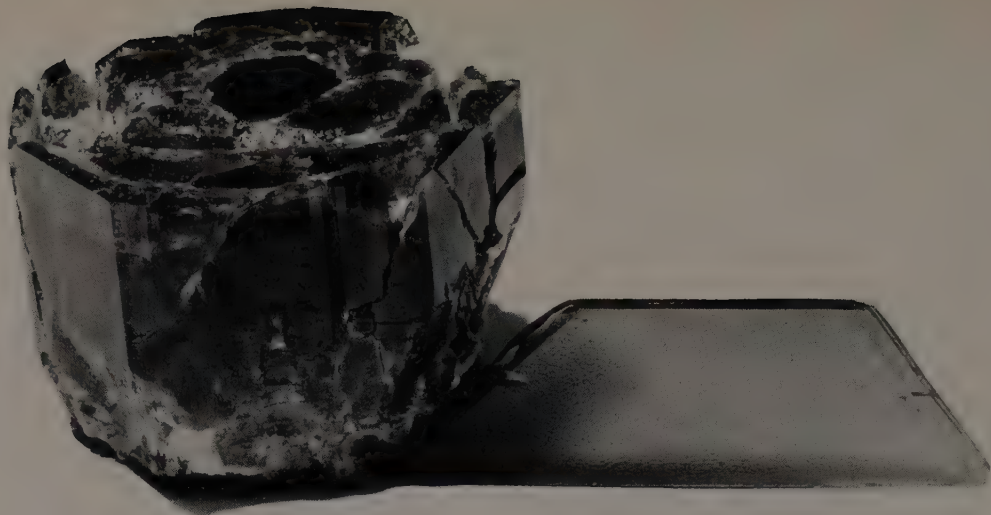
Carroll Chatham of San Francisco began experimenting with emerald synthesis before 1930, and his technique is capable of producing single crystals several inches in maximum dimension. Chatham's process is not patented, but is a closely guarded secret. It is believed that both the Chatham process and the Igmerald process are melt-diffusion techniques.

Synthetic emeralds are among the finest of man's efforts to duplicate nature's art. They do not contain curved growth lines, or Verneuil-type bubbles. They do, in fact, contain inclusions that strongly resemble those found in natural gemstones. The major distinguishing features are density (natural emeralds are noticeably heavier) and refractive index (the degree to which light is bent in a material).

Emerald has been produced more recently by Zerfass (in Germany) and Pierre Gilson (in France). Both men appear to use flux methods, and the Gilson crystals are sometimes more than an inch long and of superb color and transparency.

Emerald has also been produced by the Union Carbide Corporation, the firm re-

Emerald can be synthesized in a quality surpassing that of most natural crystals. The large crystal was grown by Carroll Chatham of San Francisco; the thin, transparent crystal by the Union Carbide Corporation.



sponsible for star sapphire and ruby production. These emeralds are grown hydrothermally, using seed plates of pale or colorless beryl. The crystals are grown to suitable thickness, the seed plates cut out, and the remaining material fashioned into gemstones. There is a great deal of advanced technology involved in growing reasonably thick crystals in this way.

In addition, a major ingredient of emerald, beryllium, is a highly toxic material. Extreme safety precautions have to be used in handling the feed chemicals and in monitoring growth processes. Such safety measures are very expensive. Manufacturing costs have thus limited the output of hydrothermal emerald.

A variation on emerald synthesis involves simply coating a plate of poor-color beryl with a thin layer of emerald. Such gems, produced by J. Lechleitner in 1960, are made by starting with a faceted gemstone and subjecting it to hydrothermal treatment. The color of the outer layer then appears to be the color of the entire stone. The only way to detect the true origin of the gem is by careful investigation along the edges, where a network of fine cracks can be seen. In some cases it is possible to see the layered effect of hydrothermal deposition.

Synthetic emerald brings high prices in spite of its laboratory origin. In most cases synthetic gems are finer in color and transparency than any but the highest quality natural emerald. This fabulous gemstone, one of those considered most desirable by man for centuries, is now within the reach of almost anyone's budget.

OTHER GEMS

The mineral rutile, titanium oxide, occurs in nature as red, brown, or black, elongated or chunky-looking crystals. It is nearly always opaque and gems cut from natural crystals are extremely rare, and always very dark. In 1948 synthetic rutile appeared on the market. Cut gems, fashioned from Verneuil-grown boules, were colorless, pale yellow, yellow, orange, red, and blue. Sold as "Titania," the material was one of the first diamond imitations to have internal flashes of color ("fire") resembling those of a diamond. The fire is caused by a phenomenon known as *dispersion*, the ability of a material to break up white light and separate it into its component colors.

The dispersion of Titania is, in fact, six times higher than that of diamond, giving cut gems an almost unbelievable saturation of dazzling colors. The effect is breathtak-

ing, but unnatural in the sense that no diamond ever produced such pyrotechnic brilliance. In addition, the hardness of Titania is just below that of quartz, or many times less than that of diamond. The stones have thus never been considered suitable for rings, where a durable gem is required.

Imitation diamond is made not only from synthetic rutile, but from such materials as synthetic sapphire and spinel, strontium titanate, YAG, and yttrium aluminate. Trade names for these imitation diamonds are listed in the appendix.

Many other crystals have been grown in the laboratory that are counterparts of natural minerals, but so far none of these have been cut commercially as gems. This picture may change in the years to come.



This gem of synthetic rutile blazes with myriad colors. A similar material, strontium titanate, displays almost as much fiery brilliance. Gems such as the Wellington Counterfeit Diamond (strontium titanate) are among the most effective diamond imitations.

Transistors,

Lasers,

and

Bubbles

Breakthroughs and major advances in science occur only after sufficient background knowledge has been acquired. Great strides in areas of technology do not occur without advances in many other, sometimes apparently unrelated, disciplines. Interchange of ideas among scientists and engineers leads to fruitful collaboration, and sometimes to startling new discoveries.

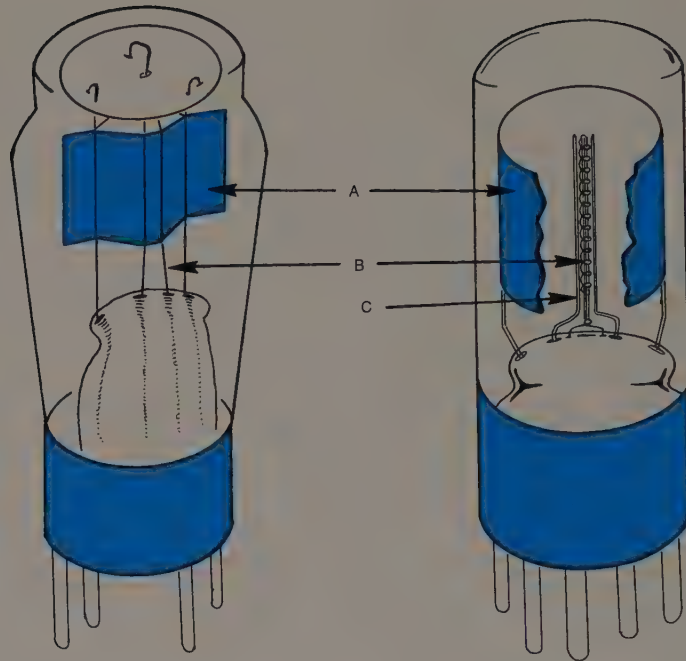
The most significant technological events of the 20th century have been in the fields of electronics and optics. The single most revolutionary device invented in the last fifty years is the transistor. More recently, considerable attention and publicity have been accorded the laser. Equally exciting to scientists is the potential afforded by the development of "bubble technology," a study of phenomena observed in certain types of magnetic materials.

Single crystals are essential in all these technologies. Without the ability to grow perfect crystals of such esoteric substances as silicon, germanium, and YIC, the technological progress seen in recent decades would not have been possible. It is also evident that future developments in electronics and optics will depend on the successes of crystal growers. The demand for more and more new crystals has already exceeded all expectations. Our society has reached the point where major scientific achievements no longer occur at a steady rate; technology is advancing exponentially, with no end in sight.



The laser is one of the most revolutionary inventions of the 20th century.

TRANSISTORS



The diode (left) and triode (right) tubes have been supplanted by solid-state devices. Both the diode and triode contain a plate (A) and a filament (B). The triode contains an additional element, the grid (C), and the very name tri-ode implies a three-element tube.

The electronic age began in the early part of the 20th century. A key development was the invention of the *triode* electron tube by Lee De Forest in 1907. Previous tubes, called *diodes*, consisted of two components (a filament and an *anode*, or positively charged plate) inside an evacuated glass bulb. De Forest's triode contained a third element, a piece of wire mesh called a *grid*, located between the filament and the anode.

The triode was a major advance because this tube could act as an amplifier of electric current. Triode amplifiers made possible the improvement of radios and switches in special types of circuits. Radios for home use, all containing vacuum tubes, were soon to be found in almost every city in the United States.

But vacuum tubes have several disadvantages. They are relatively large, easy to break, and generate a lot of unwanted heat. The heat, produced as current passes through the filament, destroys much of the efficiency of the tube. In addition, the tube has to be made large to avoid damage to the glass envelope, and tubes have to be spaced relatively far apart in an electric device for cooling purposes. In spite of these drawbacks, electron tubes of advanced design (containing 4, 5, 6, and more elements) were responsible for considerable progress in radio and communications equipment during the 1930s and 1940s.

In 1948 Bell Telephone Laboratories announced a breakthrough in the development of small, compact, and efficient power amplification and transmission devices. A group headed by William Shockley had been working with crystals of silicon and germanium, investigating the flow of electrons (the small particles that make up an electric current)

in crystalline materials. This research led to the invention of very small electronic amplifiers called *solid state*—that is, they incorporated bits of single crystals. A paper published by W. H. Brattain and John Bardeen in 1948, entitled “The Transistor,” was expanded the following year in an account by Shockley. The transistor age was born—and a modern era in electronics was launched.

Transistors were the logical outcome of work with materials called *semiconductors*. A conductor is a material that allows the passage of electricity with relative ease; examples are copper, aluminum, and gold. A nonconductor blocks the flow of an electric current; examples are rubber and plastics. A semiconductor is a very poor conductor of electricity, its conductivity depending on temperature and the presence of specific types of impurities. A semiconductor whose resistance to electricity decreases as temperature increases is called *intrinsic*. An *extrinsic* semiconductor has similar electrical properties, but is produced by doping certain types of materials; that is, by adding impurities in small and carefully controlled amounts.

The amount of current that can pass through a bit of semiconductor material is extremely sensitive to such factors as voltage (one can think of voltage as a kind of “pressure” that forces electrons along a path).

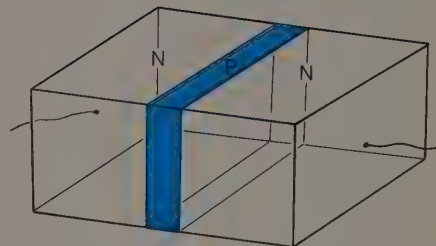
By sandwiching together slices of two different types of semiconductor materials, scientists created the *semiconductor diode*. Such a device is capable of *rectification*—converting AC (alternating current, as is tapped in a wall outlet) to DC (direct current, such as comes from a flashlight battery). The advantage of the semiconductor device is small size and no generation of heat.

A more elaborate sandwich was then tried, using three slices of two different types of semiconductor materials (thus producing A-B-A and B-A-B composites). These devices were capable of tremendously amplifying electron currents, the same job done by the bulky and inconvenient triode tubes. It was this three-layer sandwich that was dubbed the *transistor*. As with the diode rectifier, it was very small, efficient, and produced no heat. It could take mechanical vibration and shock (unlike tubes), its lifetime was rather long, and it was less sensitive to fluctuations in temperature than were electron tubes. Transistors provided the key to shrinking the size and extending the life of all electronic devices.

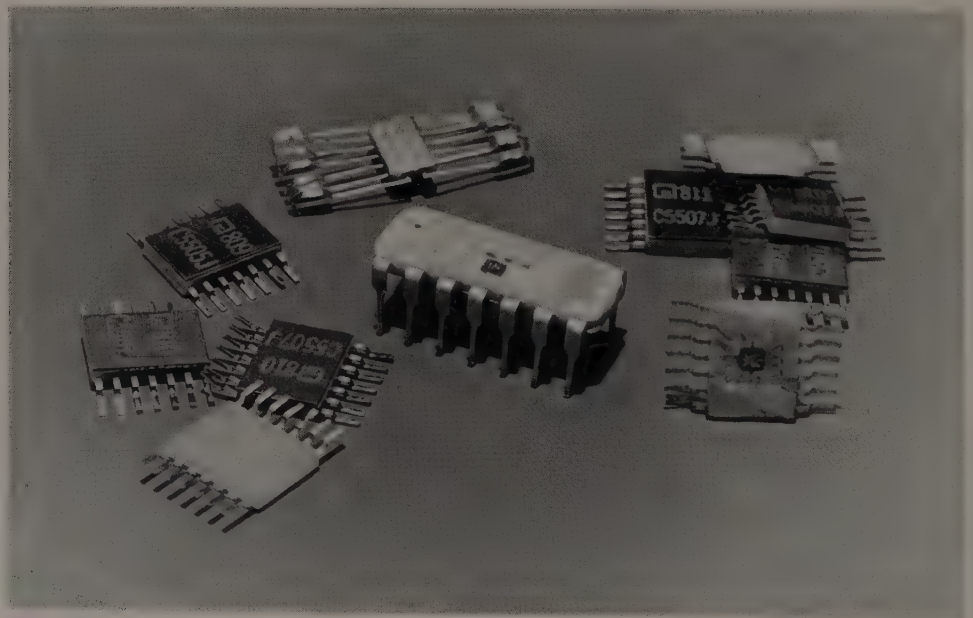
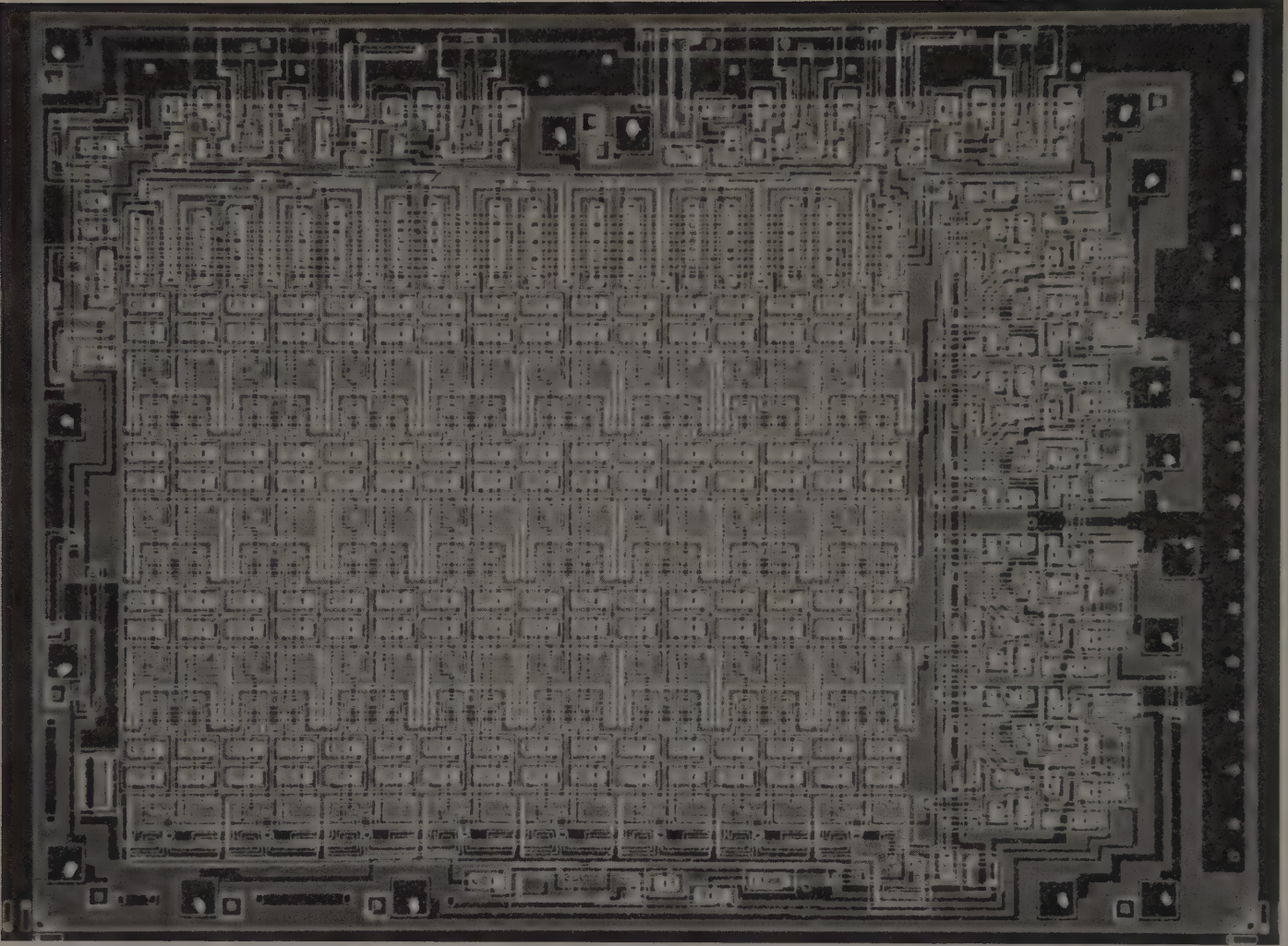
Making a transistor requires extremely pure single crystals, and crystal growers went to work to perfect ways of producing such crystals in large volume. The major development of transistors involved the element germanium, but silicon was later found to have more desirable properties. Germanium is now gradually being phased out as a major material of the electronics industry.

Silicon technology led to the invention of ways of further miniaturizing solid-state devices. Transistors had previously been made and soldered to circuit boards along with other components, such as resistors, capacitors, and switches. Why not “grow” all the components and interconnections on a single slice of crystal material? This would eliminate the need for wires, soldering, and the manufacture of individual parts.

