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**Factors Related to Laboratory
Production and Evaluation
of Berlinite Crystal**

By D. J. MacDonald

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm ²	square centimeter	mol/L	mole per liter
cm/s	centimeter per second	MPa	megapascal hour
C/N	coulomb per newton	m/s	meter per second
g	gram	nm	nanometer
g/cm ³	gram per cubic centimeter	N/m ²	newton per square meter
K	kelvin	pct	percent
kJ/mol	kilojoule per mole	ppm	part per million
kW·h/kg	kilowatt hour per kilogram	wt pct	weight percent
L	liter	°C	degree Celsius
M	molar concentration	°C/d	degree Celsius per day
MHz	megahertz	\$/kg	dollar per kilogram
mm	millimeter	¢/kW·h	cent per kilowatt
mm/d	millimeter per day		

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FACTORS RELATED TO LABORATORY PRODUCTION AND EVALUATION OF BERLINITE CRYSTAL

By D. J. MacDonald¹

ABSTRACT

This U.S. Bureau of Mines report reviews published information on synthetic berlinite (AlPO_4) and suggests experimental conditions requisite for its production. Berlinite is a piezoelectric material with potential use as a substitute for quartz in the crystal oscillators, which are components of electronic and electroacoustic equipment.

Information gathered here (mostly from published sources) includes historical background, physical properties, end-use applications, criteria of quality, and physio-chemical factors involved in berlinite crystal growth. It is concluded that growing large high-quality berlinite crystal would require high-purity starting materials in an autoclave equipped with a noncorrodible liner and operated with temperature control of ± 0.005 °C over a range of 250 to 350 °C.

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INTRODUCTION

DISCOVERY OF NATURALLY OCCURRING BERLINITE AND EARLY EXPERIMENTS ON SYNTHETIC BERLINITE

As part of the U.S. Bureau of Mines' (USBM's) mission to help ensure that the United States has an adequate supply of mineral-based materials, scientists at the USBM's Reno Research Center did a literature survey and conducted preliminary experiments on the formation of berlinite (AlPO_4), a potential substitute for quartz crystal in electronic and electroacoustic applications.

The mineral berlinite was first described in 1868 after its discovery in a Swedish iron mine and was named after N. J. Berlin, a pharmacologist at the University of Lund in Sweden. The natural material is massive and granular (1).² Berlinite, unlike quartz, does not occur naturally in macrocrystalline form. By 1941 it was established that the mineral is chemically identical with anhydrous aluminum phosphate and isostructural with quartz ($\alpha\text{-SiO}_2$) (2).

Development of quartz-crystal oscillators for radio communications equipment in World War II led to a search for other materials that possess the useful piezoelectric property of quartz but which might be more readily available than quartz, which at that time was produced only from natural sources located outside the United States. One such material is berlinite, which could potentially be produced synthetically from inexpensive materials in virtually unlimited quantity. Properties of synthetic berlinite and methods of growing berlinite crystals by a hydrothermal method were investigated by the U.S. Army Signal Corps Engineering Laboratories and were described in a 1954 publication (3).

At about that time, development of synthetically grown quartz crystals for use as crystal oscillators proved successful on a commercial scale. Synthetic quartz met the need, and as a consequence, work on berlinite lay dormant for the next 20 years.

SYNTHETIC BERLINITE

Since about 1976 there has been renewed interest in berlinite as an oscillator or electroacoustic material, with emphasis on the growth of large crystals (more than 100 mm long) having favorable physical properties.

Researchers have grown crystals of berlinite from aqueous solutions of phosphoric acid saturated with aluminum phosphate confined under pressure at temperatures from 140 to 270 °C. Growth of berlinite from a

molten salt medium is not considered feasible because of its high melting point, >1,500 °C.

For growth of berlinite from aqueous solution, it is necessary that the solution be strongly acidic, otherwise precipitation of basic aluminum phosphates, such as the mineral wavellite [$\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$], or augelite [$\text{Al}_2\text{PO}_4(\text{OH})_3$], or trolleite [$\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$], would be expected rather than berlinite. Similarly, the solution must be high in phosphate and low in other anions, so as to avoid formation of solids, such as amblygonite (LiAlPO_4F).

PIEZOELECTRIC PROPERTIES

A solid material is said to be piezoelectric if the application of a mechanical stress induces a net separation of positive and negative electric charges within the solid. The converse is also true of a piezoelectric solid, wherein the application of an external electric field causes a mechanical deformation of the material. The effect, first discovered by Pierre and Paul-Jacques Curie in 1880, is exhibited by any crystalline solid, which lacks a center of structural symmetry (4). The magnitude of the effect is described in terms of the piezoelectric modulus (e) with dimensions of coulombs per newton. The magnitude of the piezoelectric modulus does not have a single value for a given substance, but is a function of direction relative to a crystal's crystallographic axes.

APPLICATION IN ELECTRONIC OR ELECTROACOUSTIC DEVICES

The piezoelectric effect is put to work in practical devices in two ways. One class of applications is in crystal oscillators for time and frequency standards and in band-pass filters for radio and telephone communications equipment. In these applications, it is necessary that the crystals have low energy dissipation (corresponding to a high Q value) and a stable frequency of oscillation, not sensitive to fluctuations of temperature. The numerical value of Q is defined as the number of oscillations that occur in a freely oscillating specimen before its amplitude of oscillation decays to 0.368 of its initial amplitude. For example, a golf ball has high Q ; a softball has low Q .

The other class of applications is in underwater sound equipment (sonar) and in ultrasonic cleaning devices. These applications make use of the rapid and forceful change in dimensions that the crystal undergoes upon application of an oscillating electric field. For this purpose, factors of energy consumption and frequency stability are not crucial.

²Italic numbers in parentheses refer to items in the list of references at the end of this report.

RECENT IMPROVEMENTS IN QUALITY OF BERLINITE APPLICABLE TO ELECTROACOUSTIC DEVICES

Discussion of quality factors that are relevant for berlinite requires an understanding of how quality factors for quartz are defined and optimized. The most important factors are the piezoelectric modulus and the energy dissipation or Q factor. Because the crystal is anisotropic, the piezoelectric modulus is not a simple constant, but a tensor whose numerical value depends on spatial orientation and temperature. The temperature effect, expressed as the temperature coefficient of the crystal's resonant frequency, is an important factor in frequency control, time measurement, and band-pass applications.

Figure 1 (taken from reference 4) illustrates how a quartz crystal is cut to yield oscillators having the best shape and orientation for different applications. The *x*-cut is used for expansion or contraction in thickness upon application of an electric field in the *x* direction; the *y*-bar expands and contracts in length when the field is applied in the *x* direction. The plate *at* shows shear in side faces when the field is applied in the thickness direction; it has superior freedom from temperature variation of resonant frequency. Berlinite, being isomorphous with quartz, would be cut in a similar way, but its optimum angles of orientation would not be the same as those of quartz. For the *at* cut in berlinite (the cut whose orientation gives the smallest temperature coefficient of resonant frequency at or near room temperature), the angles are approximately 30° from the *y* axis and 0° from the *x* axis.

For different applications, different properties need to be optimized. These properties include temperature coefficient of frequency, piezoelectric modulus, Q factor, piezoelectric coupling, power flow angle, and possibly others. The situation is further complicated by the question of whether the crystal is to be excited in the bulk acoustic wave (BAW) mode or the surface acoustic wave (SAW) mode.

Some of these properties are intrinsic to the overall crystal structure and independent of the presence of impurities or lattice defects. A macroscopic crystal structure defect that seriously impairs a crystal's piezoelectric response is twinning, somewhat like the albite twinning commonly found in plagioclase feldspar. This defect is sometimes found in plates cut from natural quartz, but seldom found in synthetic quartz. In quartz and berlinite, this kind of twinning produces what are called Brazil twin lamellae, but their occurrence in synthetic berlinite was reported to be rare (5). However, berlinite crystals grown

from a solution of sodium aluminate in phosphoric acid by repeated cycles of heating showed considerable twinning (3).