Such a feat of engineering took years to accomplish, but is now an industrial fact. Chips of single crystals that contain transistors, diodes, resistors, and other components



A transistor consists of three adjoining layers of a material such as silicon. Alternating layers contain different types of impurities that give different semiconducting characteristics. These are referred to as “n-type” and “p-type” semiconductors. The transistor performs the same functions as older and bulkier vacuum tubes.



Integrated circuits come in a wide variety of shapes and packages.

Modern integrated circuits are extremely complex and contain many electronic components, all on a tiny piece of semiconducting material. The area shown is about $\frac{1}{2} \times \frac{1}{2}$ inch.

are called *integrated circuits*. The technology that produces them borders on science fiction. These minute crystal chips are revolutionizing our way of life.

In making an integrated circuit, a single crystal of silicon is sliced into wafers a fraction of an inch thick. The wafers are then polished and subjected to a detailed photographic procedure. This "images" the desired circuits onto a photosensitive layer deposited on the wafers. The imaging technique resembles a microscope in reverse, so the final circuits are almost invisible to the naked eye!

Next, the photosensitive coating is etched away, and the wafers are put through a very complex series of etching and vapor-deposition steps. (Vapor deposition is a way of coating an object with a thin layer of a specific material, with exact control of the thickness of the coating and its composition.) These deposition and etching steps create the transistors and other components in the wafers according to the original circuit design. The astonishing thing about such circuits is their incredibly small size. A device containing several dozen transistors, diodes, and other components can go easily through the eye of a needle!

THE 'MIRACLES' OF INTEGRATED CIRCUITS

Integrated circuits are the most vital ingredients in modern electronics manufacture. They are responsible for most of the developments in miniaturization and sophistication in all areas of electronics application. We may examine this progress in terms of individual aspects of society and its functioning.

Communications: Much of the impetus for research in electronics for communications has come from Bell Telephone Laboratories. Early communication was by word of mouth or written letter only. Then, in 1876, came the telephone, an electromechanical device (containing both electrical and mechanical components). The triode opened the way for electronic communications, such as radio and television. But the telephone is still a primary communications vehicle in our society.

A need has always existed for better telephone switching facilities. The newest accomplishment in this area is ESS, the electronic switching system. This system is linked to a large computer, and automatically chooses the right path for a call after recognizing the number dialed. Telephone switching systems must be able to handle millions of new phones in years to come, and improvements are being made continually.

Microelectronics were developed primarily by the armed forces, but found popular domestic use in such items as the television sets built with integrated circuits (ICs) that appeared on the market in 1966. The solid-state circuits in these units are many times more reliable than older equivalents.

Integrated circuits will make possible advanced devices such as wrist radios, TV sets that will fit inside a woman's pocketbook, radios the size of earplugs that can actually be inserted in the ear rather than carried in the hand, portable telephones,



telephone switching systems are extremely complex. Solid-state equipment, such as that shown, is currently being installed to replace older, less efficient systems. Ultimately, laser communication devices may replace even the most sophisticated electronic networks.

picture-phones in every home, and remote telephones for automobiles.

Solid-state technology has made possible such things as communications satellites that are many times cheaper than telephone cables and offer more reliable service. Every time you make a telephone call, watch a TV show, listen to a radio, or reserve an airline ticket you are reaping the benefits of solid-state technology.

Computers: There were about 700 computers in the United States in 1955 and about 22,000 by 1964. Today there are many times this number in use and the figure is growing rapidly. The first electronic computer was developed at the Massachusetts Institute of Technology and called ENIAC. It contained about 19,000 vacuum tubes, some of which would burn out every few days. This computer completely filled a large room, and the cost of the electricity to run it was enormous. Early computer memories required 10,000 to 20,000 watts of power, enough to run a small factory. Today's miniaturized wonders operate on 60 watts, about the same as a small light bulb!

With integrated circuitry, computers have truly come of age. Modern high-speed machines are capable of handling calculations in billionths of a second. Engineers found that the only way to appreciably shorten calculation times was simply to reduce the length of electric circuitry that electrons had to travel. This was done by compressing and miniaturizing the circuits themselves, with a technique known as *large-scale integration* (LSI).

There is not a sector of the American economy that is not dependent on computers in some way. Check and credit-card processing and all bank accounting, as well as stock transactions, and even retail purchases in some large stores are computer-controlled. All forms of transportation depend on computers, and even monitoring of rail freight is now computerized in many places. Library retrieval would be a nightmare job if it were not for the rapid searching capabilities of high-speed computers.

In industry, mass production techniques are supervised by small computers, and many installations (such as power-generating stations) are automated. Telephone switching, as mentioned previously, is computer-run. Scientists and engineers rely on computers for solutions to problems that could not even be attempted if computers did not exist!

The space program and all related research is tied to computing power. Only the availability of very large machines made it possible to put a man on the moon. The calculations involved just in putting a spaceship in orbit are so complex that humans could not attempt them in reasonable time, let alone the split seconds required when the ship is actually on its way into space. In the future, computers will be used extensively in teaching children via programmed instruction. The day is not far off when every housewife will rely on a small computer to handle the shopping and even to run the more routine household chores.

Medicine: Major advances in medical knowledge have been achieved through the use of miniaturized devices designed to be implanted in the body. The field of *implant*

Crystals are used extensively in medical technology. This instrument uses sodium iodide detector crystals to evaluate the condition of a patient's lungs. The magnetic tape unit and control box contain solid-state electronic components.



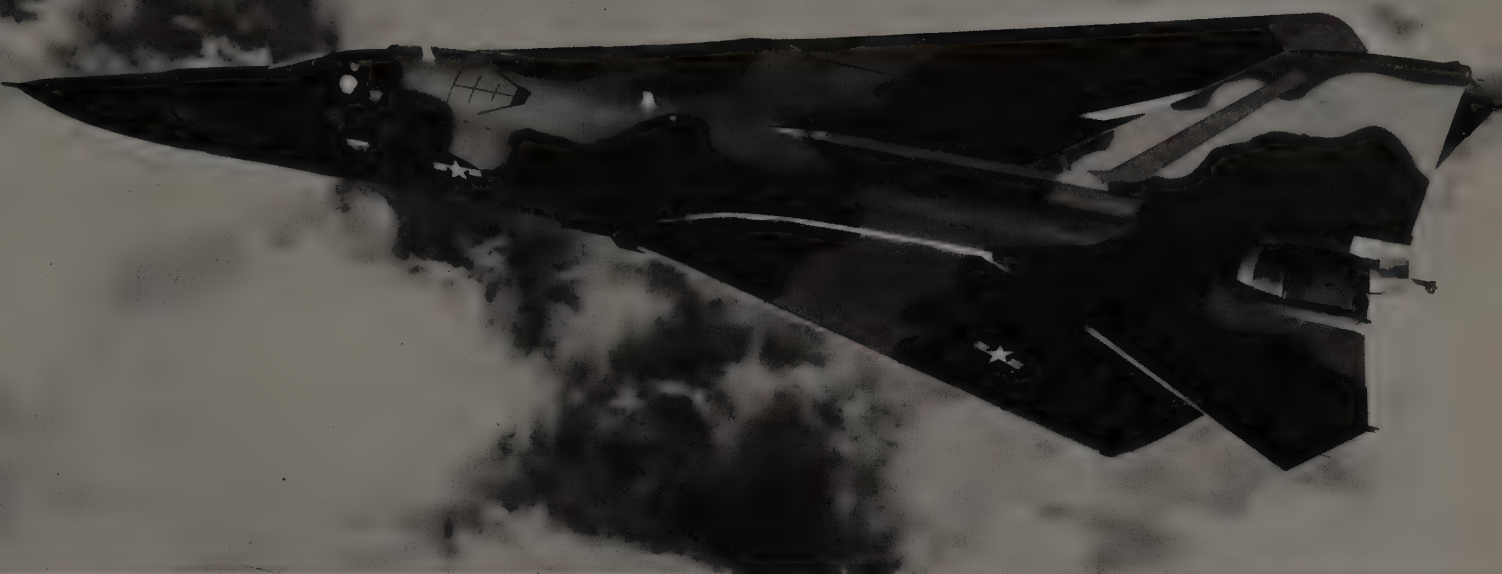
biotelemetry involves tiny radio transmitters that are swallowed or surgically embedded in tissues. They monitor key body functions and report to control units with vital diagnostic information.

Pill-sized transmitters have been used successfully to predict disturbances of the stomach and intestines. Electrocardiography (study of heart function) uses tiny sensing devices taped to various parts of the body to detect faint electric signals, and thus provide information about the state of a person's heart. Artificial limbs will be made realistic and much more useful through miniaturized electronic controls.

In hospitals and wards, portable electronic diagnosis and treatment units will save lives daily; computers will help diagnose disease and prescribe treatment. Remote sensing stations will interpret and evaluate data supplied by radio devices that monitor vital functions on all patients. The efficiency of the doctor will be vastly enhanced.

Transportation: Automobile manufacturers are already turning to solid-state devices for improved reliability and performance in such products as car ignition systems. High-speed railroad trains will rely on advanced electronic devices to maintain safety conditions at speeds up to 200 mph. Airline traffic could not be handled safely, even today, if it were not for extremely sophisticated control devices. Radar is a critical necessity at airports, and advanced electronic flight systems will make possible landings even in "zero-visibility" weather conditions. Flight instruments are made with solid-state circuits, as is most of the electronic equipment in both airplanes and traffic-control towers.

Automobile traffic control will someday be run by computers linked to traffic-light systems and even to automobiles themselves. Radar in cars and highway strips will



regulate distances between automobiles, supervise lane changes, and even guide cars to preset destinations automatically. Such systems are far from dreams—they are being developed today in many laboratories.

Transistor sales were practically nil in 1952, about \$37 million in 1958, more than \$300 million in 1968, and are nearing a billion dollars in the decade of the 1970s. The transistor and its descendants are so vital to modern industry that without them almost all factories and scientific establishments would shut down. There would be no communications, no transportation, and no economic functions (banks, credit card purchasing, stock transactions) left in operation. We cannot reverse the trend of progress. Our society is fully transistorized, and thus able to embark on paths of research and advancement unknown in previous history.

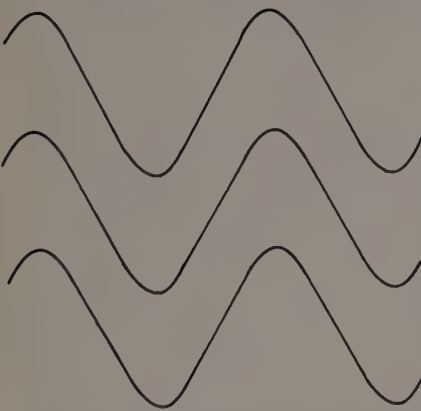
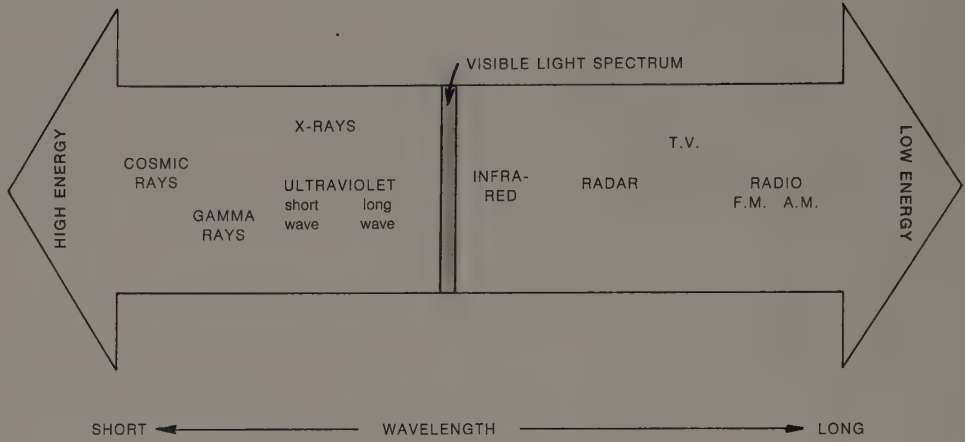
Transportation systems of the present and the future will rely heavily on solid-state electronic components.

Television and FM radio are transmitted via carrier waves with very high frequencies (100 million cycles per second, abbreviated 100 MHz). Very little of the energy transmitted by these waves is reflected by the atmosphere. Consequently, FM and TV broadcasting utilizes very tall aerials in order to cover as wide an area as possible with direct (line of sight) beams.

Radar signals travel as waves that are much shorter than FM or TV carrier waves. These waves, called *microwaves*, also travel in straight lines and penetrate the atmosphere very readily. In 1951 E. M. Purcell and R. V. Pound published a report of their investigations on the production of microwave radiation. They suggested it

LASERS AND MASERS

The electromagnetic spectrum consists of all the different types of radiation that exist in the universe. These types of radiation are distinguished on the basis of wavelength. Cosmic rays are the shortest and radio waves among the longest waves that man has measured.



The waves making up a beam of laser light are "in phase;" that is, the crests and troughs of all waves in the beam match up with each other. This characteristic makes laser light "coherent."

might be possible to devise an efficient mechanism for producing a powerful beam of such radiation by creating a self-amplifying chain reaction within the emitter material.

In the mid-1950s, Charles Townes reported the construction and operation of such a device, which he called a MASER (acronym for *Microwave Amplification by Stimulated Emission of Radiation*). Masers are capable of producing intense, highly directional beams of high-frequency microwaves that have proved most useful in radio astronomy, communications with satellites, and space probes.

The principle of the maser, however, is a general one and can be applied to other regions of the electromagnetic spectrum. All forms of radiant energy, including light, heat, ultraviolet, radio waves, and x-rays belong to different portions of this spectrum.

In 1960 T. H. Maiman of the Hughes Aircraft Company described the operation and construction of an optical maser, appropriately dubbed the LASER (*Light Amplification by Stimulated Emission of Radiation*).

Maiman's laser used a rod of synthetic ruby and emitted an intense beam of red light. The light produced by a laser is *monochromatic*—that is, composed essentially of one wavelength. Wavelength differentiates parts of the electromagnetic spectrum. Different colors of light, for example, have different wavelengths. Monochromatic light tends to be highly *collimated* (does not diverge much with distance from the source), and laser light is also *coherent*. This means that its waves are not only all one wavelength, but are also *in phase*. Waves that are in phase are essentially superimposed with coincidence of similar portions of the waves, resulting in *amplification*.

LASER APPLICATIONS

Because of its coherence and monochromaticity, laser light has found many applications. Laser beams are straight and can be used to align pipeline to an accuracy of

1 inch in 15 miles. The Stanford Linear Accelerator (for research in particle physics) was aligned by lasers to an accuracy of about one-fiftieth of an inch in a mile.

Lasers are used to measure the height of ocean waves; this information is needed in offshore drilling for petroleum. In a similar fashion, laser beams can be used for measuring terrain profiles. A laser in an airplane flying at 10,000 feet can detect the difference in elevation between a street and the adjacent sidewalk!

A laser gyroscope is being developed that will be ten times more accurate than conventional mechanical gyroscopes, as well as immune to gravity and acceleration forces, and less expensive than spinning-wheel devices.

Laser radar is in active use for extremely accurate distance measurements. A so-called "laser yardstick" will allow measurement of the speed of light with an accuracy never before possible. Similar applications have already provided new standards for length.

Laser beams can be focused to very small pinpoints that contain the *full energy* of the light beam. This feature has led to a wide range of applications, such as eye surgery. The intense heat generated by a focused laser beam is capable of welding a detached retina, or burning away tumors on the retina of an eye. The beam passes through the lens of the eye without damaging it and can be precisely positioned at the desired spot.

Larger and more powerful lasers are used for welding metals and for cutting fine wires in complex circuits. Focused laser beams can drill holes in steel or even in diamond. This greatly reduces the cost of making diamond dies for drawing thin metal wires, and the laser can even burn out tiny carbon inclusions in diamonds that detract from the value of cut gems.

Laser cloth cutters have a tolerance of 5-thousandths of an inch—the thickness of a single thread. Garments made this way can be guaranteed to have a "perfect fit." High-power lasers are used to cut holes in ship hulls, drastically reducing the costs of shipbuilding and reducing the time of construction by many days. Yet laser action can be finely enough controlled to burn clean holes in rubber nipples for baby bottles. The process is fast and sanitary.

Laser ranging devices may ultimately allow prediction of earthquakes, by accurately mapping the positions of features in fault zones in the Earth's crust. Shifting of these faults is associated with earthquake activity. Night surveying is now possible because of the small divergence of the laser beam. A typical gas laser has a divergence factor of 1 part in 2,000. The unfocused beam would thus spread out to a diameter of about 12 inches, at a distance of 2,000 feet. But the beam can be focused to a much smaller diameter than this. The beam of the helium-neon laser is visible in daylight, although the total output of the laser is equivalent to that of a small flashlight!

A major use of lasers is and will continue to be in the field of communications. Radio channels are very crowded today because every transmitter is assigned specific frequencies and there are not many frequencies left open that can be handled by existing receiving and transmitting equipment. The laser opens up a new range of



A laser in action. Lasers are currently used in many applications, ranging from eye surgery to cutting and welding, aligning tunnels, and measuring pollution.

frequencies equivalent to 10 million TV channels! The wide range of frequencies in laser emission capabilities would allow a single laser beam to carry all the communications now borne by telephone lines between the west and east coasts of the United States.

This staggering fact depends on a principle called *modulation*. Every communications device uses modulation to carry information. The most primitive example is the measured beat of a jungle drum, and more sophisticated examples would include Morse code. A modulator impresses such coded information onto a carrier signal. In AM radio transmission, the modulation is in the form of changes in the amplitude (strength) of the signal over a pre-assigned range. In FM transmission, the frequency of the carrier wave is varied. The range of channels available depends on the range of frequencies available and the effectiveness of modulator devices.

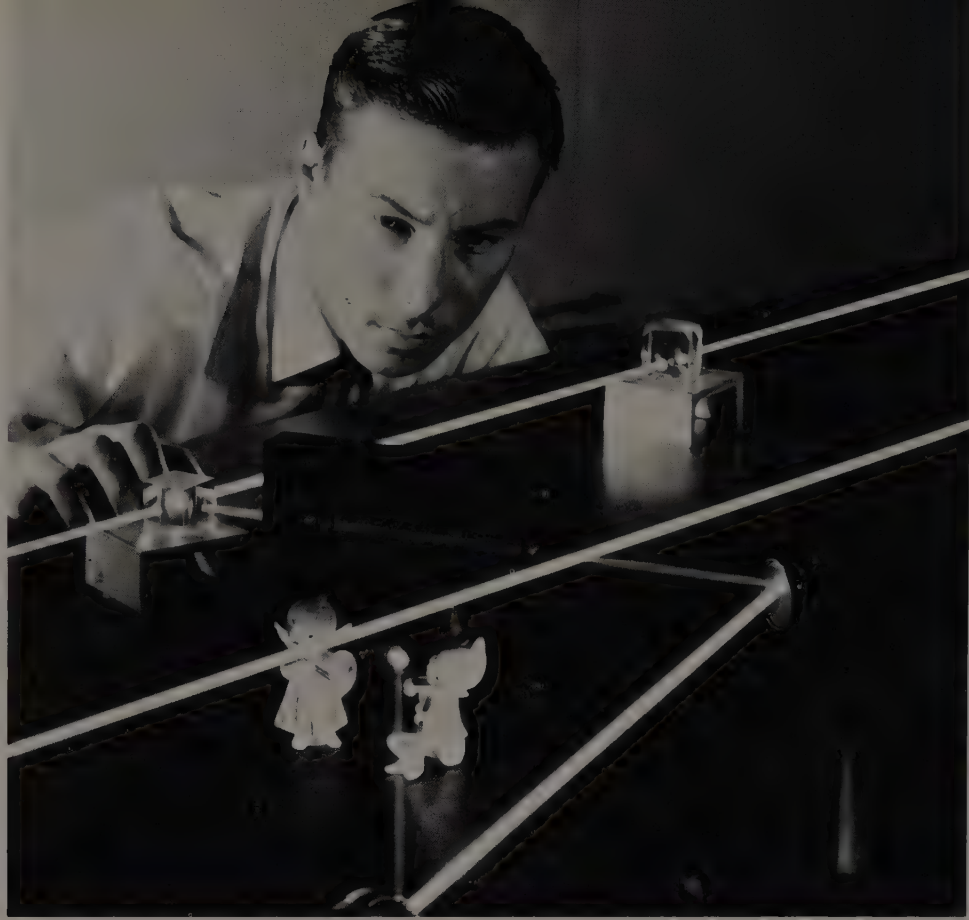
The potential of the laser is in the enormous range of frequencies laser beams can carry, and in the speed of laser modulators. Such modulators are crystal devices, some of them quite sophisticated, and both laser transmitters and modulators are being actively developed in various laboratories. Demonstration TV transmission laser systems have already been constructed. Further refinements will make such systems a practical reality.

The high power of focused laser beams may ultimately provide the key to the generation of limitless power on Earth, through hydrogen fusion. This is the process that occurs on the sun (and other stars) for conversion of matter into energy. The fuel is hydrogen, present in the oceans of the Earth in almost limitless quantities. The obstacle in controlled fusion is in actually starting the fusion reaction. This requires extremely high temperatures in a confined space, generated in extremely short times. The laser can provide such conditions. A bank of high-power lasers, all focused at the same spot, could generate a temperature of 50 million degrees in a billionth of a second. Such lasers are now being developed and will doubtless be available within a few decades.

A much-publicized use for lasers is in *holography*, a technique for recording three-dimensional images on ordinary photographic materials. An object is photographed in laser light in a carefully arranged way. The resulting photo, or *hologram*, can then be viewed in light of the same frequency as that which exposed the photograph. When this is done, the viewer sees a three-dimensional image of the photographed object that appears to float in space behind the hologram. Rotating the hologram causes the image to rotate, so that it can be viewed from all sides as if the object were actually present.

In addition to their dimensional qualities, holograms have potential as information-storage devices. A single piece of photosensitive material can store many holograms by simply rotating and exposing it in different orientations. A 2x2-inch piece of film can thus store thousands of page images. Holographic storage will be useful in library information retrieval and in high-speed computer processing. Computer applications will involve the "writing" and "erasing" of information on the same photosensitive medium thousands of times. Such systems have already been developed and tested.

Holography is a means of storing and reproducing three-dimensional images without the use of a lens. A Hughes Aircraft Company scientist is shown recording a hologram of some small figurines.



Laser beams carry information because they are modulated (systematically varied) by means of sophisticated crystal devices. Very high information-transmission rates are possible, and laser beams may one day carry voice, television, and data channels simultaneously. Continuous wave operation of a ruby laser is demonstrated above.



LASER DESIGN

Although lasers can be made that operate with glass, gases, and even liquids, the original laser and many current devices use crystals. In design, the laser is basically simple. Its heart is a crystal rod, polished perfectly flat at both ends, and surrounded by a coiled lamp called a *flash tube*. Current sent through the flash tube produces an intense burst of light. With a ruby laser, the flash tube is chosen to emit green light, which is strongly absorbed by the red laser rod. The flash tube light excites atoms in the rod, causing them to *fluoresce*. (Fluorescence is the "glow" of some paints and coatings when struck by ultraviolet light or other energy sources. Fluorescent *phosphors*—materials that emit light when properly stimulated—are responsible for the bright image on a TV screen and the light produced in a fluorescent lamp.)

In a laser, this fluorescent light travels within the rod and excites other atoms, causing them to emit light of exactly the same wavelength as the stimulating (fluorescent) light. The waves emitted by all of these atoms are said to be in phase, which accounts for the coherence of the laser's light. Most of the radiation produced within the rod escapes out the sides; some, however, travels along the length of the rod, stimulating atoms as it goes. When this light strikes the polished end of the rod, it is reflected back inside and continues to accumulate fluorescent output from all the atoms in its path.

One end of the laser rod is heavily mirrored, and all light striking it is reflected back inside. The other end is given a thinner mirror coating. The light traveling back and forth within the laser rod eventually reaches sufficient strength to burst through the partially mirrored end in a powerful burst (pulse) of light. This *pulse mode* is typical of some crystal lasers. It is possible, through the use of rather sophisticated techniques called *Q-switching* and *mode locking*, both to increase the power of these pulses and to make the output of the laser continuous, termed *cw* for *continuous wave*.

Laser output power is measured in units of energy per unit of time; for example, watts. Large carbon-dioxide gas lasers are capable of powers measured in thousands of watts. But the awesome capabilities of lasers are seen in the expression of such powers in terms of time units. Laser pulses are extremely short—as short as a billionth of a second. When a kilowatt power output (continuous rating) is divided by such tiny fractions of a second, the *instantaneous* power becomes enormously high. One of the largest power figures reported to date is 2 trillion watts, or more than six times the total electric power generating capacity of the United States.

THE SEARCH FOR FLUORESCENT CRYSTALS

The search for laser materials is in effect a search for suitable fluorescent materials. Ruby can be made to fluoresce red and is an excellent laser crystal. Other laser ma-

materials can be made by doping crystals with suitable impurities (generally rare earth elements) to make them fluorescent.

Many excellent laser crystals have been invented. Some of the most widely used are calcium tungstate, yttrium aluminum garnet doped with neodymium (YAG-Nd), strontium molybdate, calcium niobate, yttrium vanadate, yttrium aluminate, magnesium oxide, calcium fluor-phosphate (fluorapatite, or FAP), and various fluorides. Laser crystals are grown by a variety of techniques. All of the above crystals must be doped with suitable impurities to make them fluoresce.

Laser modulators are all crystals, such as lithium niobate, lithium tantalate, barium titanate, gallium phosphide, cadmium sulfide, and ammonium dihydrogen phosphate. Laser modulators and deflectors probably represent the most sophisticated technology achieved in "crystal design"—growing crystals with specific properties to meet device requirements. (Laser modulators are discussed in the next section.)

In the 1960s, research scientists devised lasers made of semiconductor materials, such as gallium arsenide, indium phosphide, cadmium selenide, zinc sulfide, zinc oxide, indium antimonide, and lead selenide. Semiconductor lasers are about the same size and cost as transistors, convert 50 percent of the electric input energy into light, and can be run on small current loads. These devices will operate for an estimated million hours or more without failure on the power supplied by a flashlight battery. They yield more light per unit of input power than any other device made by man. It is theoretically possible to make solid-state lasers with dimensions measured in microns (a micron is a millionth of a meter, or about 0.00004 inches).

Laser technology is still in its infancy. There is no doubt that its potential impact will be as great as that of semiconductor research twenty years ago. It will not be long before lasers are affecting society as visibly as do transistors. We will become dependent on their availability and usefulness as primary tools of our technological civilization.

LASER CONTROL CRYSTALS

The control of laser beams is based on the fact that these beams are nothing more than highly coherent light waves. When light passes through any medium other than a vacuum, its path is bent because of a small decrease in the speed of light through the medium. This bending, called *refraction*, is what makes a pencil held in a glass of water appear broken.

Modulation can be impressed on a laser beam (thereby adding information to the beam) by turning the beam on and off in a coded fashion. This is not easy to do at the laser source, but can be accomplished in another way. If the beam passes through a transparent material to a receiver, the beam can be modulated simply by periodically deflecting it away from the receiver. One might think of inserting a small mirror in the path of the beam at a very rapid rate, but there is an easier way to do the job.

A class of materials exists whose *refractive index* (measure of refraction power)

changes in an electric field, or when a mechanical strain occurs within the crystal. These crystals are called *electro-optic* and *elasto-optic*, respectively. They can be used as effective laser modulators because the path of the laser beam through them depends strongly on their refractive index. If the index is made to change (for example, by applying an electric field), the path of the laser beam will change. Even a tiny change will cause the beam to miss the receiver because of the coherence of laser light. The electric field or stress can be applied with the speed of electronic devices (that is, light speed) and so laser beams can carry information at very high frequencies.

Laser modulators are crystals chosen for their strong electro-optic or elasto-optic effects. Other materials (also suitable for modulators) are *piezo-optic*: they experience a change in refractive index when an external stress is applied. A similar effect is observed in *acousto-optic* materials, which react to acoustic (sound wave) vibrations.

A new field of physics has developed around laser light applications and control devices. Laser beams are so intense that they actually can change the physical properties of the transparent materials through which they pass. Specifically, the intense light itself modifies the refractive index of certain materials. This simulates the action of a lens, because a lens focuses by bending parallel light beams through differences in the thickness of the refracting medium. Self-induced refraction changes actually allow laser beams to focus themselves in appropriate materials! The study of such effects is called *nonlinear optics*, because the properties of the transmission medium change as the transmitted light becomes more intense.

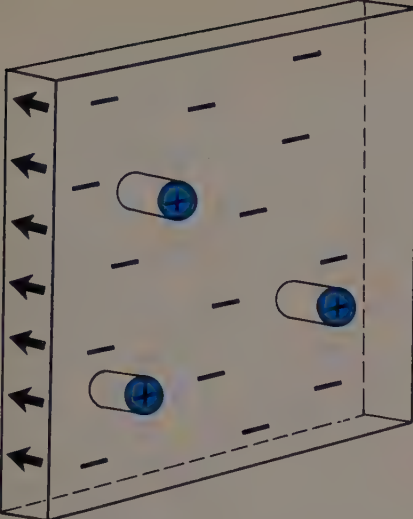
Electronic computers are vital to our society. Their cost and speed are limited by the capacities, reliability, and cost of their memory systems. Currently, there are two types of computer memories in widespread use. One consists of tiny doughnut-shaped rings, or *cores*, made of substances called *ferrites*, strung on a fine wire mesh. A second involves the use of magnetic recording media, such as tape, for information storage.

BUBBLES

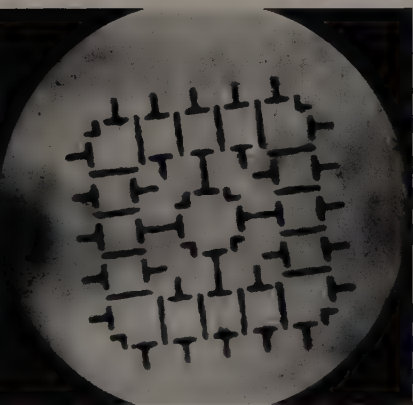
A more recent development, still largely experimental, uses solid-state circuitry, with many tiny transistor circuits embedded in chips of silicon. The large computer memories needed in telephone switching systems are very expensive by standards based on available memory systems. In searching for cheaper, more reliable devices, Bell Telephone Laboratories discovered what has come to be called "bubble technology."

Bubbles are actually tiny regions, called *domains*, of magnetically aligned (*polarized*) material. They can move about within a film of magnetic material that has been polarized in the opposite direction. The bubbles are created in the film by applying a strong magnetic field. Magnetic bubble memories are expected to be cheaper than ferrite core memories, and many times faster than other systems now widely used for information storage in computers. Bubble devices have no moving parts and should work reliably for years, though this has not yet been verified by experimentation.

Bubble materials have esoteric magnetic properties and considerable searching has been done for suitable crystals. Typical bubble materials are substances called *ortho-*



When certain types of magnetic materials (such as YIG) are subjected to a magnetic field (direction of arrows), portions of the material align themselves in opposite directions. This produces regions of opposite alignment or "polarity." As the strength of the applied magnetic field increases, these regions—called "domains"—shrink down to small cylinder-shaped areas of magnetism that look like tiny "bubbles" in cross section, hence the name "bubble" technology.



In this photomicrograph, a bubble (magnetized cylinder) can be seen as the round light area at upper right of center. Such bubbles are formed in certain materials (orthoferrites) by applications of strong magnetic fields, and they can be moved about magnetically, thus making possible efficient information-handling equipment.

ferrites, usually grown by flux methods. More recent advances have been made with *plumboferrite* and with yttrium iron garnet (YIG), also grown from flux. These materials are discussed in greater detail on page 87.

All computer memories operate by storing information in coded form as *binary digits* (abbreviated *bits*), which are either ones or zeros. Every number can be given binary representation, and the key to computer operations is the ability to represent 1 by a switch in the "on" position and 0 by the switch in the "off" position. By analogy, the presence of a magnetic bubble in a certain location might represent a one, its absence there a zero. Since bubbles can be moved around in magnetic films at very high speed, with very little power, their potential in computer memories is very exciting.

Bubbles operate in thin magnetic films; advanced technology has been developed for depositing films with appropriate characteristics on suitable substrates. Yttrium iron garnet is now routinely deposited as a thin film by growth from a vapor. Experimental data storage devices have already been built that pack as many as 2.5 million bits of data into a square inch of material, and can process information at rates up to a million bits per second!

Advances in this new technology in years to come will provide tremendous reductions in size—and increases in performance—of computers. Bubbles may someday make it possible for every man and woman to carry a computer the size of a pack of cigarettes, able to do calculations now limited to very large scientific and business machines. Technology is catching up so rapidly with the science fiction of less than a decade ago that even speculation as to what developments lie ahead is becoming harder to produce.

Case

Histories

Materials science frequently advances through what might be called a “brute-force” approach. Theory may predict how a specific type of material may perform, but the only way to prove the theory right or wrong is through experimentation. The brute-force method is: “try it first—if it works, let’s figure out why afterward.” A recent example of this approach will be discussed later.

By means of brute-force methods and exhaustive testing of many different materials, technologists have developed crystals with outstanding characteristics for specific applications. When a material is found that seems to have desirable properties, a growth technique is first perfected that will yield crystals of suitable size and quality. Then, crystals are grown that incorporate a wide variety of dopants, or even complete substitutions of elements present in the original crystal. Usually, one such derivative compound has properties superior to the originally grown crystal.

The procedure of growth and testing continues until all reasonable combinations have been tried, and the one with the best characteristic for a given function is chosen. Thus, for each type of compound there is usually one (or, at most, a small number) that can be considered “superior.” The less outstanding compounds are shelved and seldom mentioned in the literature. But the field of “crystal design” is so young that only a tiny fraction of the known types of compounds have been investigated. The “winners” in the field so far will be briefly mentioned in the following pages.

Silicon carbide, SiC, was the first synthetic abrasive. It was made by Dr. Edward G. Acheson in 1891 in a special type of electric furnace capable of reaching very high temperatures. The “feed mixture” in making SiC is rather unsophisticated: sand, coke, sawdust, and salt. When this mixture is heated to 2,400°C., the coke reacts with the quartz sand to form silicon carbide and carbon monoxide. The sawdust burns away to create vent holes to allow the escape of gases produced in the reaction of the salt with impurities in the mixture. The silicon carbide is then picked out and crushed.

SILICON CARBIDE



Silicon carbide, once used exclusively as an abrasive, now finds application in semiconductor technology.

When first grown, silicon carbide was found to be one of the hardest abrasive substances known—second only to diamond. It was first used extensively in grinding, but soon other uses were found. Its thermal stability allows it to be used in furnace muffles and linings, in fire bricks and crucibles for high temperature processing, as a foundry additive, and in making furnace heating elements. In the 1920s, scientists discovered that the resistance of SiC to an electric current decreased as voltage increased. This was an ideal condition for a lightning arrester, in which huge currents must be carried away very rapidly. The millions of volts of a lightning bolt made the silicon carbide a very efficient conductor for dissipating the electric energy of the bolt itself, whereas many other types of materials would simply vaporize as a result of rapid heating.

In recent years, it has been found that SiC is extremely strong. Whiskers (fine, hairlike crystals) of SiC have a strength modulus (a measure of strength) of millions of pounds per square inch, compared to 600,000 pounds per square inch for steel. In addition, SiC whiskers have a stiffness modulus twice that of steel.

When such whiskers are embedded in a matrix of another material, they impart their strength and stiffness to the matrix, and SiC composites have many uses.