The most defect-free crystals of berlinite have been grown at constant temperature, without stirring, in phosphoric acid solution, in a manner similar to the method by which synthetic quartz is grown hydrothermally from lasca (6). Lasca is the term for the type of naturally occurring quartz that is used as the raw material for industrial production of synthetic quartz.

Other properties, particularly the Q factor, depend only partly on the intrinsic crystal structure, but are also influenced in part by the presence of dislocations, inclusions, and point defects, all of which are produced in the course of crystal growth. Dislocations and inclusions can be minimized by maintaining a slow steady rate of crystal growth. Rapid growth produces poor quality (7). Episodes of growth, followed by partial redissolution, followed by more growth, are especially prone to produce inclusions (3). In the case of growth from hydrothermal solutions, inclusions consist primarily of water. The Q factor for quartz crystals is inversely related to the growth rate (8). The logarithmic relationship is shown graphically in figure 2, taken from a National Academy of Sciences report (9).

Point defects have a different origin. The point defects responsible for part of the decrease in Q factor for berlinite consist of interstitial H⁺ or OH⁻ ions or substitutional H₂O molecules, with four H₂O molecules substituting for one AlPO₄ unit (5) and/or with Al-OH HO-P substituting for the Al-O-P group (8). These defects arise from the adsorption of H₂O at a molecular level upon the surface of the growing crystal. It is an equilibrium effect, wherein the concentration of such defects is inversely related to the temperature prevailing during crystal growth. The defect concentration, which may be referred to as the "solubility" of water in the crystal, is proportional to the exponential e^{-kT} , where *k* is the Boltzmann constant, 1.3805×10^{-16} erg per kelvin; and *T* is the absolute temperature in kelvins. Thus, the defect concentration is expected to be smaller in berlinite crystals grown at higher temperature. This is borne out by experiment (6), as shown by data in figure 3. Higher Q factor correlates with higher crystal growth temperature even more strongly than crystal water concentration, as shown in figure 4. Most quartz products for electronic use require a Q factor of 1.5 to 2.2 million (10).

Pressure also affects the point defect water concentration, but not as strongly as temperature. Higher pressure during crystal growth is expected to produce a greater water concentration, approximately 50 pct greater at 48.3 MPa than at 10.3 MPa (5).

FACTORS AFFECTING CRYSTAL GROWTH RATE

SOLUBILITY AND SOLUBILITY RATIO

Good crystal growth of a solute substance from solution requires that the solubility be neither too great nor too small. A desirable range of solubility for crystal growth from aqueous solution is 200 to 1,000 g solute per 1,000 g solvent (11). Too low a solubility gives too slow a rate of growth; too great a solubility leads to inclusions, defects, and multicenter crystal growth. A pertinent parameter for crystal growth is the solubility ratio, defined as the ratio of solubility-temperature gradient to solubility, i.e., $(dS/dT)/S$, where S is solubility and T is absolute temperature. A desirable range for the solubility ratio is 0.01 to 0.03, where temperature is expressed in degrees Celsius and solubility is expressed as grams of solute per 1,000 g of solvent. If the solubility ratio is too great, minor fluctuations of temperature (e.g., 0.01 °C) may produce bursts of rapid and uncontrolled growth, thereby generating defects. Other things being equal, there is a tradeoff between growth rate and crystal quality. Slower rate of crystal growth is better. Typical rates of crystal growth observed for berlinite ranged from 0.1 to 0.3 mm/d per face (5).

Figure 5 shows the solubility ratio for berlinite as a function of temperature, derived from data reported by Goiffon (12). For each solvent indicated, i.e., 9Mol/L H_2SO_4 , 8 mol/L HCl, and 9.5 mol/L H_3PO_4 , the solubility ratio is in or near the desired range, although in 9 mol/L H_2SO_4 at 300 °C, it is somewhat smaller than desired. Figure 6 shows the solubility of berlinite in each of the above-mentioned solvents.

In the supercritical fluid region for aqueous solution (i.e., pressure greater than 22.1 MPa and temperature greater than 374 °C), the solubility of most solutes is greater than at subcritical conditions. An example of this is the solubility of quartz in water, as shown in figure 7 (13). Note that at temperatures above the critical point, the solubility of quartz may be normal or retrograde, depending on the pressure. Berlinite probably exhibits similar behavior, even though it shows retrograde solubility under subcritical conditions. Crystal growth rates are generally rapid under supercritical solvent conditions because of the combined effects of high solubility and high diffusivity. Commercial synthetic quartz crystal is grown at a temperature just below the critical temperature and at pressures of 70 to 210 MPa, well above the critical pressure.

TEMPERATURE

Crystals grow faster at higher temperature. In the case of quartz, the relation of growth rate to temperature

indicates that the activation energy for crystal growth from aqueous solution is about 84 kJ/mol. Numerous measurements of the activation energy for diffusion in liquids indicated values about 13 kJ/mol (14). This makes it possible to distinguish between two alternative hypotheses regarding the rate-determining step, as depicted in figure 8. The approximately 84-kJ/mol magnitude of observed crystal growth activation energies strongly suggests that the rate-determining process involves migration of adsorbed ions or clusters of ions across the flat surface of the growing crystal until they encounter step dislocations, where they lodge permanently and add to the regular structure of the crystal lattice. The diffusion mechanism is not rate-determining except under conditions where growth is so rapid as to deplete the concentration of solute ions in a laminar boundary layer near the crystal surface.

SOLUTION VISCOSITY

If crystal growth rate were diffusion controlled, viscosity of the solution would be a pertinent factor in growth rate. Presumably, viscosity would be a rate-controlling factor only if solute concentration were small enough so that the crystal surface would be starved of its supply of adsorbed mobile ions.

STIRRING OR AGITATION

Stirring that imparts to the solution a velocity of 10 to 100 cm/s relative to the crystal surface is sometimes used to overcome local fluctuations in the degree of supersaturation. But stirring is difficult or impossible to achieve in a high-pressure system used for hydrothermal crystallization as in the growth of quartz. Under conditions near or above the solvent's critical point, however, diffusivity is large enough that stirring is not necessary. Greater diffusivity makes the temperature control requirement less stringent.

Convective circulation even in the absence of stirring can be significant if the vessel containing the fluid is hotter at the bottom than at the top, as is the practice in growing synthetic quartz (7). This convection can be very rapid and actually becomes turbulent under supercritical conditions.

USE OF MINERALIZERS TO FACILITATE CRYSTAL GROWTH

Geochemists have long speculated that ore deposition and crystal growth in hydrothermal deposits are facilitated by the presence in hydrothermal fluids of dissolved

constituents, such as chloride, sulfide, carbon dioxide, etc., which do not themselves precipitate. These constituents, referred to as "mineralizers," are believed to function by increasing the solubility of ore minerals, thereby increasing their rates of diffusive mass transfer and hence their rates of crystallization. Experimental evidence for increased solubility from this cause has been found in the case of anhydrite (CaSO_4). The relationship of anhydrite to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is like the relationship of berlinite (AlPO_4) to variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$). Figure 9 shows how the solubilities of anhydrite and gypsum vary with temperature (15). (The substance of lowest solubility is the stable solid phase at any given temperature.) As shown in figure 10 [adapted from Holland (16)], higher concentrations of NaCl in solution cause much greater concentrations of anhydrite in solution, hence presumably greater rates of anhydrite crystallization. Pressure also affects equilibrium solubility, thereby influencing the rate of

diffusive mass transfer of the solute. As an example, figure 11 (17) illustrates the pressure effect in the case of anhydrite. Other things being equal, higher pressure means higher rates of crystal growth.

In the production of cultured quartz crystal, NaOH and Na_2CO_3 are used as mineralizers to increase the solubility of quartz (18). With regard to berlinite, both HCl and H_2SO_4 are expected to be good mineralizers for crystal growth, because both acids increase the solubility of berlinite, as shown in figure 6. A mixture of HCl and H_2SO_4 might be better than either acid alone.