Very pure crystals of SiC can now be made. With the attainment of high purity came the discovery that SiC could be used to make semiconductor diodes. A whole

technology has developed around SiC semiconductor devices. Some of the most exciting aspects of this technology are the improvements SiC offers over germanium and silicon. Germanium's chief drawback is that Ge semiconductors can operate well only up to 100°C. and Si only to 300°. SiC devices can operate at 500°, thus greatly extending the service capabilities of semiconductor circuits in unfavorable environments.

In addition, SiC diodes will convert electric current to visible light, thus making possible such devices as ultrasensitive "pens" for recording sound tracks on movie film. Silicon carbide diodes have a much longer useful life than tungsten lamps for this purpose, and they are less variable.

Many growth techniques are employed for making very pure SiC, including sublimation (growth from a vapor); epitaxial growth (*epitaxy* is growth on a substrate material, where the crystal structure of the deposited material closely matches that of the substrate); growth from solution (in liquid silicon); and growth by gaseous cracking (decomposition of a vapor of a silicon or carbon compound). Abrasive material is still prepared by reaction in an electric furnace.

Quartz, silicon dioxide (SiO₂), is one of a family of materials that exhibit an effect called *piezoelectricity*, the ability to convert a mechanical vibration or oscillation into an electric current. This effect was observed as early as 1881 by Pierre and Jacques Curie, but remained a laboratory curiosity until World War I. At this time Paul Langevin, a French physicist, conceived the idea of using quartz plates to detect submarines. An electric current sent through the quartz would produce a beam of sound waves far beyond the range of a human ear (ultrasonic) that would travel underwater and bounce off any submarine that might be present. This method of producing sound waves is, in effect, inverse piezoelectricity. The echo of the sound would reveal the distance and direction of the craft.

At about the same time, A. M. Nicholson of Bell Telephone Laboratories experimented with another piezoelectric material, Rochelle salt (sodium potassium tartrate), for use in phonograph pickups and microphones. In 1921 W. G. Cady showed that quartz plates could be used to control the oscillations produced by vacuum tubes in radio, thus offering a precise method of stabilizing and controlling the transmission frequencies of radios. Quartz was used rather than materials with a greater piezoelectric effect because of the superior chemical and physical stability, strength, and availability of quartz. By 1939 the quartz oscillator plate industry in the United States had reached a volume of 50,000 units per year.

Langevin's ideas later became the heart of what we know today as sonar. Although crystal devices were not used extensively in World War I, research was expanded in many laboratories, and by the second world war their value in military devices was well established.

When the United States entered World War II in 1941, the demand for quartz oscillator plates soared. Tens of millions of such plates were needed, creating a severe industrial supply problem. The major source of high-quality electronic quartz was

QUARTZ



Slices of quartz are essential in frequency-control devices, such as the ones shown. Millions of "crystal units" were produced during World War II. Current demand is for ever higher quality quartz for specific electronic applications.

In growing quartz crystals, the process starts with seeds. These are hung on racks and loaded into a hydrothermal autoclave.



Brazil, and German submarines greatly endangered the security of this supply. A method was therefore sought for manufacturing quartz on a large-scale production basis.

This industry did not develop quickly enough to meet the wartime need, however, and the 55 million quartz plates made between 1941 and 1944 were fashioned entirely from natural quartz. The pressing demands of war did, however, rapidly enlarge scientific knowledge of the function and operation of quartz oscillators. The research completed during the war tremendously advanced the sophistication of oscillator devices, and paved the way for the growth of an industry founded on the use of quartz and other piezoelectric materials.

Certain kinds of crystals are, in some respects, similar to a tuned piano string in that they have natural frequencies. Although a tuned piano string may have only a few vibrational frequencies, a crystal such as quartz may have hundreds of harmonic frequencies, in addition to the fundamental frequency. If an electric current is introduced into a crystal that has a natural frequency identical to that of the current, the crystal is said to be *in resonance*. In piezoelectric materials, the current actually causes the crystal to vibrate at the same rate as the current. The vibration can be strong enough to destroy the crystal, just as a singer's voice can shatter a resonant glass.

The vibrations of crystals occur at rates (frequencies) far beyond the range of the human ear. The way a crystal plate vibrates depends on the way it is cut. Some crystal bars actually flex up and down like the plates of a xylophone when driven by an electric current. Other types of piezoelectric plates oscillate in a *shear mode*, and become alternately longer and shorter as they vibrate. Crystals resonate at frequencies measured in terms of millions of cycles per second.

During World War II a major effort was launched to develop production techniques for making quartz oscillators for radios. The frequency of vibration of crystals is strongly dependent on the thickness of resonator plates. Therefore, production depended on devices for thinning quartz plates to exactly the right dimensions. Machines were built that could grind down a quartz plate and check its vibrational frequencies in an almost continuous operation.

Crystal oscillators are extremely sensitive to the frequencies of the current that forces them to vibrate. When the frequency of the current exactly matches the resonant frequency of the crystal, the latter's vibration is most acute. This effect is used in reverse, to control radio wave frequencies and hold them constant. A tiny quartz crystal can maintain the frequency of a powerful radio transmitter broadcasting at powers of thousands of watts.

The regularity of vibration of quartz crystals makes them useful in timing devices, such as watches. A small battery drives a carefully cut crystal that will maintain great accuracy in its frequency output. This frequency provides a precise measure of elapsed time.

The sensitivity of crystal resonators to frequency makes them useful as "channel

filters" for communications devices. Every separate message transmitted through a cable is modulated on a distinct frequency. A properly "tuned" crystal can be made selective for a single frequency, and crystals are superior to other devices for this purpose.

Quartz is popular for many electronic and optical uses because it has extremely sharp resonant frequencies, is mechanically durable, and resists attack by most chemicals. Some cuts made from quartz crystals have vibrational frequencies that vary little with changes in temperature, a key factor in constructing a stable electronic tuning or transmitting device. The demand for quartz is thus very great, and natural material of the requisite quality is scarce. Brazil still remains the chief source of supply of high quality crystals.

The manufacture of quartz for commercial purposes began in the late 1950s. The process does not use simple oxide or element starting materials to produce the finished crystals, and is therefore not a "synthesis" in the true sense of the word.

Rather, low quality natural quartz is crushed and cleaned in acid and dissolved in large hydrothermal autoclaves. The solution is passed through racks containing seed crystals in a cooler part of the autoclave, and the quartz in solution is deposited on these seeds.

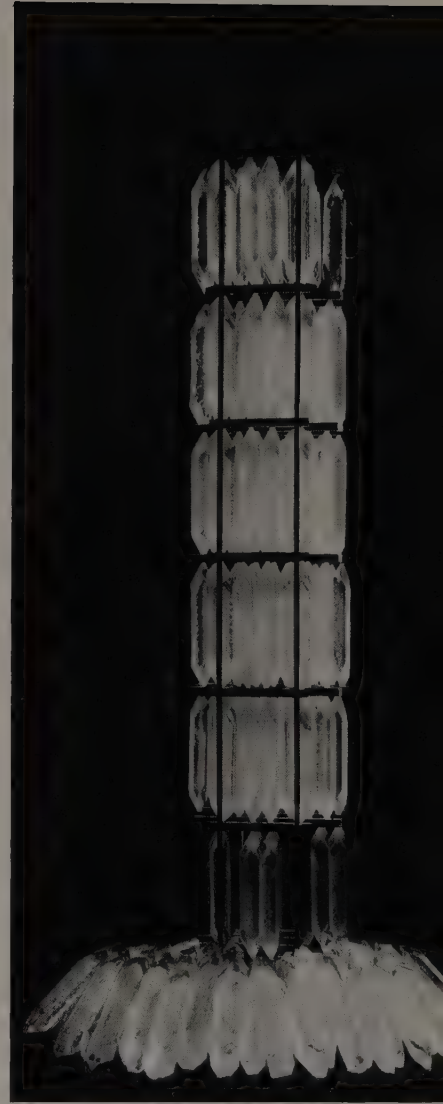
The method is simple cooling of a saturated solution to induce supersaturation and precipitation of excess dissolved material, as discussed earlier. Manufacturers therefore prefer to call their product "cultured quartz" rather than "synthetic quartz" because the process is, in effect, a "reworking" of natural quartz to yield crystals with optical and electronic properties superior to those of the starting material.

The primary advantage of cultured quartz is in control of growth conditions and seed orientations. Man-made crystals are generally free of twins (oriented intergrowths of two or more crystals) and visible flaws and inclusions. Seeds can be cut in such a way that crystal growth produces almost 100 percent usable material. If slices of a specific orientation are required for a particular frequency device, crystals can be made that allow maximum yield of the desired slices with almost no waste.

This advantage makes the cultured quartz industry competitive with natural quartz. Although natural quartz is less expensive, much more of it has to be examined to obtain material of the quality desired, and considerably more cutting and waste removal must be done. This adds greatly to the cost and narrows the difference between the natural and the cultured product.

Resonators continue to be the primary end-product use for cultured quartz. *Transducers* (devices that convert one form of energy into another) made of cultured quartz have been used to measure the pressure of shock waves.

The optical properties of cultured quartz are excellent. Its transparency in the ultraviolet region of the spectrum makes quartz a desirable material for windows in scientific instruments. Lens elements and prisms made from cultured quartz are of very high quality.



At the completion of a run, racks originally loaded with seed crystals are removed from the hydrothermal autoclave. The seeds have grown into full-sized quartz crystals.

SILICON AND GERMANIUM

Few materials have had as great an impact on the societies in which they first appeared as have silicon (Si) and germanium (Ge). We might compare their significance to that of bronze or iron in ancient times, and to uranium in recent decades.

Neither of these two elements occurs in nature in pure, uncombined form. Crystal preparation is the key to their usefulness in industry and science. Germanium is recovered as a byproduct of the smelting of certain zinc ores. It is refined and made into standard ingots that are about 15–17 inches long and weigh about 3½ pounds. These ingots are not single crystals, but rather are *polycrystalline* (masses of intergrown, tiny crystals). For use in electronic devices, germanium must be highly purified, normally by zone-refining techniques. Transistor-grade germanium contains less than one part of impurities in 10 billion parts of Ge!

Silicon recovery is somewhat more complex. The chief “ore” of Si is sand, worth about a penny a pound. This is heated in an electric furnace with coke (carbon) to yield a product that is about 99.7 percent pure Si and worth about 20 cents a pound. Intermediate purification steps produce very pure Si worth about \$3 per ounce.

This is the “feed material” for Czochralski growth of very large single crystals that are not only very pure but have perfect internal crystalline structures as well. Zone refining further improves the purity and allows fabrication steps to commence.

Very thin slices of single-crystal Si, worth about \$3 each, are polished and used to make such devices as diodes and rectifiers. A brief history of single crystal electronic devices will highlight the significant improvements achieved through the use of Ge and Si.

The original crystal rectifiers (a rectifier is a device that converts AC to DC current) consisted of a slice of crystal and a fine, hairlike wire called a “cat whisker.” Such a rectifier would conduct electricity well only when the wire was held against the crystal in a “sensitive spot,” and therefore came to be called a “point-contact rectifier.” The very earliest radios had crystals of galena (lead sulfide), and operators had to move the wire around on the surface of the crystal to find the best spot for reception.

Eventually, vacuum tubes replaced crystal rectifiers in radios, and from then until the early 1940s such rectifiers were merely laboratory devices. Experiments were conducted using silicon crystal rectifiers and tungsten wires.

In the late 1930s the advent of radar began to spur new interest in crystal rectifiers because vacuum tubes didn’t work well at radar frequencies. But rectifiers still gave poor results because they lacked homogeneity, and it was difficult to determine the “best spot.” The solution to this problem came with the introduction of very high-purity silicon. It was found that even small amounts of unwanted impurities adversely affected device operation. In the following years very high-quality silicon and germanium began to be produced.

Germanium for rectifier use was doped with tin to produce suitable conductive properties. Eventually, scientists learned that the tin itself was having little effect; the desired properties were being created by impurities in the tin, most likely arsenic and



A typical Czochralski-grown crystal of silicon, suitable for transistor use.

antimony. Silicon and germanium diodes were greatly improved in the period 1940–1948. When the point-contact transistor was devised by Bardeen and Brattain in 1948, interest in silicon and germanium became even greater.

In the late 1940s G. K. Teal and J. B. Little at Bell Telephone Laboratories began to grow single germanium crystals by crystal pulling. Repeated crystallization resulted in large and very pure crystals. When Shockley demonstrated that “sandwiches” of semiconductor material containing different impurities in different layers would give both rectifying and transistor effects, Teal modified the growth technique to introduce such impurities during the crystal-pulling operation itself. These crystals were described as *grown junction* semiconductor crystals. Bell Labs not only predicted the effects to be expected in semiconductor devices, but also made the first transistors and announced them to the world in 1951.

W. G. Pfann developed special zone-refining techniques to make ultrapure silicon and germanium crystals. In 1952, in a now-historic symposium, Bell Labs released the details of the grown junction transistor process to a selected group of licensed manufacturers. But the Labs were continuing to work on silicon, which has a higher melting point than germanium, and greater reactivity. These factors created problems in finding a suitable crucible in which to melt it. The problems were so great in the early 1950s that only the Texas Instruments Company produced silicon commercially.

The introduction of the *float zone refining* process solved many manufacturing problems. In this technique, the silicon crystal is held vertically and a heated zone is made to travel up and down the length of the crystal. This molten zone collects impurities and pushes them to the ends of the crystal, where they can be cut away. The availability of super-pure silicon was a major advance in device technology.

A major obstacle to the improvement of semiconductor materials was in the addition of impurities in carefully controlled amounts. A major improvement came with the sophistication of diffusion techniques. In diffusion, the impurities are allowed to “work their way” into a host crystal (like the gradual mixing of a layer of cream floating on a cup of coffee). Diffusion technology allowed the field of semiconductor devices to truly mushroom, and today improvements are made almost daily in solid-state laboratories.

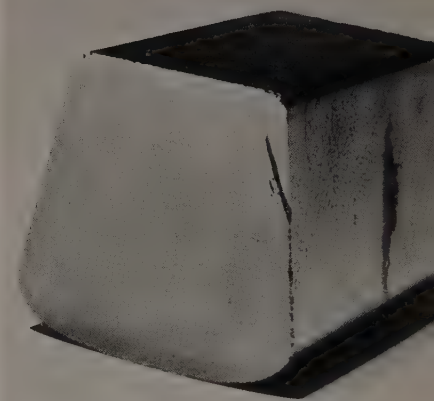
Silicon oxidizes to form silicon dioxide (SiO_2), which is known in nature as the mineral quartz. Controlled oxidation of a silicon slice allows quartz to form in pre-designated areas, where it impedes the diffusion of impurities. This allows regions with different conductive properties to be deposited on a crystal wafer.

A major advance in transistor production came with the advent of *epitaxial junctions*. Epitaxy, as noted earlier, is the crystal growth of a substance on a substrate with similar structural characteristics. Epitaxy makes it possible to start with a very pure silicon substrate and add impurities as needed. Epitaxy also allows the production of a wide variety of semiconductor devices, many of which do not employ silicon.

Germanium doped with lithium is used in making detectors for various types of radiation, including gamma rays, cosmic rays, and x-rays. For such applications



Germanium crystals are purified by zone refining in “boat-shaped” containers. The resulting material has very few impurities.



A transistor consists of adjoining layers of semiconductor material containing different chemical impurities, which are added by a diffusion process. Before this process was developed, the impurities were added during crystal growth. The silicon crystal shown here is termed a “grown junction” crystal, and the two layers of different composition are clearly defined.

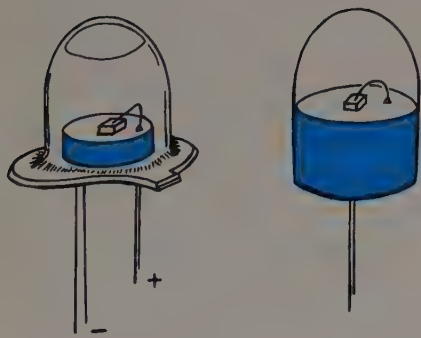
Light-emitting diodes are used in the display panels of many types of electronic instruments and control consoles, such as those used by telephone companies. In this picture, LEDs made of gallium phosphide provide the operator with information stored in an electronic switching machine.



“ultrapure” Ge is needed, and several companies are capable of refining the purest available crystals to have less than one part of impurities in a *trillion* parts of germanium. This is done by a series of zone-refining and crystal-pulling operations.

Silicon is considered superior to germanium in many respects for semiconductor use. Its chief asset is the ability to operate at higher temperatures than germanium. There are other materials that have even better operating characteristics than silicon. Nonetheless, it is clear that silicon will be a primary semiconductor material for many years to come.

LIGHT-EMITTING DIODES



Light-emitting diodes are simple in design, but require expensive and highly sophisticated materials for their operation.

Light-emitting diodes (LEDs) are semiconductor devices that convert electric energy into light. They are rated in terms of power input (watts) and light output (lumens). The chief advantage of LEDs is small size and high conversion efficiency. Their lifetimes are very long compared to other light sources, such as incandescent lamps, and they can be designed to produce a wide variety of colors.

The energy output of LEDs can be converted to visible light by coating them with a suitable phosphor (a material that emits light when properly stimulated). The most widely used LEDs are made with gallium arsenide (doped with silicon), gallium arsenide-phosphide, gallium phosphide (doped with zinc), gallium aluminum arsenide, gallium phosphide (sometimes doped with nitrogen or zinc), gallium indium phosphide, and silicon carbide.

Typical phosphors are halides (see next section). LED devices that emit a wide variety of colors—including red, green, and yellow—are finding use in all types of instruments for both scientific and consumer applications.

Halides are compounds containing the halogen elements; fluorine, chlorine, bromine, and iodine. Included in this group are chemicals vital to life (salt) as well as to industry. The most popular optical window material in use today is halite, sodium chloride, the same salt that we use on our food.

Halide crystals are grown today almost exclusively by the Bridgman technique. This method is capable of producing single-crystal ingots up to a yard across and weighing over half a ton. Such giants have specific applications in scientific devices.