Preliminary experiments, conducted at the Reno Research Center, in which copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was added as a mineralizer produced not berlinite, but beautiful bright green crystals of libethenite [$\text{Cu}_2(\text{PO}_4)(\text{OH})$]. This result illustrates the principle that any substance that is to be effective as a mineralizer must not incorporate itself into the solid phase being formed.

FACTORS RELATED TO END-USE APPLICATIONS

Piezoelectric materials may be used in two different kinds of devices for electronic circuits; BAW devices and SAW devices. The two different modes of vibration are illustrated in figure 12. The physical properties that are most important in SAW applications are different from those that determine a material's suitability for BAW applications. For BAW devices, crucial physical properties are the temperature coefficient of resonant frequency and the Q factor. For SAW devices, temperature coefficient and Q factor are important, but the most crucial factor is the piezoelectric coupling coefficient. Q factor determines power dissipation or propagation loss, while the piezoelectric coupling coefficient determines the insertion loss.

The temperature coefficient and piezoelectric coupling are properties intrinsic to the crystal structure and highly dependent on the orientation of the test specimen with regard to crystallographic axes of the crystal from which it was cut. Temperature coefficient and piezoelectric coupling are also somewhat dependent on the test specimen's temperature and on the frequency of excitation. All of this complicates the evaluation of a specimen's quality because it is not possible to define a single "figure of merit." The suitability of a crystal sample has meaning only in connection with a particular application.

The vulnerability of piezoelectric devices to nuclear weapon effects has been mentioned in connection with quartz crystal in military applications (9). Under the influence of nuclear weapon effects, a quartz crystal may temporarily cease oscillating even in the absence of any other damage to the electronic system that contains it. That would disable equipment such as communications

networks, computers, and navigation and gunnery fire-control systems.

If that disruption of function is caused by prompt neutrons from a nuclear weapon, berlinite would be more vulnerable than quartz because of aluminum's larger cross section for neutron interactions. Table 1 gives the numbers. (The cross sections are given in barns, where 1 barn equals 10^{-24} cm^2 .) Per mole, AlPO_4 would absorb and/or scatter thermal neutrons to an extent 12 times as great as SiO_2 .

Table 1.—Thermal neutron (2,200 m/s) cross sections for elements in AlPO_4 and SiO_2 , barns (19)

	Absorption	Reaction	Scattering	Total ¹
Element:				
Al	241	0.21	1.4	243
O	<0.0002	Nil	4.2	4.2
P	0.2	0.19	5	5.4
Si	0.16	Nil	41.7	1.9
Compound:				
AlPO_4				265
$2(\text{SiO}_2)$				21

¹Rounded.

If the disruption of oscillation were caused by electromagnetic (EMP) pulse from a nuclear blast, berlinite would again be at a disadvantage relative to quartz because of its greater piezoelectric coupling coefficient. The current interest in berlinite probably does not derive from any consideration of resistance to nuclear weapon effects.

FACTORS IN SELECTION OF EQUIPMENT AND METHODS

According to Stanley (3), berlinite does not form below 132 °C, and according to Caporaso (20), it does not form below 150 °C. At lower temperatures, hydrated materials, presumably variscite, constitute the stable phase. Stanley cited an upper limit of 315 °C for preparation of berlinite, but it is not clear whether that was a limit imposed by his equipment or a limit intrinsic to berlinite.

Berlinite, like quartz, occurs in different polymorphic crystal forms depending on temperature. The α -polymorph is the stable form at temperatures below 586 °C, whereas the β form is the stable form at higher temperatures. Therefore, the α - β transition point at 586 °C constitutes an intrinsic upper limit because, although the transition of the β form to the α form upon cooling is rapid (21), the phase change promotes lamellar twinning.

Because of the need to minimize point-defect water in the crystal, the highest possible temperature for crystal growth is desirable. However, excessively rapid cooling from the growth temperature before harvesting crystals is to be avoided so as to prevent cracking caused by thermal shock.

By analogy with the process for growth of cultured quartz, temperatures and pressures at or beyond the critical point of water should be considered. This means temperatures at least 375 °C and pressures at least 20.7 MPa. The effect of pressure per se on the water content of synthetic berlinite is not known, but if the concentration of point defect water depends on equilibrium adsorption of water on the crystal surface, greater pressure would be expected to correlate with greater water content.

Chemical properties of aluminum in solution require that berlinite crystals be grown from acidic solutions only. From neutral or alkaline solution, aluminum ions precipitate as $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ rather than AlPO_4 , even at high temperature. Because of increased dissociation of H_2O at higher temperatures (22), the concentration of acid required to prevent aluminum oxide formation is greater the higher the temperature. Even though H_3PO_4 is only slightly dissociated to PO_4^{3-} in strongly acid solutions, high acid concentration is not an impediment to formation of AlPO_4 .

The necessity of using an acidic system so as to precipitate AlPO_4 rather than $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ influences the selection of materials for containment of the system at elevated temperature and pressure. For growing quartz crystal from alkaline solution, autoclaves made of low-carbon steel are satisfactory (9), but would not be suitable for use with acid solutions. Acid solutions, especially at high temperature, rapidly consume steel to produce Fe^{2+} and hydrogen gas.

For growth of berlinite crystal, some investigators have used flame-sealed tubes of fused silica with demountable seals of fluorocarbon polymer and Viton fluorinated synthetic rubber (23). Others have used autoclaves with liners of platinum (20) or Teflon fluorocarbon polymer (24).

Tantalum might be suitable as a corrosion-resistant liner, but tantalum is subject to air oxidation above 260 °C.

Gold would be suitable as a flexible liner to be used inside another vessel, which would provide the necessary mechanical strength, or as a plated coating on the inside of another vessel. A gold-plated version of a stirred autoclave is commercially available, but its working pressure is limited to not more than 1.2 MPa.

Teflon fluorocarbon polymer is a suitable material for gaskets or liners up to about 200 °C, but at higher temperatures it becomes too soft. Some investigators used a sealed tube of fused quartz contained in a metal autoclave within which a counter pressure (from liquid water and water vapor) was applied to balance pressure developed inside the quartz vessel where crystals were being grown (12). The counter-pressure method provides satisfactory containment of acidic solutions, but arranging to fill the outer vessel with a noncorrosive fluid that will provide adequate counter pressure over a wide range of temperature involves considerable guesswork. If the inner vessel of glass failed, the outer vessel of metal would be destroyed by corrosion.

To grow crystals with good purity requires pure starting materials. High-purity alumina or aluminum hydroxide proved more satisfactory than aluminum phosphate for preparing saturated solutions for growing berlinite (25). Naturally occurring variscite would not be a satisfactory starting material because of its lack of purity. In any event, the starting materials are not expensive. Reagent-grade aluminum hydroxide is listed at \$21/kg, and reagent-grade phosphoric acid is listed at \$12/kg contained H_3PO_4 (26).

The energy cost for making cultured (i.e., synthetic) quartz has been estimated to be \$120 kW · h/kg,³ which at 6¢/kW · h would amount to only \$7/kg. In the case of quartz, the largest cost of production is the capital cost of the autoclaves, typically \$250,000 for a 4-m by 0.4-m-diam autoclave (10) capable of producing a hundred kilograms of quartz in a 15- to 30-day period (7).

For either quartz or berlinite, the cost of a finished electronic device would depend primarily on the cost of fabrication, not on the cost of raw cultured crystal.

Cultured quartz is not in short supply in the United States, as indicated by the fact that sometime during 1987-88, one of the major U.S. producers, AT&T Network Systems at North Andover, MA, suspended production.⁴ Six other domestic producers remained active, but, worldwide, Japan was the leader among countries producing cultured quartz (27).