One of the most important uses of halide crystals is in windows and prisms for *spectrophotometers*. These are instruments that pass a beam of infrared radiation through a liquid sample (either an unknown compound or a solution). The infrared beam is absorbed to some degree by the sample, and interaction of this beam with components in the sample allows identification and analysis. Halides are needed for spectrophotometer optics because they transmit infrared radiation extremely efficiently.

Almost every manufacturer of products we use and need daily depends on a spectrophotometer in his research laboratory or his quality-control laboratory. Almost every manufactured product, therefore, depends on an infrared spectrophotometer at some point in its manufacture. Without this instrument, it would have been impossible or extremely difficult to develop synthetic rubber, aviation gasoline, and many other materials desperately needed during World War II.

Other materials that transmit infrared radiation well are potassium bromide, potassium chloride, thallium bromo-iodide ("KRS-5"), and cesium iodide.

Halides that are used as windows and prisms for ultraviolet light transmission include the fluorides of calcium, barium, and lithium. Cadmium fluoride, when properly treated and doped, is a semiconductor material.

Calcium fluoride occurs in nature as the mineral fluorite. It is one of the few optical materials that have been obtained in nature in sufficiently high quality for direct fabrication.

Fluorite has many uses. It is one of the best known infrared transmission materials. Its optical characteristics make it extremely useful in microscopes, telescopes, and other types of lens systems. It is a superior host material, for rare-earth dopants, in making lasers (dopants include neodymium, holmium, erbium, thulium, dysprosium, and uranium). Laboratory synthesis of fluorite has provided information, obtainable in no other way, on the mechanisms of coloration in this material.

Halide phosphors are valuable in the preparation of light-emitting diodes. The most widely used compounds for this application are lanthanum fluoride and barium yttrium fluoride, activated with erbium.

Sodium iodide, when *activated* (sensitized to emit light when irradiated) with thallium, is a vital component of detectors used in medicine and the petroleum industry. In nuclear medicine, sodium iodide crystals *scintillate* (emit flashes of light) when struck by gamma radiation. The light output of a sodium iodide detector can be measured to indicate the strength of the radiation. A similar detector lowered into an oil-well hole detects nuclear radiation that is often associated with petroleum deposits.

The giant-size crystals mentioned earlier (30-inch diameter) are scintillation crystals of sodium iodide, developed for use in high-energy accelerators.

Halides are relatively inexpensive, have desirable optical and physical properties,

An initial operation in the manufacture of halide windows for optical devices is called cleaving. Here, a block of halite is being cleaved before further fabrication.



Many halide crystals are soluble in water. Cutting a large ingot can thus be accomplished simply by means of a string that runs through a pan of warm water. Solution action of the water does the cutting.



and can be prepared in large sizes while maintaining purity and optical quality. They are extremely useful materials with a wide variety of applications and, in some cases, there are no suitable substitutes. Their continued success as popular technological materials is assured for some time to come.

The gem uses of corundum (ruby and sapphire) have already been discussed, but corundum has found wide applications in modern solid-state technology as well.

Ruby was the material used in the first operating laser, made by Maiman in 1960. Since ruby fluoresces red, this laser produced red light. The ruby laser is still widely used, although newer materials have supplanted it in certain areas.

Corundum was originally grown by flux methods (Frémy) and later by the Verneuil technique. Gem corundum is still grown primarily by Verneuil methods, but Verneuil crystals have optical defects that make them unsuitable for laser use. The Czochralski method is now applied almost exclusively to produce ruby laser material and sapphire for semiconductor devices.

The chief advantages of sapphire are its good optical and physical properties. It is the hardest of available oxides. It is inert, and can therefore be used in "hostile" environments. It has effective zero-porosity, and is very stable in high temperatures. In addition, sapphire is a semiconductor itself. A relatively new device-applications field called MOS (metal oxide semiconductor) relies on sapphire as a primary material. As a substrate for semiconductor devices, sapphire is superior in some respects to silicon. Devices and circuits implanted on sapphire operate up to 100 times faster than such devices on silicon.

Sapphire is five times stronger than most glass. It has been grown in large, specially shaped Czochralski crystals, and cut into plates for helicopter windows. Such windows are extremely efficient armor plate, and will deflect projectiles that could pierce steel of equal thickness.

Resistance to abrasion makes sapphire windows additionally useful in aircraft flying at supersonic speeds, and as transparent covers for such devices as solar cells. Transparency makes sapphire ideal for solid-state devices that produce light. The light-emitting unit is actually deposited on the sapphire window, which serves as a protective cover, substrate, and display window all in one. Sapphire is very transparent to ultraviolet radiation, making it useful in windows and cells for spectrophotometers. Sapphire also transmits well in the infrared region of the spectrum.

Its temperature resistance makes sapphire ideal for observation windows in high-temperature processing equipment. It resists the damage that can be produced in many materials by powerful laser beams, and therefore is useful as a laser reflector. Sapphire's hardness gives it value in cutting edges, wear pads, washers, bearings, and balance knife edges.

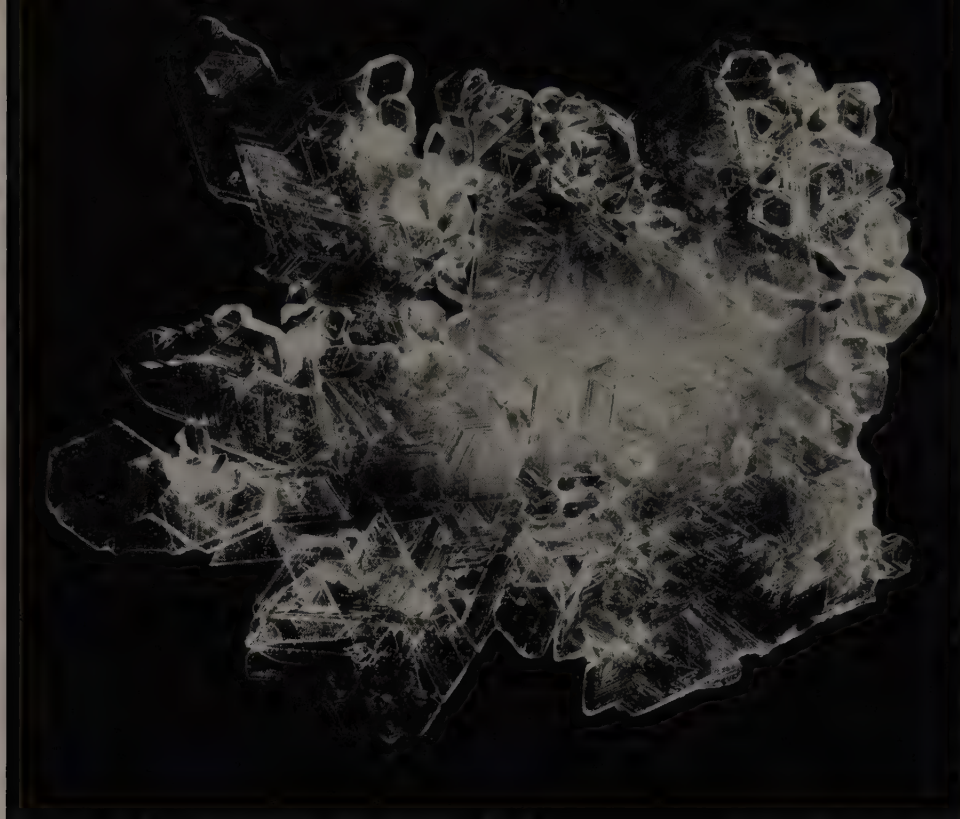
Czochralski growth of corundum is a highly developed art. The Union Carbide Corporation has reported crystals weighing over 12 pounds and containing useful, op-

CORUNDUM

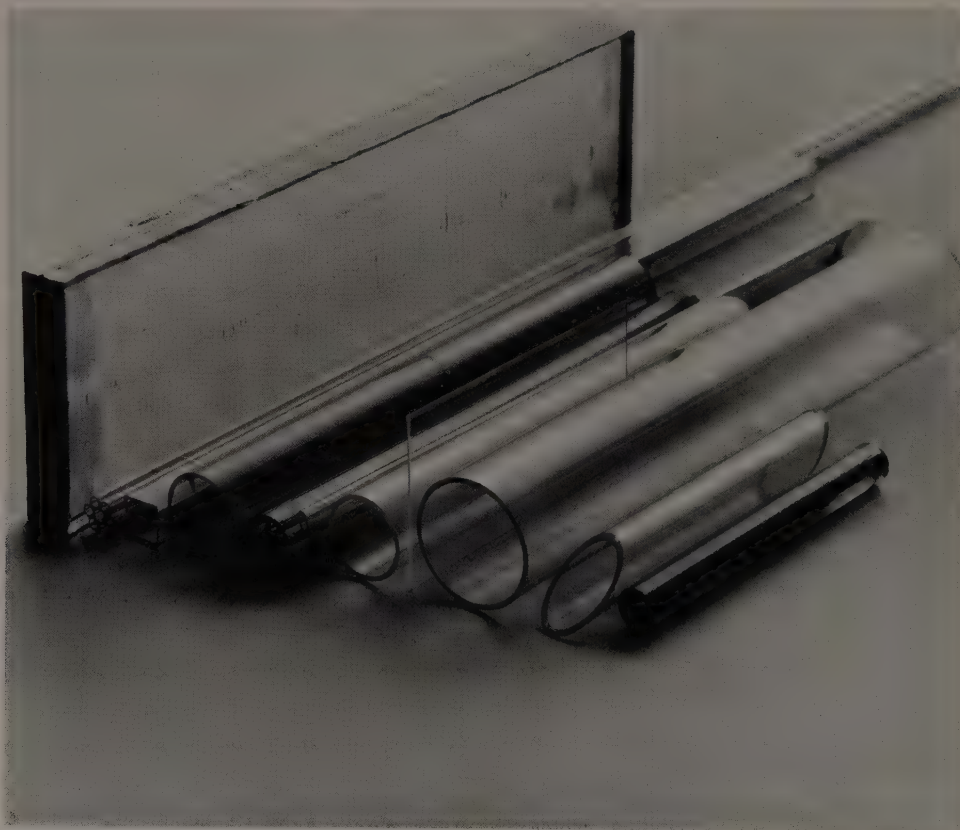


These large colorless crystals of corundum (sapphire) were grown by the crystal-pulling technique. Sapphire "windows" are hard and durable.

Flux-grown ruby crystals.



Saphikon is shaped sapphire. Intricate tubes, rods, and ribbons are formed during the growth process in a manner similar to pulling metal through a die. At left is a sapphire plate.



tically perfect areas up to 8 inches long and 4½ inches in diameter. Ruby crystals for laser rods up to 20 inches long have been grown. "Shaped" boules for specific applications have also been made by careful design of the crucible in a pulling apparatus.

A new technique called EFG (edge-defined film-fed growth) has been developed by Tyco Laboratories, and applied to sapphire growth. This material, called "sapphikon," can be prepared in rods, tubes, ribbons, and complex cross-sectional shapes in a continuous pulling operation. The technique promises the availability of specialized sapphire components for a wide variety of applications, at modest cost. Applications of the EFG technique to other materials are still in the experimental stage. Simply stated, EFG involves the pulling of a material as it emerges (in a molten state) through the openings of a specially shaped die.

Other corundum growth techniques include vapor deposition (very limited in application and capable only of very small crystal sizes), hydrothermal and flux growth, and a new method called the *Schmid-Viechnicki technique*, after its two American inventors. This process, similar in basic approach to the Bridgman technique, involves directional solidification from a melt, and is capable of producing single crystals of corundum 6 and even 8 inches across. For optical purposes, Czochralski corundum remains superior, although the other techniques produce material for a wide variety of scientific applications.



This crystal of ruby was grown hydrothermally by the Airtron Corporation.

Spinel has many of the same advantageous properties as corundum, but is even more desirable for logic and memory semiconductor applications. Spinel's crystal structure is similar to that of silicon, a far closer match than that between silicon and sapphire. Spinel thus has greater potential as a substrate for the deposition of silicon for device manufacture. In addition, it is easier to fabricate than sapphire, and silicon-on-spinel circuits have the same speed as silicon-on-sapphire. One major disadvantage of spinel is its thermal sensitivity. Sudden changes of temperature cause it to crack or shatter.

Spinel is less expensive than sapphire for application in microwave devices, although cost advantages have not yet been realized because spinel is not yet commercially manufactured for these uses. Spinel is transparent and would make excellent lenses if internal strain could be eliminated. It is efficient at conducting heat away from a circuit imprinted on it (although only half as efficient as sapphire). Both sapphire and spinel are reusable; the metal circuits deposited on them can be stripped off and the substrate used over again.

In the field of optoelectronics, spinel may become the most widely used material. Light-emitting diodes can be made by direct deposition on a spinel substrate. Since spinel is transparent, the light emitted by the diode is visible through it, and the spinel further serves as a cover for the device. Manufacturers are turning to spinel as a significant addition to the array of available materials for semi-conductor use.

SPINEL

**ROCHELLE SALT, ADP,
KDP, AND EDT**

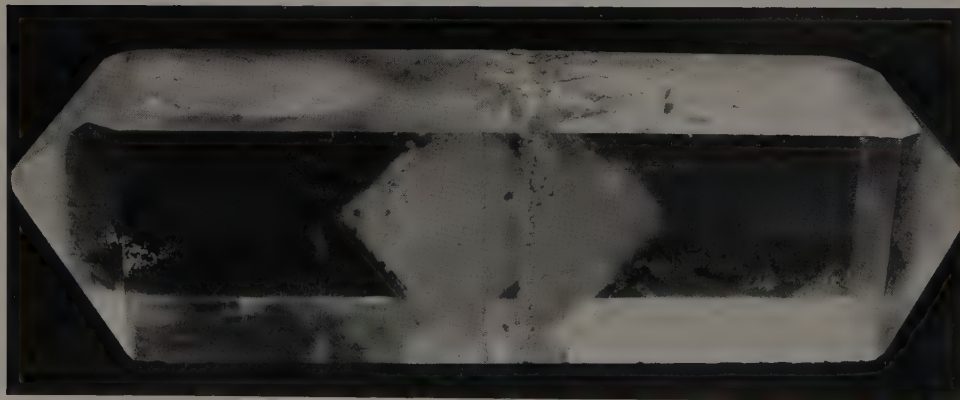


Rochelle salt (sodium potassium tartrate) is obtained by refining a residue that accumulates in wine casks during fermentation. It is thus supplied in granular form, but for device applications it is recrystallized, normally from water solutions at low temperature. Crystals can be grown up to 2 feet long and 3 inches wide in about a month's time.

Similar giant-sized crystals of ADP (ammonium dihydrogen phosphate), KDP (potassium dihydrogen phosphate), and EDT (ethylene diamene tartrate) are grown from water solutions. They are all useful for their piezoelectric properties. Rochelle salt in particular is widely used in such devices as radio earphones, microphones, speakers, phonograph pickups and record-cutting machines, pen motors for chart recorders, and in hearing-aid earphones. Most of these piezoelectric applications have been taken over by materials, such as barium titanate, that have mechanical properties superior to those of Rochelle salt.

ADP has been used in sonar transducers and in hydrophones. More recently it has been used as an electro-optic light modulator. Its rapid switching speed makes it useful in high-speed camera shutters, "light valves" for producing sound tracks on motion-picture film, tunable optical filters, and in infrared absorption plates. KDP also has electro-optic capabilities.

Very large crystals of ADP (ammonium dihydrogen phosphate) have been prepared from water solutions. Because of its piezoelectric properties, this material was widely used in such devices as phonograph tone arms.



Rochelle salt crystals are easily grown from water solutions. They were once used extensively in phonograph pickups and other electronic devices.

The term garnet refers to a group of silicate minerals that all have the same atomic structure, but differ widely in composition. The basic formula of garnet is $A_3B_2C_3O_{12}$. In natural garnets, A is calcium, iron, manganese, or magnesium; B is aluminum, chromium, or iron; C is silicon; and O is oxygen. Scientists have learned to make garnets in the laboratory with much more esoteric compositions than nature's. Few of the garnets grown for technology have compositions that even faintly resemble those of naturally occurring garnets. They are, nonetheless, termed garnets because they have the same atomic structure.

The best known man-made garnets have already been briefly discussed. YAG (yttrium aluminum garnet) is grown chiefly by flux methods and by the Czochralski technique. YAG grown by hydrothermal and Verneuil methods has proven less suitable for laser use than Czochralski YAG. YAG doped with neodymium is an excellent laser material, capable of continuous wave operation at room temperature. Other chemical dopants that result in laser action with YAG are lutecium, chromium, erbium, thulium, and ytterbium.

YIG (yttrium iron garnet) is typically grown from flux (the most suitable flux is a mixture of lead iodide, lead fluoride, and boron oxide). YIG is a black, optically opaque material, but is transparent to infrared radiation and serves as infrared "windows." Tiny spheres and rods cut from YIG are used in microwave devices, for tuning, modulation, and switching.

Gadolinium gallium garnet (GGG) is valuable in bubble technology because of its structural similarity to YIG. The latter can be deposited on a GGG substrate by vapor-deposition techniques.

Ferrites are oxides that are useful because of their magnetic properties. Orthoferrites have the general formula $XFeO_3$. They are suitable for bubble devices, but a chief drawback is that they produce bubbles with a somewhat large diameter. This reduces the total number of bubbles that can fit in a unit area of material, and limits the use of orthoferrites in mass storage devices. For example, $SmTbO_3$ (samarium terbium orthoferrite) has bubbles 0.0015 inch in diameter, yielding 25,000 bits of information per square inch, whereas estimates of minimum packing densities for useful storage materials call for over 1 million bits per square inch.

Another class of oxides called the *magnetoplumbites* is characterized by the general formula $PbX_{12}O_{19}$. Pb is lead and X is generally gallium, aluminum, or chromium. Magnetoplumbites are usually grown from flux. They will form small magnetic bubbles, but the mobility of the bubbles in the material is low, limiting the speed of computing and switching devices in which they are used.