³OFR 117(1)-76. Energy Use Patterns in Metallurgical and Non-metallic Mineral Processing (Phase 6—Energy Data and Flowsheets, Low-Priority Commodities), by Battelle Columbus Laboratories.

⁴Communication from J. A. Ober, USBM commodity specialist, Feb. 19, 1989.

PHYSICAL PROPERTIES AND OTHER DATA

Table 2 lists some of the measured physical properties of berlinite that are pertinent to its use in electroacoustic devices. Variation in numerical values from one source to another probably reflects variation in the purity and crystalline quality of materials under investigation. There

is no single criterion of quality. Table 3 lists other physical properties of berlinite. Table 4 gives a comparison of berlinite versus quartz for use in piezoelectric devices. Thermodynamic properties of berlinite are given in table 5.

Table 2.—Physical properties of berlinite by year crystal was grown

Constant ¹	1950 (28)	1976 (28)	1983 (29)	1986 (28)
Elastic constants, 10^{10} N/m ^{2,2}				
C ₁₁	10.50	6.40	6.93	6.34
C ₃₃	13.35	8.58	8.82	5.58
C ₄₄	2.31	4.32	4.30	4.32
C ₆₆	3.79	2.84	2.94	3.06
C ₁₂	2.93	0.72	1.05	0.23
C ₁₃	6.93	0.96	1.35	0.58
C ₁₄	-1.27	-1.27	-1.30	-1.21
Dielectric constants (dimensionless):				
ε ₁₁	6.05	NAp	4.7	4.60
ε ₁₄	NA	NAp	4.8	4.48
Piezoelectric constants, 10^{-12} C/N:				
e ₁₁	-0.27	-0.30	0.14	-0.22
e ₁₄	0.12	0.13	0.02	0.15

NA Not available.

NAp Not applicable.

¹Subscripts used with symbols for the elastic constant, dielectric constant, and piezoelectric constant denote the tensor's relation to crystallographic axes.

²For comparison, steel has an elastic constant (Young's modulus) about 7×10^9 N/m². Berlinite is up to 10 times as stiff as steel.

Table 3.—Crystal properties of berlinite (1)

Crystal structure	Trigonal-trapezohedral, crystal class 32.
Crystal habit	{1011}, {0111}, {1010}.
Unit cell dimensions	0.493 nm a ₀ , 1.094 nm c ₀ .
Hardness	About 6.5 on Moh's scale.
Density (calculated)	2.62 g/cm ³ .
Refractive index	Ordinary ray = 1.524, extraordinary ray = 1.530, uniaxial, positive.
Chemical composition ..	41.80 pct Al ₂ O ₃ , 58.20 pct P ₂ O ₅ .

a₀ Unit cell length on x axis.

c₀ Unit cell length on z axis.

Table 4.—Comparison of berlinite with quartz for use in resonators operating in thickness excitation mode (29)

Property	Berlinite relative to quartz
Piezoelectric coupling coefficient	40 to 50 pct greater. ¹
Bandwidth of filters	Double.
Sensitivity of first-order coefficient of frequency as a function of temperature, sensitivity to angle of cut	Smaller.
Q factor or propagation loss	Depends on berlinite's freedom from water impurity and freedom from twinning.
Vulnerability to mechanical shock	Unknown.
Vulnerability to thermal shock	Do.
Vulnerability to ionizing radiation from detonation of a nuclear weapon	Do.

¹Some authors report a piezoelectric coupling coefficient four times that of quartz. Wide variations occur between individual specimens of berlinite.

Table 5.—Thermodynamic properties of berlinite (30)

Formula weight	121.9529.
ΔH_f° (0 K)	-1,721.3 kJ/mol.
ΔH_f° (298.15 K)	-1,733.8 kJ/mol.
ΔG_f° (298.15 K)	-1,597.0 kJ/mol.
S° (298.15 K)	90.8 J/(K·mol).
C_p° (298.15 K)	93.2 J/(K·mol).

EQUIPMENT FOR LABORATORY-SCALE PRODUCTION OF BERLINITE CRYSTAL

Other investigators have used two methods for growing berlinite crystals. One method employed an autoclave containing a suspended seed crystal immersed in solution held at a constant temperature together with a mass of granular berlinite held at a temperature 25 to 50 °C lower. This is called the constant-temperature method. To produce good results, the zone containing the suspended seed crystal must be held at a closely controlled temperature over a period of several weeks.

The other method used an autoclave containing a seed crystal suspended in a solution saturated with respect to berlinite and slowly heated so as to make the solution slightly supersaturated with respect to the seed crystal. This is called the slow heating method. This method requires that the temperature be carefully controlled while being slowly programmed upward at a rate of 1 to 2 °C/d, over a period of 2 to 4 weeks.

Both methods require precision temperature control, e.g., ± 0.005 °C, absence of power outages or serious variations in the ambient temperature of the laboratory, and a highly corrosion-resistant pressure vessel or autoclave liner. Corrosion resistance is important because any

corrosion of the container would impart to the solution impurities, which would then be incorporated into the crystal. Because the required temperature range is well above the boiling point of aqueous solutions, a pressure vessel is necessary. It cannot be done at ambient pressure. The possibility of rupture of the pressure vessel poses a safety hazard. For example, rupture of a vessel containing 1 L of aqueous solution at only 0.8 MPa and 170 °C, undergoing adiabatic expansion, would involve an explosive energy release equivalent to detonation of 20 g of trinitrotoluol (TNT). The fact that the solution would consist of a corrosive strong acid gives an added dimension to the hazard. Precautions to ensure the safety of personnel are essential.

For the proposed duty (i.e., containment of concentrated acid solutions at temperatures and pressures up to the critical point), a counter-pressure technique is recommended, comprising a sealed Pyrex glass ampoule inside an electrically heated autoclave with a platinum or gold liner between the glass ampoule and the metal (e.g., stainless steel) autoclave. This would be similar to what other investigators are using.

METHODS FOR TESTING BERLINITE CRYSTAL

Line defects, dislocations, cracks, and inclusions are detectable in berlinite by a technique called X-ray topography (6, 23, 29). Twinning in berlinite is detectable by transmission electron microscopy (28). Water content of berlinite, like that of quartz, is measurable by infrared

spectroscopy (31-32). The Q value can be measured directly by insertion of a specimen into an appropriate resonator circuit or by a logarithmic decrement procedure in which the decaying amplitude of vibration is displayed on an oscilloscope (32).

CONCLUSIONS

To produce synthetic berlinite crystal having a suitably high Q factor and usefully large dimensions would require high-purity starting materials (aluminum hydroxide and phosphoric acid) and a controlled-temperature autoclave equipped with a noncorrodible liner (such as platinum, gold, fluorocarbon polymer, or fused silica). Containment

of pressure up to 20.7 MPa at temperatures up to 375 °C may be necessary. Use of natural variscite as a starting material is ruled out by its lack of purity. Temperature during crystal growth would need to be very closely controlled (i.e., ± 0.005 °C) while being held constant or slowly programmed upward over a period of days or weeks.

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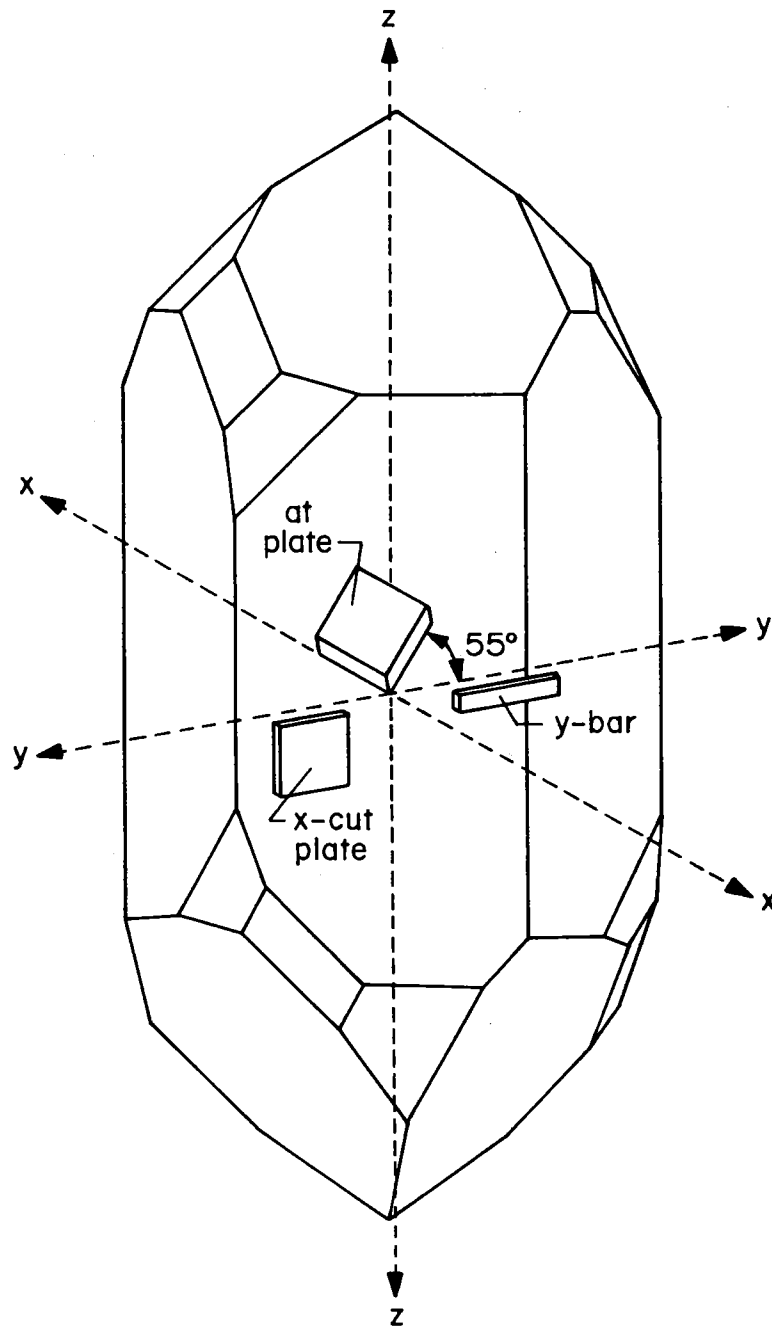
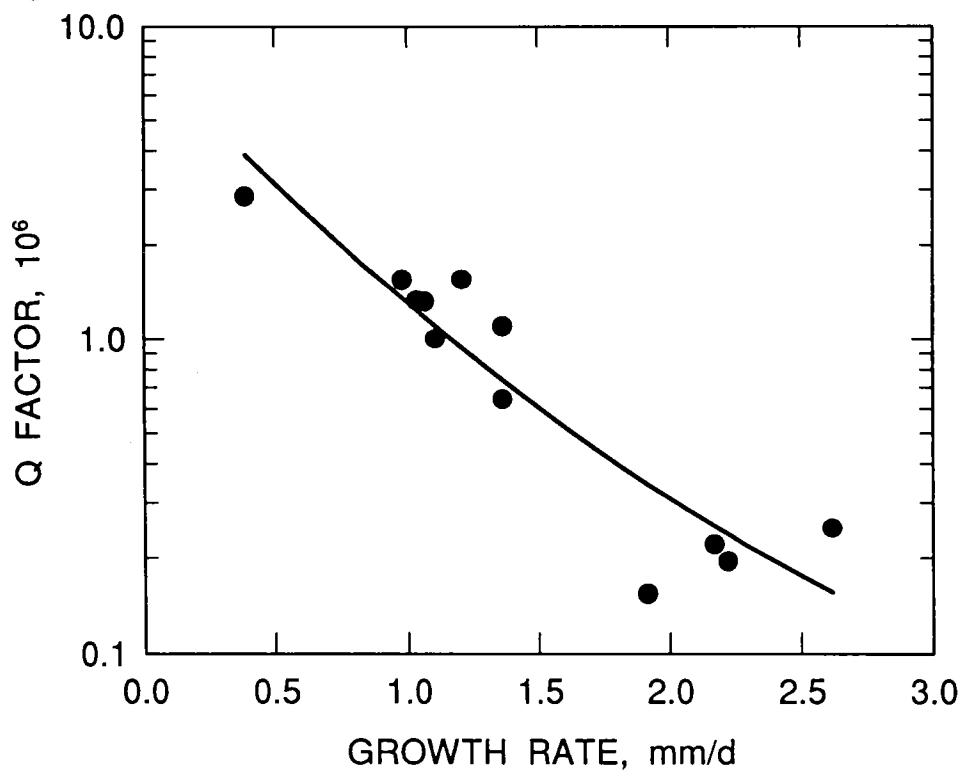
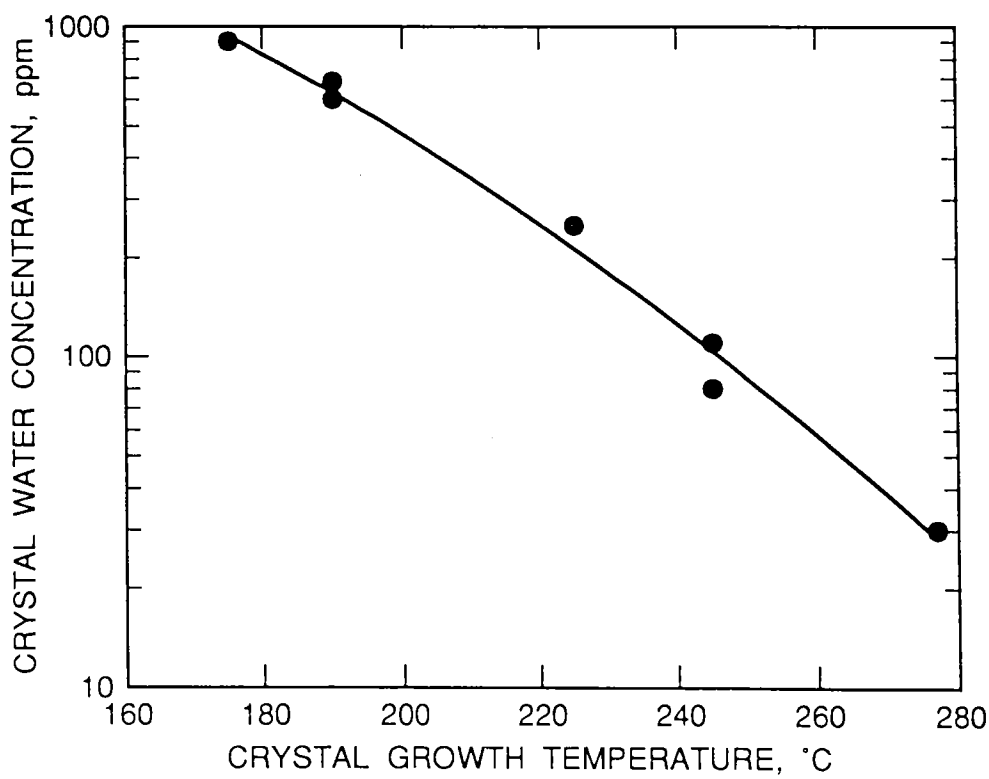
Figure 1*Quartz crystal with three of the most important piezoelectric elements.*