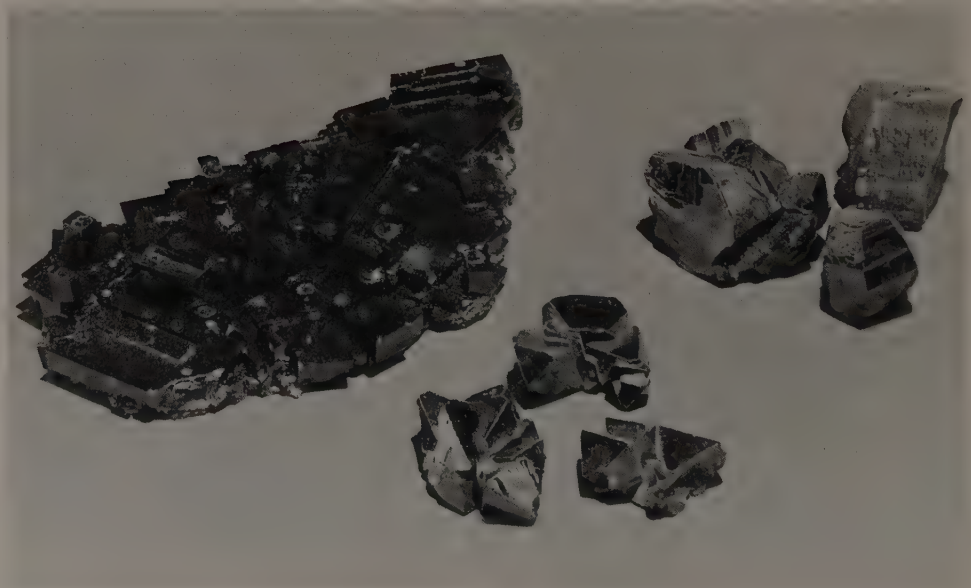
A suitable bubble host has been found in YIG doped with rare earths. These materials can contain upward of one million bits per square inch and bubble mobility is high. They offer an excellent compromise in properties between the orthoferrites and magnetoplumbites.

GARNETS AND FERRITES

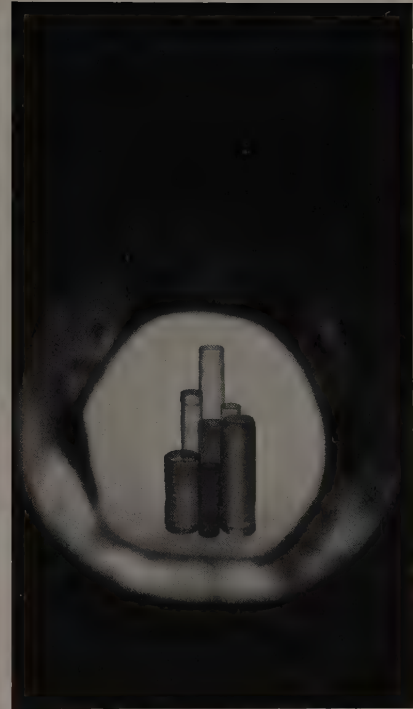
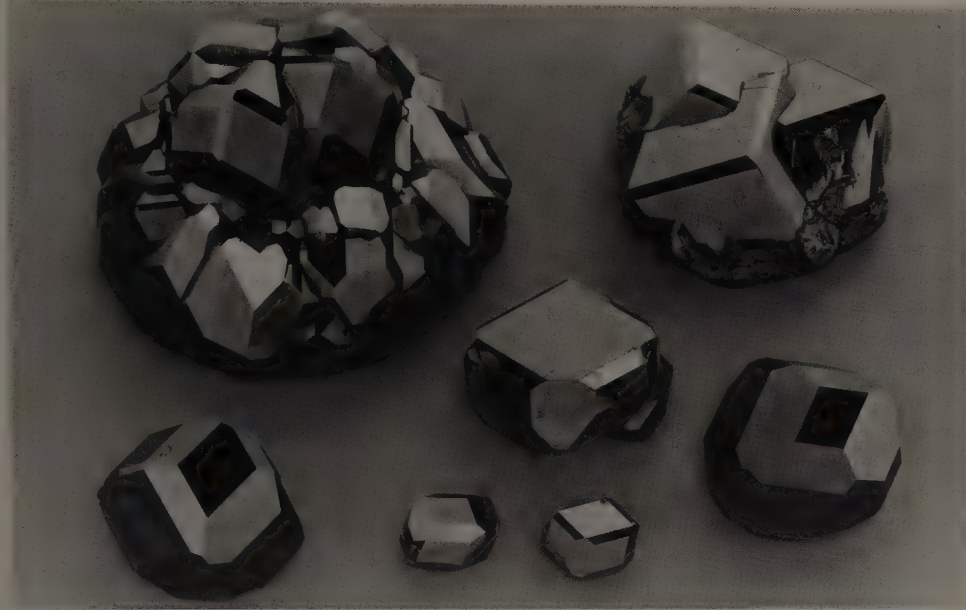
YAG (yttrium aluminum garnet) can be grown in various colors that make attractive gemstones.



Materials for bubble technology are somewhat esoteric. Here, from left to right, are orthoferrite, lithium ferrite, and magnetoplumbite—all grown at Bell Telephone Laboratories.



These crystals of γIG (yttrium iron garnet) were grown from a flux, and can be used in bubble technology or microwave applications.



These boules of GGG (gadolinium gallium garnet) were grown by the Czochralski technique. The photograph was taken through the entire length of a crystal such as those shown!



This large crystal of γIG (yttrium iron garnet) was grown from a flux by the Airtron Corporation.



**MOLYBDATES,
NIOBATES,
TANTALATES,
TUNGSTATES,
AND BANANAS**

The use of nonlinear optical materials has already been briefly discussed (page 71). In past years, one of the best of these materials was KDP. Many newer materials have proven far superior to KDP and similar crystals, such as ADP. One of these recent success stories is *lithium niobate*, which has a useful nonlinear optical coefficient ten times better than KDP. But lithium niobate has problems when used with certain types of lasers, and better crystals have therefore been sought. One crystal found superior to lithium niobate in many respects is *barium sodium niobate*, $\text{Ba}_2\text{NaNb}_2\text{O}_{15}$, whose unpronounceable acronym has led to the more fanciful name "bananas."

Lithium niobate and *lithium tantalate* are both strongly piezoelectric. *Calcium niobate* has been found excellent for microwave applications. Recent work on *strontium niobate* has revealed that this material has a nonlinear electro-optic effect 75 times greater than lithium niobate! *Barium niobate* has similar characteristics. Another useful crystal is *barium strontium niobate*.

Scheelite (*calcium tungstate*), when doped with rare earth elements, is a useful laser material. Scheelite and other tungstates are normally grown by the Czochralski method.

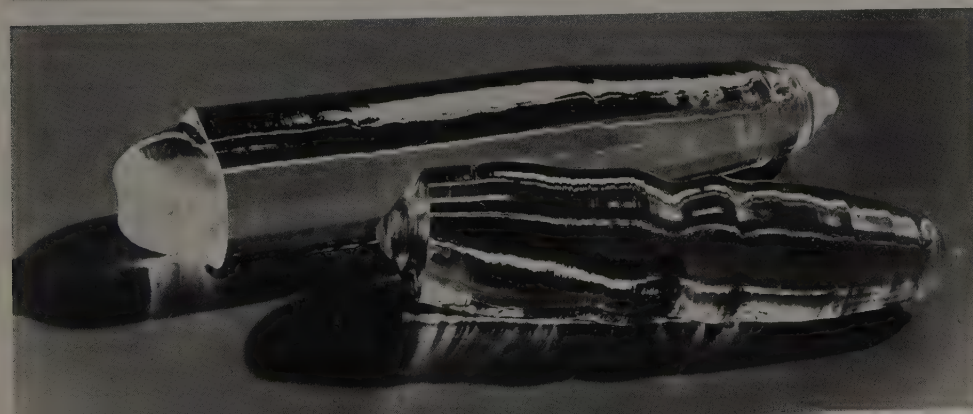
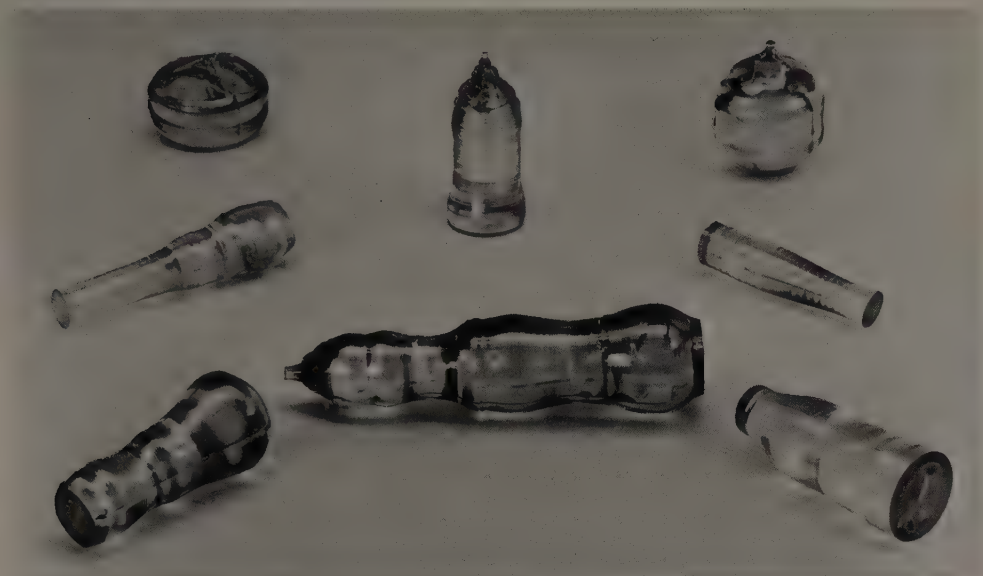
Lead molybdate is an efficient acousto-optic material used in control devices for lasers. *Bismuth germanium oxide* is strongly piezoelectric and elasto-optic, and is widely used in radar. *Potassium tantalate niobate* (KTN) is a useful laser modulator.

An example of the action of a laser modulator can be found in an experimental arrangement involving information transmission via laser beam. A high-speed digital information system was connected to a helium-neon gas laser, modulated by a lithium niobate crystal. This one laser transmitted data at high speed, without error, on a beam equivalent to 3,500 voice channels or two TV channels. The same system also was used successfully to demonstrate color TV transmission via laser beams. These tests did not use the full capacity of an optical beam, however, because the transmission involved only one channel sending 224 million bits of information per second.

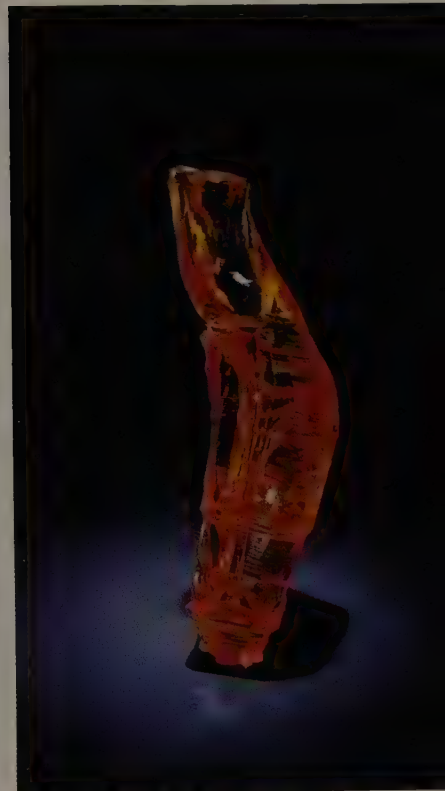
It is estimated that a neodymium-YAG laser could operate at 10,000 million bits per second, or almost forty times as great a data transmission capability! This would mean that the single laser beam could handle more than 140,000 voice channels! Even higher capacities will be available in the future.

Lead molybdate occurs in nature as the mineral wulfenite (left), usually in yellow, orange, or red crystals. The man-made equivalent (right) is gemmy, transparent, and yellow.

Lithium niobate crystals of exceptional size and transparency are grown routinely by the Czochralski method.



Bismuth germanium oxide is a spectacular deep orange color. The material is used in laser control devices.



Calcium tungstate (top) and calcium molybdate are regularly grown by the Czochralski method. Both materials are used in lasers.

*Man-made crystals are not only useful,
but can also be spectacularly beautiful.*

*This dendrite of silicon has no
commercial use, but is one of the
artistic masterpieces that occasionally
emerge from the laboratory.*



The Future

Solid-state technology advances at such a rapid rate that even textbooks explaining basic theory have to be rewritten every few years. Only a year (sometimes less) normally passes between the introduction of new theories and the emergence of devices based on them. By the time such devices are commercially popular, new ones are already reaching the production stage. This has given rise to the somewhat fatalistic statement: "if it works, it's obsolete."

The "brute-force" approach mentioned earlier ignores theory and simply relies on experimental observation to produce new devices. One such advance is the observation of laser action (or what seems to be) in the x-ray region of the spectrum. This work has met with wide skepticism from theorists because no ready explanation can be found for the observed effects. But if the experiments are reliable, the implications are truly awesome.

The x-ray laser would have enormous significance in all areas of science, one of the most obvious being holography. X-ray holograms would make it possible actually to photograph the atomic structure of crystals, revealing the marvels of nature's architecture in a way only dreamed of in recent decades.

Crystal growth has provided the mechanism whereby materials scientists, physicists, and engineers can "tailor-make" crystals with specific properties. In a sense, this represents the fulfillment of an ancient alchemical wish. But this "modern alchemy" is far from maturity. The next decade will see advances in the art not even imagined today.

Synthetic gems are becoming more and more popular, as natural gemstones are becoming scarcer. The day may not be far off when only synthetics will be available to the average person, the natural gems quickly disappearing into the hands of wealthy collectors. When that day comes it will probably be difficult, if not impossible, to distinguish natural from man-made gems without the most sophisticated laboratory analysis.

Man-made crystals are among the most valuable of industrial raw materials. They are incorporated in components built into almost every electronic and optical device made today.

Most of us may never see a transistor, a diode, or a laser. Nonetheless, we should be aware of the crystals glittering at the heart of most of the devices serving our modern electrified, transistorized, and automated civilization.

ACRONYMS

ADP	Ammonium Dihydrogen Phosphate
C-MOS	Complementary Metal Oxide Semiconductor
CZ	Czochralski
DCTL	Direct Coupled Transistor Logic
DTL	Diode Transistor Logic
ECL	Emitter Coupled Logic
EDT	Ethylene Diamine Tartrate
EFG	Edge Defined Film Fed Growth
ESS	Electronic Switching System
FAP	Fluorapatite
FET	Field Effect Transistor
GASH	Guanidinium Aluminum Sulfate Hydrate
GGG	Gadolinium Gallium Garnet
IC	Integrated Circuit
KDP	Potassium Dihydrogen Phosphate
KTN	Potassium Tantalate Niobate
LED	Light Emitting Diode
LSI	Large-Scale Integration
MIC	Microwave Integrated Circuit
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
MSI	Medium-Scale Integration
RAM	Random Access Memory
RC-network	Resistor-Capacitor Network
RCTL	Resistor Capacitor Transistor Logic
ROM	Read Only Module
RTL	Resistor Transistor Logic
SCR	Silicon Control Rectifier
SIS	Silicon on Insulating Substrate
SOAP	Silicate Oxyapatite
SOS	Silicon on Sapphire
SSI	Small-Scale Integration
T ² L-TTL	Transistor Transistor Logic
YAG	Yttrium Aluminum Garnet
YIG	Yttrium Iron Garnet

SOME OF THE TRADE NAMES USED FOR DIAMOND IMITATIONS

SYNTHETIC RUTILE	Wellington
Astryl	Zenithite
Brilliante	Jewelite
Diamothyst	
Gava Gem	YAG
Jarra Gem	Diamonique
Johannes Gem	Triamond
Kenya Gem	Diamonair
Kima Gem	Di'Yag
Kimberlite Gem	Linde Simulated Diamond
Lusterite	Diamonte
Miridis	Diamanite
Rainbow Diamond	Diamon-Brite
Rainbow Gem	Diabud
Rainbow Magic Diamond	Regalaire
Rutile	Diamone
Sappherized Titania	
Star-Tania	SYNTHETIC SPINEL
Tania-59	Alumag
Tiru Gem	Magalux
Titangem	Strongite
Titania	
Titania Brilliante	DOUBLET
Titania Midnight Stone	Carnegie Gem (synthetic spinel top and strontium titanate base)
Titanium	Laser Gem (synthetic sapphire top and strontium titanate base)
Titanium Rutile	
Titanstone	
Zaba Gem	
STRONTIUM TITANATE	
Bal de Feu	
Diagem	SYNTHETIC SAPPHIRE
Diamontina	Diamondite
Dynagem	Walderite
Fabulite	Crown Jewels
Kenneth Lane Jewel	Diamonette
Lustigem	Gemette
Marvelite	
Rossini Jewel	
Sorella	YTTRIUM ALUMINATE
Pauline Trigere	Diamonaura

THE CHEMICAL ELEMENTS AND THEIR ABBREVIATIONS

Actinium	Ac	Hafnium	Hf	* Praseodymium	Pr
Aluminum	Al	Helium	He	* Promethium	Pm
Americium	Am	* Holmium	Ho	Protactinium	Pa
Antimony	Sb	Hydrogen	H	Radium	Ra
Argon	Ar	Indium	In	Radon	Rn
Arsenic	As	Iodine	I	Rhenium	Re
Astatine	At	Iridium	Ir	Rhodium	Rh
Barium	Ba	Iron	Fe	Rubidium	Rb
Berkelium	Bk	Krypton	Kr	Ruthenium	Ru
Beryllium	Be	Lanthanum	La	* Samarium	Sm
Bismuth	Bi	Lawrencium	Lr	Scandium	Sc
Boron	B	Lead	Pb	Selenium	Se
Bromine	Br	Lithium	Li	Silicon	Si
Cadmium	Cd	* Lutetium	Lu	Silver	Ag
Calcium	Ca	Magnesium	Mg	Sodium	Na
Californium	Cf	Manganese	Mn	Strontium	Sr
Carbon	C	Mendelevium	Md	Sulfur	S
* Cerium	Ce	Mercury	Hg	Tantalum	Ta
Cesium	Cs	Molybdenum	Mo	Technetium	Tc
Chlorine	Cl	* Neodymium	Nd	Tellurium	Te
Chromium	Cr	Neon	Ne	* Terbium	Tb
Cobalt	Co	Neptunium	Np	Thallium	Tl
Copper	Cu	Nickel	Ni	Thorium	Th
Curium	Cm	Niobium	Nb	* Thulium	Tm
* Dysprosium	Dy	Nitrogen	N	Tin	Sn
Einsteinium	Es	Nobelium	No	Titanium	Ti
* Erbium	Er	Osmium	Os	Tungsten	W
* Europium	Eu	Oxygen	O	Uranium	U
Fermium	Fm	Palladium	Pd	Vanadium	V
Fluorine	F	Phosphorus	P	Xenon	Xe
Francium	Fr	Platinum	Pt	* Ytterbium	Yb
* Gadolinium	Gd	Plutonium	Pu	Yttrium	Y
Gallium	Ga	Polonium	Po	Zinc	Zn
Germanium	Ge	Potassium	K	Zirconium	Zr
Gold	Au				

* the RARE EARTH ELEMENTS.