Figure 2



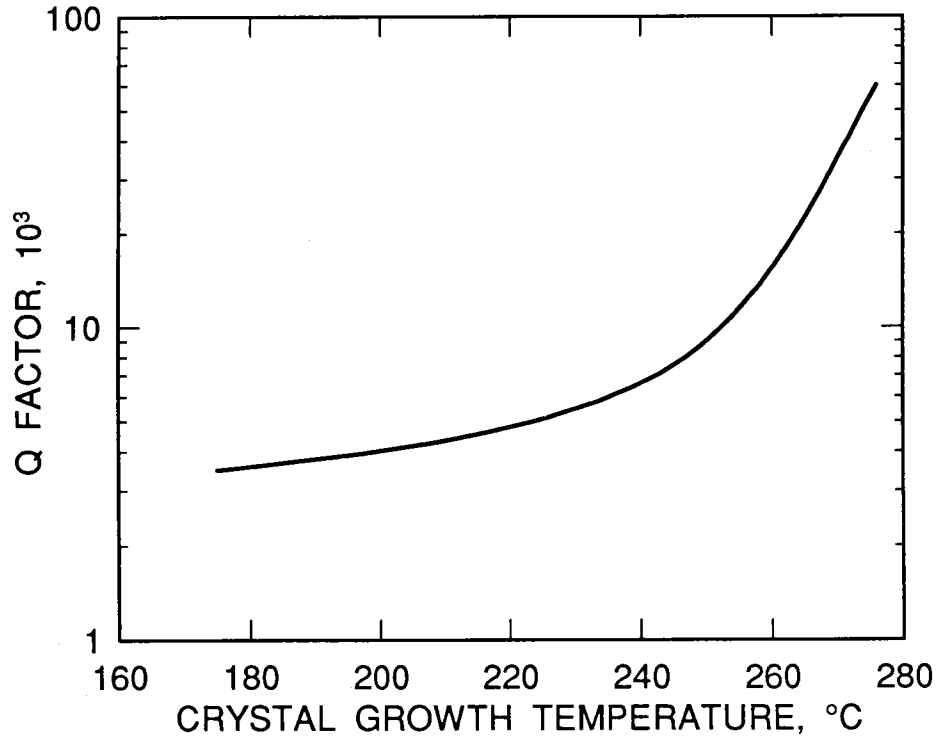
Relationship between Q and rate of growth of quartz crystals in NaOH solutions.

Figure 3



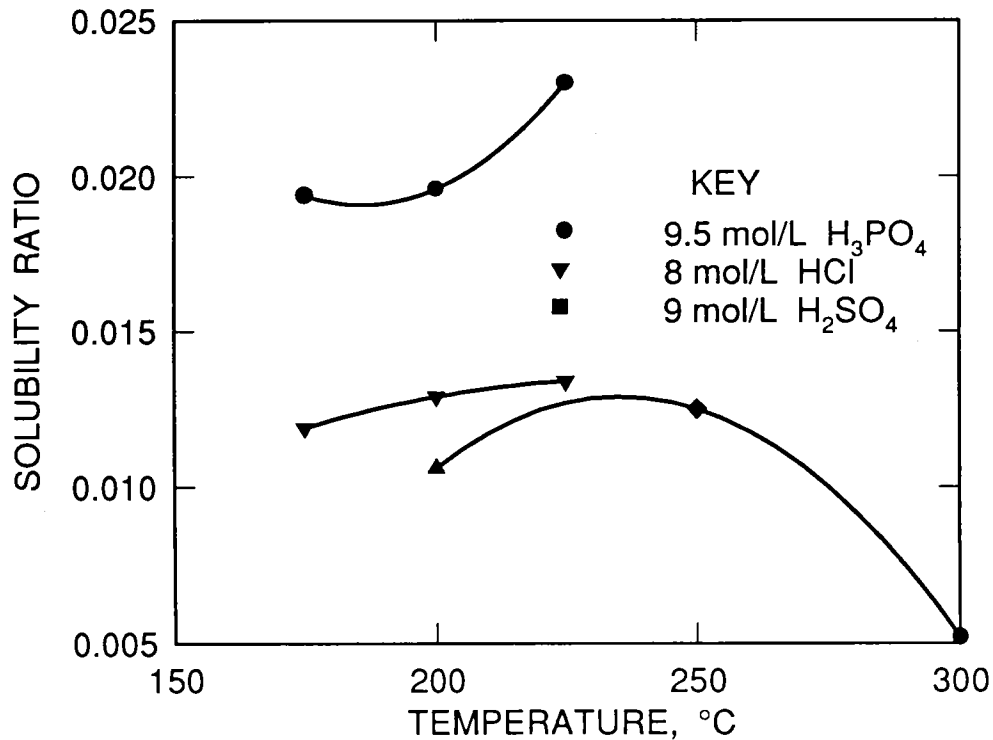
Berlinite crystal water concentration as function of crystal growth temperature.

Figure 4



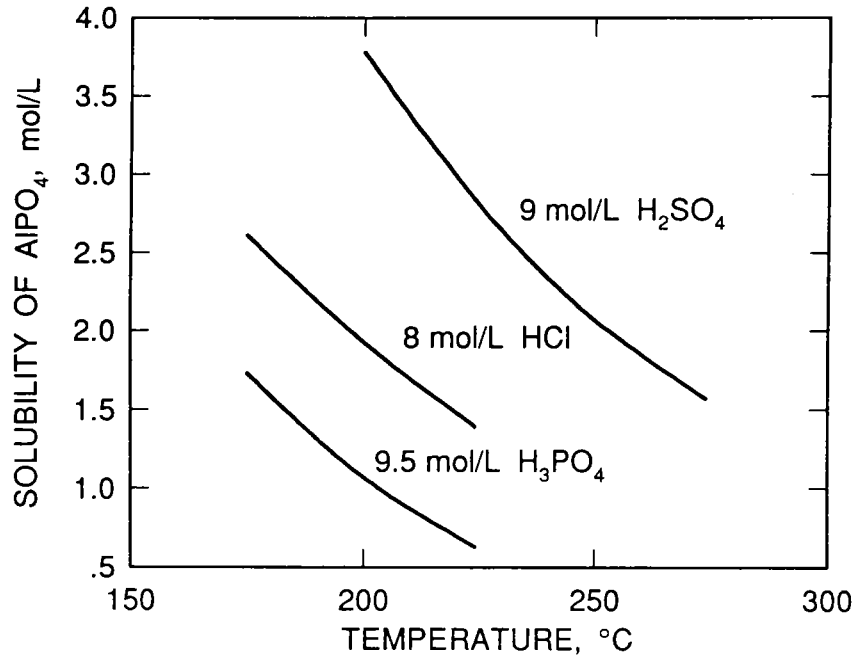
Berlinite crystal Q factor at 5 MHz as function of crystal growth temperature.

Figure 5



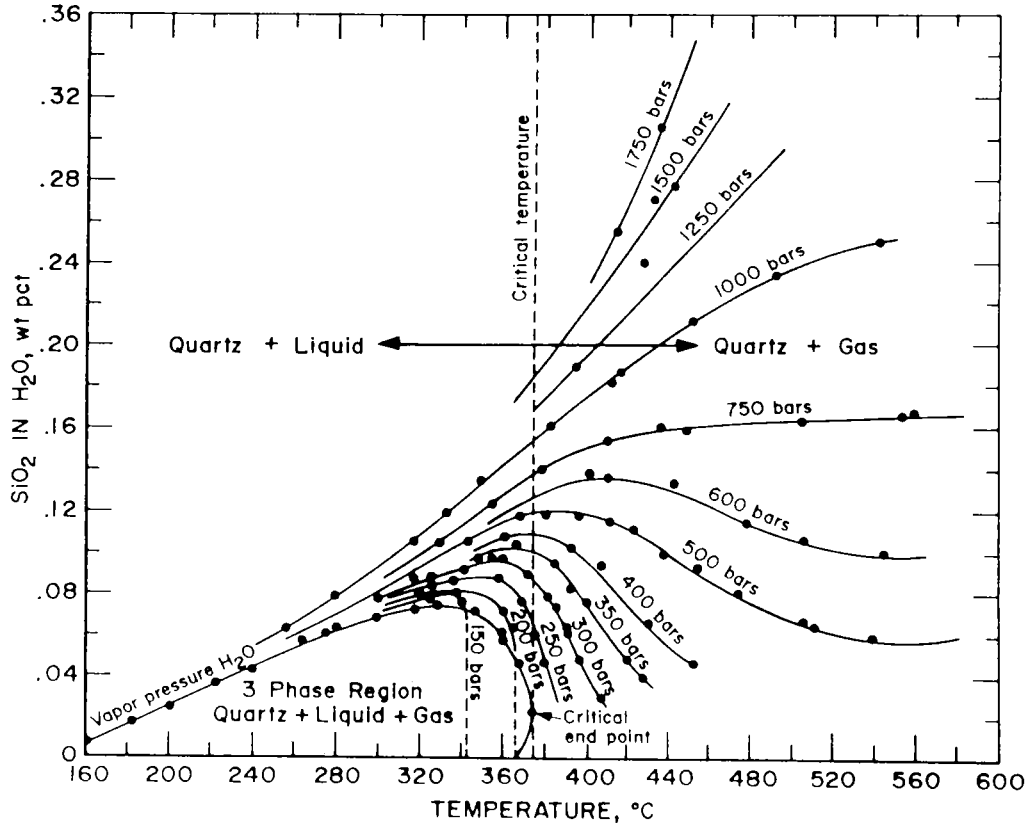
Solubility ratio of AlPO₄ in H₃PO₄, HCl, and H₂SO₄ as function of temperature.

Figure 6



Solubility of $AlPO_4$ in H_2SO_4 , HCl , and H_3PO_4 as function of temperature.

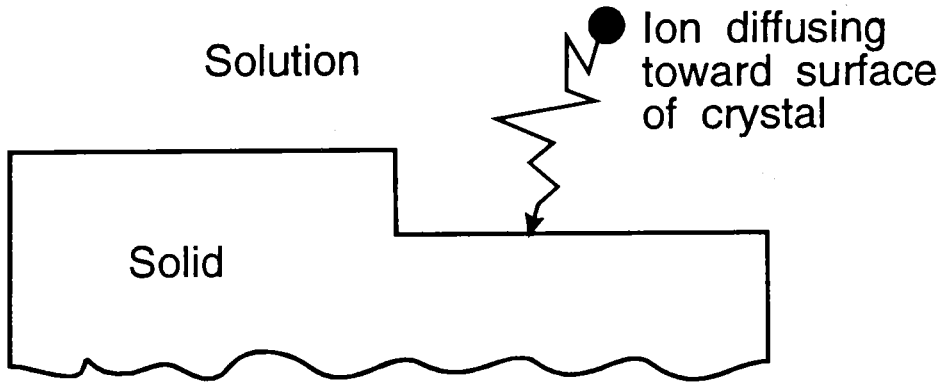
Figure 7



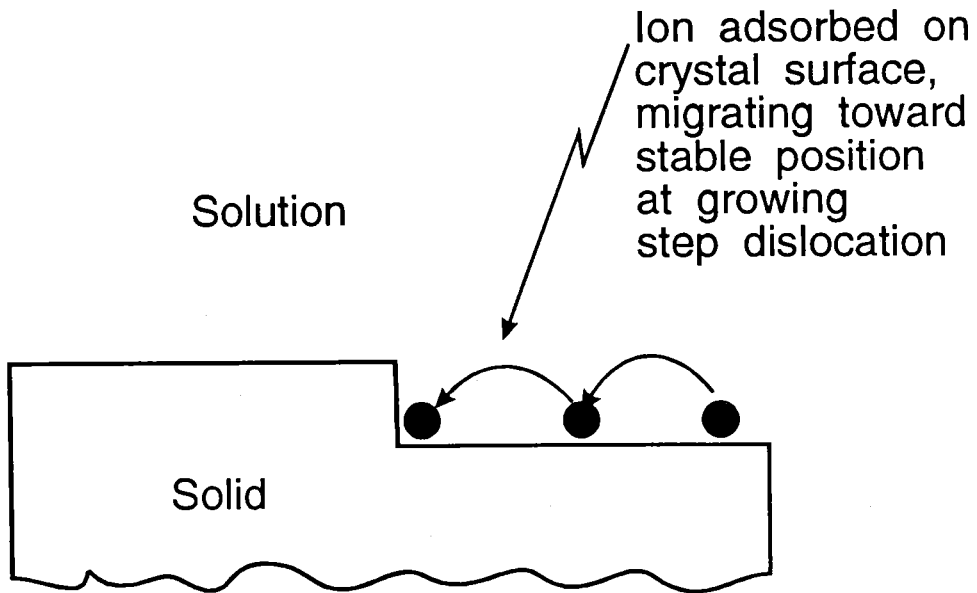
Solubility of quartz in water as function of temperature and pressure. [From Kennedy (13).] (1 bar = 0.1 MPa.)

Figure 8

DIFFUSION MECHANISM

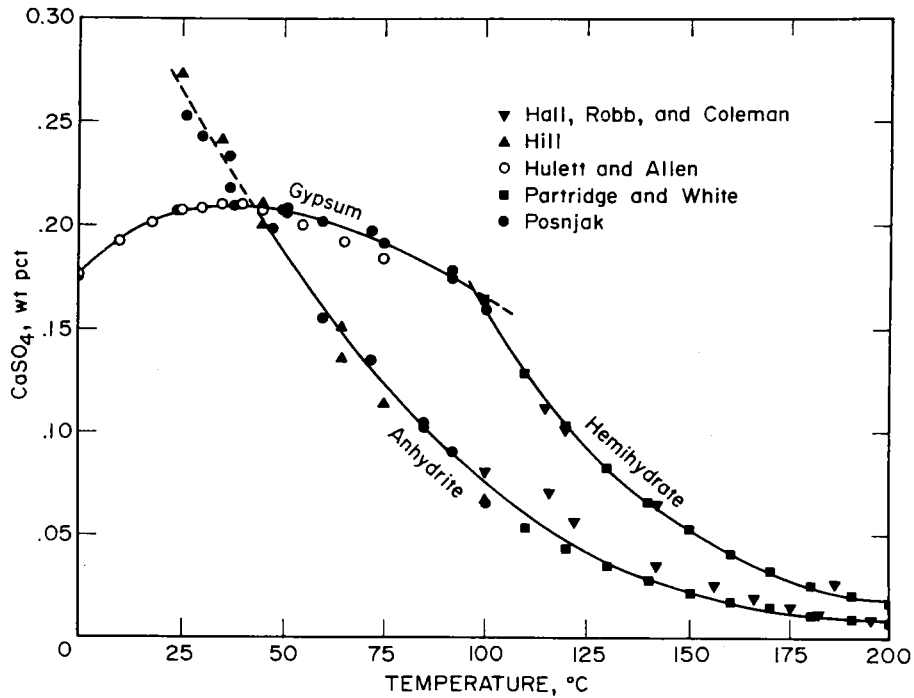


SURFACE MIGRATION MECHANISM



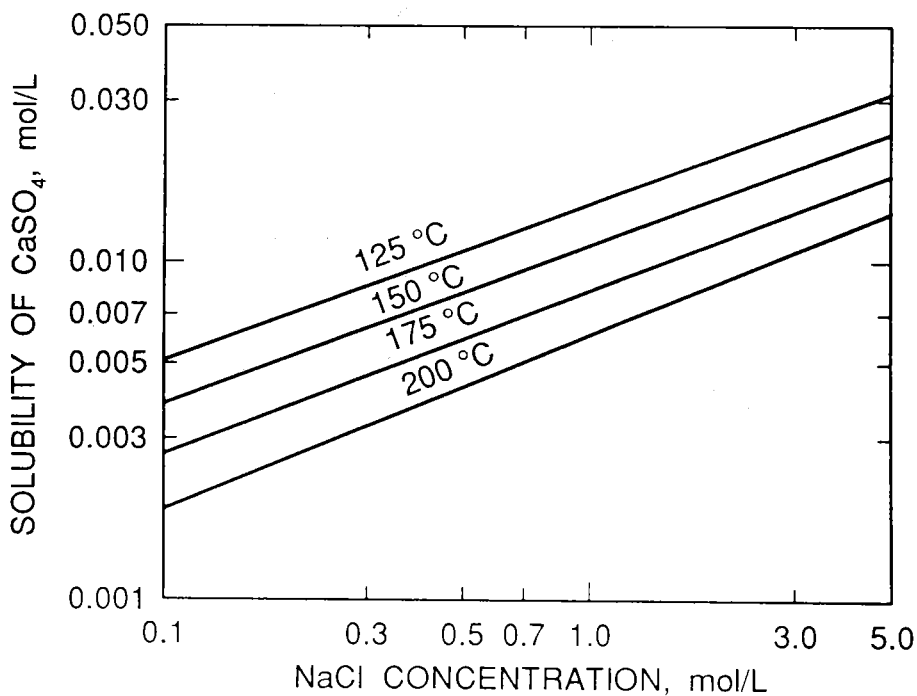
Two alternative theories of rate-controlling step in crystal growth.