Glossary

ACCELERATOR	A machine that increases the speed of electrically charged atomic particles. Such particles may attain high energies.
ACOUSTO-OPTIC MATERIAL	A material whose refractive index is affected by the influence of acoustic (sound) waves.
ACTIVATOR	A substance added to a material to make it glow when exposed to energetic radiation, such as ultraviolet light.
AUTOCLAVE	A machine that uses steam and fluids at high pressures and temperatures, for example in hydrothermal crystal growth.
BINARY DIGITS abbreviated BITS	Numbers in a counting system consisting of only two numbers: 1 and 0. Any decimal number can be represented by a string of ones and zeros.
BOMB	A vessel used for containing gases and liquids under high pressures and temperatures.
BOULE	A French term (literally meaning "ball") that was originally used to designate crystals grown by the Verneuil (flame fusion) technique. It now applies to any melt-grown synthetic crystal.
BUBBLES magnetic bubbles	Small regions (domains) within a host material, formed by applying a strong magnetic field. Bubbles are cylindrical in shape and circular in cross section, and can be moved about within the host material with magnetic fields.
CAPACITOR	An electric device capable of storing an electric charge.
CARAT	A unit of weight generally applied to gemstones, equal to one-fifth of a gram, or approximately 1/140 ounce.
COHERENT	The waves emanating from a source are termed coherent if they are in phase (which see) and of one wavelength.
COLLIMATED	Made to travel in parallel lines.
CORES	Small doughnut-shaped bits of specially made magnetic materials that are used in computer memories.
CRYSTALLITE	A minute (generally microscopic) crystal, such as one that has just begun to grow and enlarge in size.
DENDRITES	Branched and spiked crystals that sometimes resemble trees and ferns. These generally form because of the presence of impurities around a growing crystal during rapid crystal growth.
DIFFUSION	The slow migration of atoms through a solid, liquid, or gas.

DIODE	A vacuum tube containing two elements: a filament and an anode. This tube acts as a rectifier—that is, a device that allows current to pass in only one direction.
DISLOCATION	The line forming the boundary, within a crystal, of an area in which the crystalline pattern has been disturbed.
DISPERSION	The ability of a substance to separate white light into its component colors. Dispersion causes the color play seen in diamond.
DOMAINS	Regions of material that have certain characteristics, within a host material with different characteristics. Magnetic domains are magnetically aligned oppositely from the surrounding material.
DOPANT	An additive used to alter the physical properties of a substance. Dopants are added to a crystal while it is growing.
ELASTO-OPTIC MATERIAL	A material whose refractive index changes because of strain within it. Strain is the response of a material to an external stress.
ELECTRO-OPTIC MATERIAL	A material whose refractive index changes because of an applied electric field.
EPITAXY	The deposition of one crystalline material on top of another, in which there is a matching of the crystalline structures of the two materials.
EQUILIBRIUM FORM	The shape a crystal would assume if placed in an unchanging growth environment and allowed to grow for an indefinitely long time. This form would represent the shape most stable in the specified growth conditions.
FERRITES	Nonmagnetic materials (oxides) used in computers and other electronic applications.
FLASH TUBE	The coiled lamp that surrounds a laser rod in a laser. A flash of light from the coiled tube starts the optical chain reaction that produces a laser pulse within the rod.
FLUORESCENCE	The emission of radiation by a material after it absorbs radiation of higher energy. The emitted radiation is often visible light, and the input radiation ultraviolet light, electrons, or x-rays.
FLUX	A material that lowers the melting point of a material with which it is mixed. Fluxes are generally solid substances that become powerful solvents when melted.

FLUX GROWTH	In general, the growth of a crystal from a molten-salt solvent. In this respect flux growth is similar to growth from water solutions.
FREQUENCY	In wave motion, the number of waves that pass a fixed point in a given time interval. Frequency is expressed in terms of cycles (waves) per second. This unit is now called the Hertz. Thus, 100 Hertz (Hz) = 100 cycles per second.
GAMMA RAYS	Very high-energy radiation, produced in atomic reactions and present abundantly in deep space.
GEL	A spongelike network of a material such as silica (silicon dioxide) or gelatine, permeated by a liquid or a solution.
GROWN JUNCTION	A boundary created during the growth of a semiconductor crystal such as silicon. The junction separates zones within the crystal with different electrical properties. These are used in semiconductor devices.
HABIT	The characteristic external shape of a specific type of crystal.
HEAT OF CRYSTALLIZATION	The heat that must be lost by rapidly moving atoms and molecules in order for these particles to settle into the relatively fixed positions characteristic of a crystal structure.
HOLOGRAM	A two-dimensional photographic medium exposed in order to store the image of a three-dimensional scene. When illuminated in a special way the scene reappears, retaining its dimensional qualities.
HOLOGRAPHY	The art of storing and recreating three-dimensional images on flat photographic media.
IMPLANT BIOTELEMETRY	A procedure for obtaining information about the internal condition of an organism. It involves the surgical implantation (attachment) of a radio-transmitting device that continually transmits information about the organism to a remote receiver.
INCLUSIONS	Gas bubbles, liquid drops, or solid particles that are trapped in a crystal as it grows. Inclusions consist of material foreign to the crystal in which they are found.
IN PHASE	Waves consist of crests and troughs. For waves to be in phase their crest and troughs must coincide.
INTEGRATED CIRCUIT	A solid-state device consisting of a slice of semiconductor material (such as silicon) on which have been created numerous interconnected circuit elements (such as transistors, capacitors, switches, and resis-

	tors). The key usefulness of the integrated circuit (IC) lies in the number of circuit devices that can be created in a very small area.
LARGE-SCALE INTEGRATION	The miniaturization of already-compact integrated circuits into highly sophisticated circuits capable of complex jobs.
LASER	Acronym for <i>Light Amplification by Stimulated Emission of Radiation</i> . The laser produces a special kind of light that is monochromatic (one color) and coherent and collimated (does not spread out much with distance from the source).
MAGNETOPLUMBITES	Compounds with the general formula $PbX_{12}O_{19}$, where Pb is lead, and X is generally gallium (Ga), aluminum (Al), or chromium (Cr). Magnetoplumbites are useful in bubble memory systems.
MASER	Acronym for <i>Microwave Amplification by Stimulated Emission of Radiation</i> . The maser produces a microwave signal, in a manner similar in principle to the laser.
MODE LOCKING	A method of synchronizing waves of light traveling within a laser rod. This produces a very short pulse that contains the full energy of the beam.
MODULATION	The impressing of information onto a carrier signal. An example is speech: the sounds consist of alternating layers of compressed and rarified air that travel from throat to ear. AM radio transmission is a code created by varying the amplitude (strength) of the transmitted signal. In FM transmission, the frequency of the signal is varied in a coded manner.
MONOCHROMATIC	Consisting of a single frequency, or color.
MORPHOLOGY	The general study of crystal forms—that is, the geometric shapes that bound the exterior of a well-formed crystal.
NONLINEAR OPTICS	A branch of optics that deals with materials whose optical properties change depending on the intensity of light passing through them.
NUCLEATION	The formation of crystal nuclei, tiny clusters of atoms and molecules that are just barely stable in their particular environment.
ORTHOFERRITES	Compounds with the general formula $XFeO_3$, where Fe is iron and X can be one of several elements. In nature, the compound $FeFeO_3$ is the mineral hematite.

	Rare earth orthoferrites (where X is a rare earth element) are used in bubble memory systems for computers.
OSCILLATOR	A device that produces vibration, or generates waves of variable frequency.
PARABOLIC	Having the shape of a parabola, which is a special type of curve with interesting properties. Parabolic mirrors are capable of focusing light entering them at a single point.
PHOSPHOR	A substance that emits light when struck by radiation.
PIEZOELECTRICITY	An electric current generated by subjecting particular types of crystals to pressure or mechanical shock.
PIEZO-OPTIC	The property of changing refractive index with the application of an external stress, such as pressure.
PLASMA	A state of matter characteristic of extremely high temperatures, in which electrons have been stripped away from their parent atoms. The plasma thus consists of a gas of negatively charged particles (electrons) and positively charged particles (ions).
POLARIZED	Oriented in a single direction. In the case of light, polarization refers to vibration of the light waves in a single plane.
POLYCRYSTALLINE AGGREGATE	A mass of crystals joined together in an essentially random arrangement.
PRECIPITATE	Material that has separated from a solution or suspension. <i>Precipitation</i> is the process by which this occurs.
Q-SWITCHING	A means of creating a powerful light pulse from a laser. The technique involves the use of some type of shutter that opens when a pulse has built up sufficient intensity.
RECTIFICATION	The conversion from AC (alternating current, in which the direction of electron flow reverses periodically) to DC (direct current, in which electrons always flow in one direction), or vice versa.
RECTIFIER	A device that converts AC to DC current or vice versa.
REFRACTION	The bending of light when passing from one medium into another, such as from air into glass or water. This bending results from an actual change in the velocity of light, and makes an object partially immersed in a glass of water appear to be bent or broken.

REFRACTIVE INDEX	A number that indicates the relative refractive power of a substance—that is, the degree to which light is slowed down in traveling through it.
RESISTOR	An electric device that offers resistance to the flow of an electric current. A simple light bulb is a resistor. The “friction” (resistance) of electrons in the filament of the bulb causes the filament to glow, giving off light.
RESONANCE	A situation in which two or more vibrating bodies vibrate at the same frequency. When this occurs, a small vibrating body is capable of forcing the vibration of a much larger body nearby, resulting in great amplification of the vibration.
RESONATOR	A device used to produce synchronization of waves, creating resonance.
SCINTILLATION COUNTER	A device that measures radiation by means of a special type of crystal. This crystal “scintillates,” or gives off light when struck by radiation. These flashes are amplified and counted to give a measure of the amount of radiation present.
SCREW DISLOCATION	A line along which atoms in a crystal structure have been displaced so as to form a kind of “spiral ramp” within the crystal. The crystal structure, which would normally consist of parallel layers of atoms, thus has the form of an endlessly spiraling sheet of atoms.
SEMICONDUCTORS	A large class of compounds having electrical conductivities intermediate between those of metals and insulators.
SOLAR CELLS	Plates consisting of slices of semiconductors, such as silicon, that convert light into electricity.
SOLIDIFICATION	The process of formation of a solid, or crystalline material, from a liquid, a vapor, or another solid.
SOLID STATE	Consisting of devices containing chips or slices of single crystals.
SOLUTE	A substance that dissolves in another substance.
SOLVENT	A substance that dissolves another substance. When two or more such substances are mixed, the solvent is considered to be whichever is present in greater amount.
SPECTRUM	The array of various types of radiation, as differentiated according to wavelength (corresponding to the color of light, for example) or frequency (the numbers that distinguish between radio stations are frequencies of radio waves).

SPECTROPHOTOMETER	A device for measuring the intensity of light of various specific frequencies. It is useful as an analytical tool when employed to determine the loss of light intensity because of absorption by a sample compound or solution.
SPURIOUS NUCLEATION	The formation of unwanted crystals in a growth vessel containing a single, large crystal being grown. This is essentially a random process.
SUBLIMATION	The process by which a material passes directly from the solid to the vapor state.
SUBSTRATE	A substance upon which a different material is deposited, as from a vapor or solution.
SUPERSATURATED SOLUTION	A solution containing (at a specific temperature) more dissolved material than would normally be stable at that temperature.
SWITCH	A device that changes the connection in an (electric) circuit. Simple switches have only two positions: on or off.
TRANSDUCER	A device that converts one form of energy into another. The ordinary light bulb is a good example. It converts electric energy into light and heat.
TRIODE	A vacuum tube containing three elements: a filament, an anode, and a grid. This tube design allows it to act as an amplifier of electric currents that pass through the tube.
VAPOR STATE	A state of matter in which atoms and molecules are free to fly about through space (such as in a gas).
WHISKERS	Fine, hairlike crystals that contain few defects and dislocations. As a result they have mechanical strengths approaching those predicted by theoretical calculations, which are much higher than those observed in bulk materials.
ZONE REFINING	A crystal purification technique in which a molten zone is made to sweep back and forth along a crystal. This molten zone traps impurities, leaving purer material to solidify behind it.

How to Grow

Crystals

at

Home

Ice crystals are not the only ones that can be grown at home. Sugar crystals (rock candy) are quite easy to grow. In addition, sugar is inexpensive, readily available, and dissolves easily in water at low temperatures.

SUGAR CRYSTALS

The best way to grow sugar crystals is to put about 2 cups of sugar into about 4 cups of water in a pot on the stove. As the mixture heats, add more sugar slowly and stir the solution. You will have to add quite a bit of sugar because, as the water becomes hotter, more and more sugar is able to dissolve. Keep adding sugar and stirring vigorously until the point is reached when the last bit of added sugar does not dissolve, even after the solution has been stirred for a few minutes. The solution is now termed saturated at the boiling point of water and contains as much dissolved sugar as it possibly can at that temperature. But it cannot hold the same amount in solution at room temperature. If it could, it would have been possible to dissolve all of the sugar without ever heating the water.

What will happen to the excess sugar as the solution cools? The only thing that

can happen is that it is forced to come back out of solution, and it does so in the form of crystals.

After the hot solution cools a bit, pour it into a jar. Cover the jar and put it on a shelf where it will not be disturbed for a few days. Crystals will be visible on the walls of the jar after 24 hours, and they will increase continually in size during the following week. You can expect to "harvest" sugar crystals up to about one-half inch across. Repeat the experiment by adding a few tablespoons of sugar (to replace the crystals you took out) and reheating. More crystals will form, on cooling, in the same way as the first batch.

Another crystalline material that is found in every home is salt. Table salt is sodium chloride, found in nature as the mineral halite. Halite crystallizes in cubes, and also breaks up into cubes when crushed. If you examine the salt from a saltshaker through a magnifying glass, you will see that it is made up of these tiny cubes.

Salt dissolves in water—but not nearly so easily as sugar. This is because the solubility of sugar is much higher than that of salt. You will also find that very little additional salt will dissolve when the water is heated. This is quite different from the situation with regard to sugar, where much more is dissolved at higher temperatures. These relationships can be expressed in the form of simple graphs, assuming a fixed quantity of solvent (water). The curves show the solubility of materials (here, sugar and salt) as a function of temperature. It is easy to see that sugar is much more soluble than salt at room temperature, and also has a steeper *solubility curve*; that is, more sugar will dissolve at higher temperatures than will salt.

The solubility of any solute in any solvent can be expressed with such curves. But the graph shows more than relative solubilities. It gives an indication of how best to grow crystals of a specific substance. It is obvious that one can easily make a supersaturated solution of sugar by dissolving as much as possible in hot water and letting the solution cool. The excess material will simply crystallize out at lower temperatures.

The case of salt is more troublesome, however. It is not easy to make a supersaturated solution by heating, because not much additional salt will dissolve in heated water. To grow salt crystals it is therefore more prudent to use another approach: evaporation.

This can be done slowly, in a controlled manner. As the water evaporates, it supersaturates the solution in small increments. The solution never gets very supersaturated, however, because it continually dumps excess solid material. Crystal growth will thus continue as long as the solution lasts.

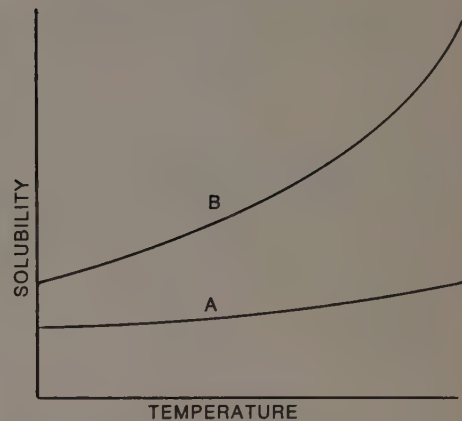
Growth by evaporation is best carried out in a basement or closet where the temperature doesn't vary too much and there are no drafts. Salt is reluctant to form good crystals no matter how much care you take, but there are better chemicals available that produce splendid crystals without great trouble.

SALT CRYSTALS

*This large crystal of maple sugar—
2 inches across—was found at the
bottom of a can of maple syrup.*



*A solubility curve shows the change in
solubility of a substance with changing
temperature. (Here, it is assumed that
water is the solvent.) A substance such
as table salt (A) is not much more
soluble in hot water than in cold
water; just the opposite is true in the
case of Rochelle salt (B).*



*Seed crystals are easily grown by
evaporation of a solution in a shallow
dish. These are alum crystals.*



OTHER CHEMICALS TO TRY

Two chemicals that are available at drug stores, or through chemical companies, are Rochelle salt (sodium potassium tartrate) and alum (potassium aluminum sulfate). Both are inexpensive, harmless, and form beautiful crystals. The following directions for growing these crystals will work just as well with nearly any chemical you may try.

Before starting, it should be emphasized that crystal growing is sure to be a disappointing experience unless scrupulous cleanliness is maintained in all operations. At the start, all pots, jars, and utensils involved in the growth experiment must be washed and rinsed thoroughly. That includes the hands.

The first objective is to prepare a saturated solution. Distilled water is preferable for crystal growing, but tap water will do. The desired amount of water is poured into the heating vessel and warmed to the correct temperature (perhaps 10–20 degrees above room temperature). While the water is heating, the solute can be added slowly, with constant stirring. Less and less should be added as it becomes obvious that it is taking longer and longer to dissolve. It doesn't matter if some solid remains at the bottom after continued stirring, because this will be filtered out. When the solution is cool enough to handle comfortably, pour it slowly through some filter papers (or a napkin) into the clean growth jar (such as a mason jar). Cover the jar and leave it in a quiet place.

In a few days the bottom will have a crust of excess solid that has precipitated, and the solution will be saturated. Save the solid material because it can be used in later growing experiments.

Take some of this saturated solution and put it into a shallow dish. Let it evaporate for a few days. Tiny seed crystals will form spontaneously. Remove the largest, and then filter the solution. The remaining smaller seeds can then be added to the chemical filtered from the jar on the first day. Put the few large seeds and the filtered solution back into the shallow dish and let the solution continue to evaporate. The seeds will grow in size until they can be handled comfortably. At this stage, cleanliness is especially critical.

A large seed crystal should next be tied to a string, preferably with several loops of thread in different directions, to form a kind of basket under the crystal. This seed will be the nucleus of a large crystal to be prepared in the mason jar. Either of the alternate methods (cooling or evaporation) can be used.

GROWTH BY EVAPORATION

To grow a crystal by evaporation, tie the loose end of the thread to a tongue depressor or a pencil. Lay the pencil across the top of the jar in such a way that the crystal hangs down into the solution, about midway between the top surface of the solution and the bottom of the jar. The string can be looped about the pencil and tied in this position. The jar is then placed in a closet or in the basement, in a spot away from drafts, open windows, or heaters.

Cover the jar loosely with some cheesecloth to prevent dust from entering. Dust

particles act as nuclei for the precipitation of small crystals. Your goal is to have all the material that precipitates from the solution settle only on the crystal on the string.

This is the reason for strict cleanliness. As the chemicals and seed crystals are handled, small crystallites adhere to the fingers. These can fall into the growth jar and act as centers for crystal growth. Such undesired growing crystals would take up material that should be joining the main crystal. The small crystals are superfluous and should be removed if they start to become abundant or very large. If the jar begins to fill up with many small crystals, it is a good idea to remove the seed crystal, pour the solution into a small glass, wash out the growth jar, and then return the solution and crystal to it.

GROWTH BY COOLING

For growth by cooling, start with a saturated solution and add solid material (a few tablespoons will do). This can be the solid recovered in the initial experiment to prepare a saturated solution. Dissolve this material in the saturated solution by heating, and filter the solution when it is cool. Tie a seed crystal and suspend it in the solution as already described. Cover the jar and set it in a quiet place. By the next day, considerable growth should be evident on the seed. The crystal will continue to grow until the excess solid is precipitated and the solution is again just saturated.

The solution will continue to deposit material on the seed crystal, however, if the jar is opened and the water can evaporate. One can thus start a crystal rapidly by cooling a supersaturated solution. Continued growth is achieved by either repeating the cooling process and adding additional solid, or by evaporation.

FREQUENTLY ENCOUNTERED PROBLEMS

Many factors conspire against growing crystals. Sudden changes of temperature, even ones you are not aware of, wreak havoc with the crystal. Such fluctuations may produce veils and milky areas or layers that make the crystal opaque. In starting a seed crystal you may go away thinking everything is fine, only to return and find your seed gone! The solution was a bit too warm and the seed dissolved. There is a way to tell, though, when the crystal is growing and when it is dissolving.

If you place a strong light behind the jar containing the growing crystal, it is possible to see faint currents moving around the crystal. These currents, which have the appearance of ripples in a pane of low-quality window glass, result from differences in density in the solution. If currents seem to be descending from the crystal, this is an indication that the crystal is dissolving. Material from the crystal is being added to

the solution surrounding it. The resulting liquid is now denser than the solution elsewhere, and thus it descends.

On the other hand, if currents seem to be rising from the crystal, this is a good sign, indicating that material is being deposited on the crystal. If the crystal is clearly dissolving in what appears to be a cool solution, remove it and let the solution evaporate for a few days. This will insure that the solution is truly saturated, and will allow growth of the seed crystal that is returned to it.

Any water-soluble chemical can be used for these growth experiments. But, as we have seen in the case of salt, the specific method to be used depends on the solubility curve of the material. With an unfamiliar compound, this is a matter of trial and error. The solubility curve is not especially difficult to determine, but it would require some laboratory equipment that is not generally found in the home.

Some frequently encountered problems that affect the appearance of your crystals can easily be corrected. One common complaint is a crystal full of veils, flaws, and milky areas. This probably results from variations in temperature, as mentioned earlier. Such variations can be prevented by putting the entire growth jar into a larger vessel full of water at room temperature (taking care that the water does not spill into the growth jar!). The outer "water bath" insulates the growth jar against sudden temperature changes.

If you are growing by cooling a supersaturated solution, the crystal that forms may be cloudy or even deformed. This is because of over-rapid growth, and it can be prevented by cooling the solution more slowly. To accomplish this with a "water bath," heat the water in the outer vessel to the same temperature as that of the growth solution and let the two solutions cool together. Slower growth can be achieved by heating the solution to a lower temperature and dissolving less additional material above saturation. This modest supersaturation will take longer to equilibrate, will yield better crystals, and can be repeated as often as desired.

To sum up: watch the density currents when starting a seed crystal to make sure that the seed will not dissolve. Make sure all utensils and your hands have been washed before handling solutions and crystals. Keep temperature changes slow and moderate. Don't continually disturb the crystal by removing it from the solution to examine it—and you may be surprised at the high quality of the results you get on your very first attempt. Crystal growing is fairly easy, once you learn what to avoid.

Index

- Acheson, Edward G. 73
Acousto-optic 71
Activated 81
ADP 36, 70, 86, 90, 95
Alexandrite 49
Alternating current 57
Alum 36, 107
Alumina 47
Aluminum 24
Aluminum oxide 47
Amethyst 51
Amplifier 56
Amplification 64
Annealing 31
Aristotle 13
Anode 56
Antioch College 17
Aquamarine 51
Arc imaging 31
Atom 9, 20, 24, 35
Atomic bonds 10
Autoclave 38, 51, 77
Bananas 90
Bardeen, John 57
Barium fluoride 81
Barium niobate 90
Barium sodium niobate 90
Barium strontium niobate 90
Barium titanate 40, 70, 86
Barium yttrium fluoride 81
Bell Telephone Laboratories 17, 35, 46,
56, 59, 71, 79, 89
Beryl 40, 51
Beryllium 24
Binary digits (bits) 72, 90
Bismuth germanium oxide 90, 91
Bomb 37
Boron-in-epoxy 24
Boron oxide 39, 87
Boule 31
Brattain, W. H. 57
Bridgman, P. W. 27
Bridgman-Stockbarger method 27-29,
81, 85
Bromellite 40
Brush Laboratories 17
Bubble inclusions 49, 51
Bubble technology 54, 71-72, 87, 89
Cadmium 24
Cadmium fluoride 81
Cadmium selenide 29, 70
Cadmium sulfide 23, 24, 29, 70
Cadmium telluride 29
Cady, W. G. 75
Calcium fluoride 81
Calcium fluor-phosphate 70
Calcium niobate 70, 90
Calcium tungstate 70, 90
Carbon 43
Cat whisker 78
Cesium iodide 29, 81
Channel filters 76
Chatham, Carroll 51
Chemical reactions 36
Citrine 50
Coherent light 64
Collimated light 64
Communications 59
Composites 24, 74
Computers 61, 71
Continuous wave (cw) 69
Copper 24
Copper sulfate 36
Cores 71
Cristallogtechnie 14
Crowningshield, Robert 46
Crucible 31, 33, 39, 43
Crystal faces 9
Crystal physics 21
Crystal pulling 31, 32
Crystal structure 10, 20, 93
Crystallite 34, 35, 107
Cultured quartz 17, 77
Curie, Jacques 75
Curie, Pierre 75
Czochralski, J. 31
Czochralski method 31-33, 46, 78, 83,
90
De Beers Consolidated Mines Ltd. 45
Defects 21, 24
de l'Isle, Romé 14
De Forest, Lee 56
Dendrites 23-25, 92
Density currents 108, 109
Diamond 15-16, 18, 40, 42-45, 95
Diffusion 36, 79
Diode 56, 75
Direct current 57
Dislocations 21, 22, 24
Dispersion 52
Domains 71, 72
Dopants 50, 73, 81, 87
Doping 50, 70, 79, 80
Driving force 21, 34
Edge-defined film-fed growth 85
EDT 36, 86, 95
Elasto-optic 71
Electric furnace 73
Electrocardiography 62
Electronic switching system 60
Electrolysis 36
Electro-optic 71
Emerald 18, 46, 51-52
Epitaxial junctions 79
Epitaxy 75, 79
Equilibrium form 36
Extrinsic semiconductor 57
FAP 70, 95
Feed material 37
Feldspar 37
Ferrites 71
Fiberglass 24
Filiform crystals 24
Fire 52
Flame fusion 15, 29, 46
Flash tube 69
Float zoning 34, 35, 79
Fluorescence 69
Fluorite 28, 81
Flux growth 39-41, 46, 83, 85, 87
Fluxed-melt growth 39
Frémy, Edmund 15, 29, 46
Fusion 67
gcc 87, 89, 95
Galena 78
Gallium arsenide 41, 70, 80
Gallium aluminum arsenide 80
Gallium indium phosphide 80
Gallium phosphide 40, 70, 80
Garnet 40, 54, 70, 72, 87
Gaseous cracking 75
Gaudin, Marc 15, 45
Gelatine 36
Gel growth 36
Gems 9, 15, 18, 42-53, 93, 95
General Electric Co. 16, 42, 43
Geneva rubies 45
Germanium 54, 56, 75, 78-80
Gilbert, William 13
Gilson, Pierre 51
Glass 11, 42, 83
Goshenite 51
Graphite 16, 31, 39, 43
Greenockite 23
Grid 56
Growth lines 49
Growth medium 21, 22
Habit 36
Halides 29, 81-83
Halite 104
Hannay, J. B. 43
Harmonic frequency 76
Haüy, René-Just 14

- Heat of crystallization 24
Heliodor 51
Holden, Alan 35
Hologram 67, 68, 93
Holography 67, 68, 93
Hughes Aircraft Co. 64
Hydrothermal growth 37-39, 46, 85
Hypo 35
Ice 11, 14, 26, 103
I. G. Farbenindustrie 51
Igemerald 51
Imitation 11, 42, 53
Implant biotelemetry 61
Impurities 29, 34, 37, 42, 57, 70, 79
Indium antimonide 70
Indium phosphide 70
In phase 64, 69
Integrated circuits 58-63
Intrinsic semiconductor 57
Iodine 23
Iridium 31, 39
KDP 36, 86, 90, 95
KRS-5 28, 81
Kyropoulos, S. 33
Kyropoulos technique 33
Langevin, Paul 75
Lanthanum fluoride 81
Lapis lazuli 49
Large-scale integration 61, 95
Laser 18, 54, 55, 63-71, 81, 83, 90, 93
Laser gyroscope 65
Laser ranging 65
Laser welding 65
Lead fluoride 39, 87
Lead iodide 87
Lead molybdate 90
Lead oxide 39
Lead selenide 29, 70
Lead sulfide 29, 78
Lead telluride 29
Lead zirconate 40
Leblanc, Nicolas 14
Lechleitner, J. 52
Light-emitting diodes 80, 85, 95
Lithium fluoride 81
Lithium niobate 90
Lithium tantalate 90
Little, J. B. 79
Long-range order 9, 20
Madeira topaz 50
Magma 26
Magnesium aluminate 40
Magnesium oxide 40, 70
Magnetic bubble memories 71
Magnetoplumbites 87, 89
Maiman, T. H. 64
Maser 64
Medicine 61-62
Melt growth 26
Metal oxide semiconductor 83
Microelectronics 60
Microwaves 63-64, 87
Mineral 10, 11, 13, 20, 37
Mixture 35
Mode locking 69
Modulation 67, 70-71, 86, 87
Moissan, Henri 15, 43
Molecule 9, 35
Molten-salt growth 39
Monochromatic light 64
Morganite 51
Morphology 10
Nacken, Richard 17, 51
Nassau, Kurt 46
Natural crystals 11
Nicholson, A. M. 75
Nickel oxide 40
Niobium oxide 24
Nonlinear optics 70, 90
Nucleation 35
Nuclei 108
Obreimov 27
Opal 18
Optoelectronics 85
Orthoferrites 71, 72, 87, 89
Oscillators 75-76
Padparadscha 45
Parabolic mirror 31
Periclase 40
Pfann, W. G. 79
Phase equilibria 39
Phosphor 69, 80
Photosensitive coating 59
Piezoelectric 75, 86
Piezo-optic 71
Plasma torch 31
Platinum 31, 40
Plumboferrites 72
Point-contact rectifier 78
Polarized 71
Polycrystalline 26, 78
Potassium aluminum sulfate 107
Potassium bromide 81
Potassium chloride 81
Potassium fluoride 39
Potassium tantalate niobate 90
Pound, R. V. 63
Pulse mode 69
Purcell, E. M. 63
Pyrite 24
Q-switching 69
Quartz 13, 16-18, 31, 37, 50-51, 75-77, 79
Radar 62-63, 78
Reconstructed rubies 46
Rectification 57
Rectifier 78
Refraction 70
Refractive index 70
Resonance 76
Rochelle salt 36, 75, 86, 107
Rock 26
Rock candy 35, 104
Rotary crystallizer 35, 36
Ruby 11, 15, 18, 29, 30, 33, 42, 45-49, 83
Ruby spinel 49
Rupture discs 39
Rutile 48, 52, 53, 95
Salt 35, 36, 105
Sapphikon 84, 85
Sapphire 18, 24, 29, 33, 37, 40, 45-49, 53, 83, 95
Saturated solution 34, 35, 107
Sawyer Research Products Co. 17
Schafhaütl 16
Scheelite 90
Schmid-Viechnicki technique 85
Scintillate 81
Screw dislocations 21
Seed crystal 14, 20, 21, 27, 107
Seeding 40
Semiconductor 57
Semiconductor diode 57, 74
Semiconductor laser 70
Shear mode 76
Shockley, William 56, 79
Shubnikov, A. V. 27
Silica gel 36
Silicon 18, 33, 54, 78-80, 85, 92
Silicon carbide 73-75, 80
Snowflakes 11, 24
Sodium chloride 105
Sodium iodide 29, 62, 81
Sodium nitrate 36
Sodium niobate 40
Sodium potassium tartrate 107
Sodium thiosulfate 35
Solar cells 83
Solidification 26
Solid state 11, 57
Solubility 34, 105
Solubility curve 105, 106
Solute 34, 35
Solution growth 34-36, 39, 75, 86, 104-109
Solvent 34
Solvent evaporation 21, 39, 40, 106
Sonar 75, 86
Spectrophotometer 81, 83
Spinel 18, 29, 30, 47, 49-50, 53, 85, 95
Spodumene 37
Spurious nucleation 34
Star sapphire 18, 48

Steno, Nicolaus 14
Stockbarger, D. C. 27
Striae 49
Strontium molybdate 70
Strontium niobate 90
Strontium titanate 53, 95
Sublimation 75
Sugar 34, 35, 36, 104
Sulfur 36
Supersaturated solution 34, 35, 40, 105
Tammann, G. 27
Tantalum 24
Tantalum oxide 24
Teal, G. K. 79
Telephone switching 59-61
Texas Instruments Co. 79
Thallium bromo-iodide 28, 81
Thin films 23
Tin oxide 24
Titania 52
Topaz 37
Townes, Charles 64
Transducer 77
Transistor 18, 54, 56-63, 79
Transportation 62-63
Triode 56, 59
Tyco Laboratories 85
Ultrasonic 75
Union Carbide Corp. 51, 83
Vacuum tubes 56, 75, 78
Vapor deposition 59, 72, 75, 85
Vapor growth 23-25
Vapor pressure 23
Verneuil, Auguste 15, 29, 46
Verneuil method 15, 29-31, 46, 83
Vibrational frequency 76
Volatile 23
Voltage 57, 74
Water bath 109
Wavelength 64
Whiskers 24, 74
YAC 40, 42, 53, 70, 87, 88, 90, 95
YIG 40, 41, 54, 72, 87, 88, 89, 95
Yttrium aluminate 53, 70, 95
Yttrium vanadate 40, 70
Zerfass 51
Zinc 24
Zincite 37
Zinc oxide 70
Zinc sulfide 24, 70
Zircon 18
Zirconium oxide 24
Zone growth 33
Zone refining 33, 78, 79

OTHER *Smithsonian Institution Press*

TITLES OF INTEREST . . .

THE SMITHSONIAN INSTITUTION

Narrative by Walter Karp. Published in association with the editors of *American Heritage* magazine.

This handsome volume tells of the strange bequest under which the Smithsonian Institution was founded, its early years, and its vast reputation among scholars around the world. Over 175 illustrations, many in full color, document the wide diversity of the Smithsonian's activities—its famed collections and its scholarly research in science, technology, history, and art.

125 pages 110 b&w, 72 color illustrations \$2.95

GEMS IN THE SMITHSONIAN

By Paul Desautels, Curator, Division of Mineralogy

A lavishly illustrated book based on the Smithsonian Institution's National Gem Collection, which includes the world famous Hope Diamond and the renowned Star of India. It covers many aspects of gemology, techniques of gem cutting, and gem lore.

74 pages 41 color plates 17 b&w illustrations \$6.95 cloth, \$2.50 paper

001000

SALE PRICE