Figure 9



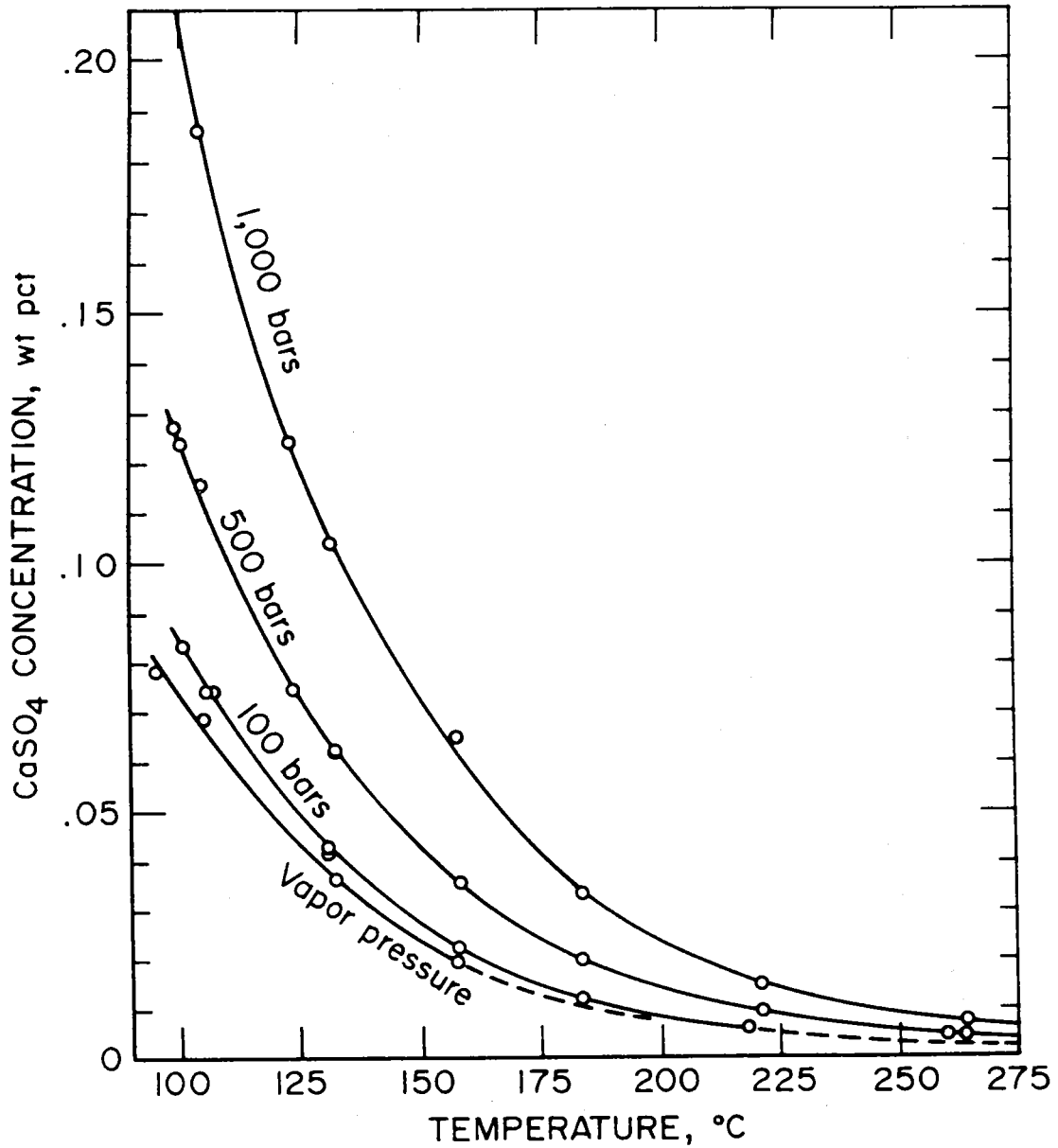
Solubility of anhydrite, hemihydrate, and gypsum in water. [From Posnjak (15).] Broken lines indicate regions of metastable equilibrium. Names listed in the key identify authors of papers quoted by Posnjak (15).

Figure 10



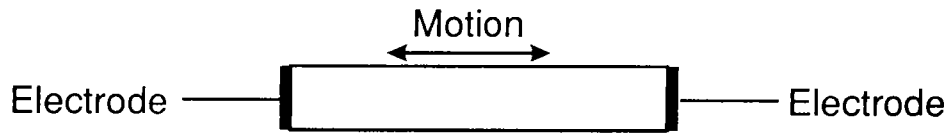
Solubility of anhydrite as function of NaCl concentration and temperature. [Adapted from Holland (16).]

Figure 11

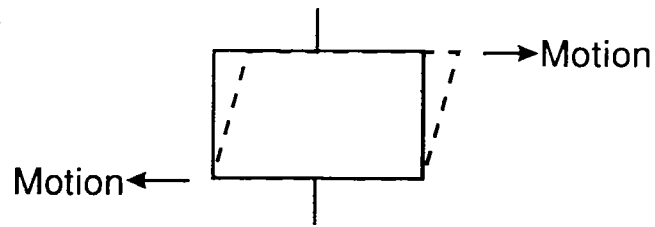


Solubility of anhydrite along lower three-phase boundary and at 100, 500, and 1,000 bars total pressure between 100 and 275 °C. [From Dickson (17).] Dashed lines denote regions in which a vapor phase may be present. (1 bar = 0.1 MPa.)

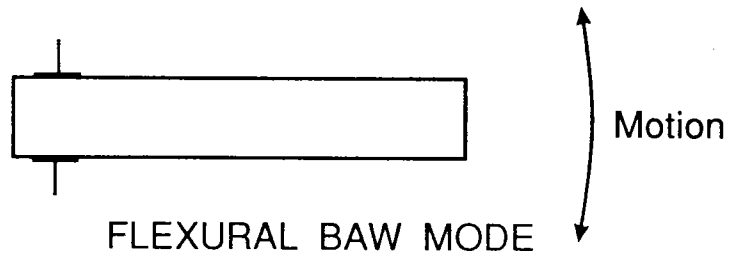
Figure 12



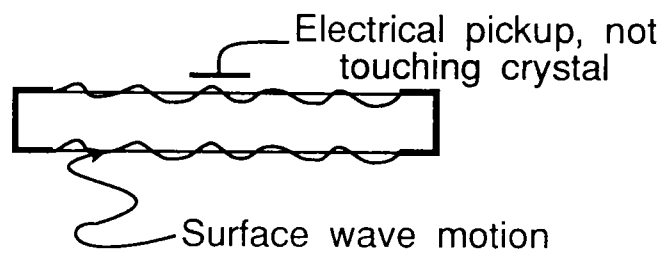
COMPRESSION BAW MODE



SHEAR BAW MODE



FLEXURAL BAW MODE



SAW MODE

BAW and SAW modes of vibration.