Case (2)

If $F>0$ and $(F)^{\frac{1}{3}}>k/A^{\frac{1}{3}}$,

$$\alpha=\left[(F)^{\frac{1}{3}}+\frac{k}{A^{\frac{1}{3}}}\right]^{\frac{1}{3}} \tag{A4a}$$

$$\beta=\left[(F)^{\frac{1}{3}}-\frac{k}{A^{\frac{1}{3}}}\right]^{\frac{1}{3}}. \tag{Ab4}$$

Case (3)

If $F<0$ compute the acute angle ϕ from the expression

$$\cos\phi=\frac{(k/A^{\frac{1}{3}})}{[(1-2k)/3]^{\frac{3}{2}}}. \tag{A5a}$$

Then

$$\alpha=\beta=[(1-2k)/3]^{\frac{1}{2}}\cos(\phi/3). \tag{A5b}$$

JOURNAL OF APPLIED PHYSICS VOLUME 36, NUMBER 1 JANUARY 1965

Synthesis of Beryl under High Pressure and Temperature

WAYNE WILSON
U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland

(Received 3 August 1964)

Clear single crystals of beryl have been obtained at pressures of 10 000 atm and above by melting beryl powder and allowing it to crystallize under the high pressure. The difficulties associated with this method of crystal synthesis are discussed in detail.

INTRODUCTION

THE present research on maser and laser materials has created a renewed interest in synthetic crystals. Crystals containing chromium are particularly adaptable for these applications and much work has been accomplished recently in growing maser quality emerald crystals. Several review papers[1] have been published on the physical properties of emerald and on the method for synthesis of this mineral. In general, the synthesis of emerald has been accomplished by either the hydrothermal technique or by the flux method. Recently, Linores, Ballman, and Von Uitert,[2] and Lefever, Chase, and Sobon[3] have independently reported on improved flux techniques for the synthesis of emerald. The newest and most recent technique, however, is the flame-fusion method employed by Gentile, Cripe, and Anders.[4]

In the present paper, a high-pressure, high-temperature method will be described which produces clear single crystals of emerald directly from beryl powder. The color of the crystals obtained can be easily controlled by substituting various amounts of metallic oxides, particularly Cr_2O_3, in the basic beryl powder. The chief advantage in this method lies in the fact that it requires only about 2 min to crystallize the beryl sample.

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[3] R. Lefever, A. Chase, and L. Sobon, Am. Mineralogist **47**, 1450 (1962).

[4] A. Gentile, D. Cripe, and F. Anders, Am. Mineralogist **48**, 940 (1963).

PRESSURE APPARATUS

The pressure vessel used in the present work is the stepped-core device shown in Fig. 1. The vessel is composed of several binding rings about the center tungsten carbide core to enable one to obtain pressures up to 60 000 atm in the test capsule. The test capsule is shown in Fig. 2. It consists of pyrophyllite material for the transmission of pressure, a carbon sleeve to serve as a furnace, and a cylindrical capsule to isolate the beryl powder from the pyrophyllite during the crystallization process. Pressure is transmitted to the test capsule through tungsten carbide pistons by means of a 300-ton press. Although this equipment has been particularly adaptable for the synthesis of beryl, there are other pressure vessels which would be easier to work with and which can provide larger working volumes than that described here. The volume available for the capsule which contains the beryl powder is about $\frac{1}{4}$ in. in diam-

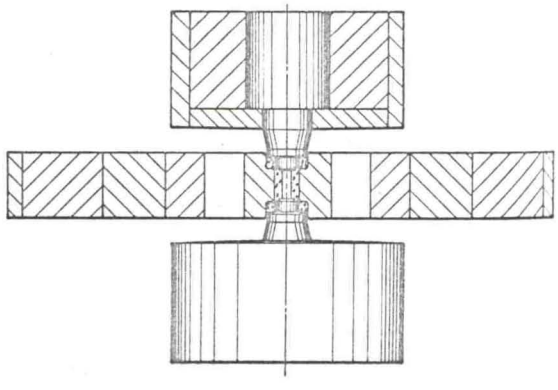

FIG. 1. $\frac{3}{4}$-in. cylindrical supported piston pressure vessel.

eter and about $\frac{3}{8}$ in. in length in the present vessel. These dimensions can easily be scaled upward to obtain larger crystals.

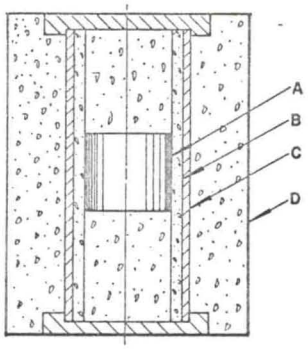

FIG. 2. Capsule design. (A) Sample, (B) pyrophyllite, (C) carbon furnace, (D) pyrophyllite.

THE CRYSTALLIZATION OF EMERALD

The procedure for the crystallization of beryl, or emerald, by the present technique is as follows: The pressure is adjusted to the proper value and the temperature is raised until the beryl powder melts. The electric current which provides power to the carbon heater is then abruptly cut off. Since there is a large mass of steel surrounding the sample, the temperature is reduced to near room temperature in a matter of a few minutes. Under these conditions the melt fuses into a clear single crystal of beryl. The quality of the crystal, however, depends upon the pressure, the time during which the temperature is applied, and the material of the capsule which contains the beryl powder. At pressures of 5 kbar, for example, one obtains translucent grey crystals of beryl which tend to disintegrate for several minutes after the pressure is relieved. Pressures of 10 kbar, however, are adequate for producing good quality clear crystals which retain their form after the pressure is released. One must compromise, however, in regards to the temperature and pressure that is used. The change in the temperature of melting with pressure is about 40°/kbar for beryl powder. The melting point of beryl, at atmospheric pressure, is about 1410°C. Consequently, at 10 kbar, the melting point is around 1800°C, and at 15 kbar, beryl melts at about 2000°C. Although these conditions are not difficult to obtain in the present apparatus, one must also be concerned with the material which confines the beryl powder. Platinum, for example, melts at 1774°C at atmospheric pressure and at about 1800°C at 15 kbar. Single crystals of emerald have been obtained in this Laboratory by using platinum containers at 10 kbar; however, the melting of the beryl had to be accomplished by a carefully controlled flash heat to prevent the platinum from fusing with the molten beryl. Although the rate of diffusion in materials normally decreases as the pressure about the sample increases, it has been found in this work that diffusion occurs extremely rapidly at the temperatures required to melt beryl powder. Most of our work has consequently been accomplished in tungsten capsules. Although tungsten can easily withstand the required temperatures, there is considerable diffusion of tungsten into the beryl. It is apparent that properly sintered Al_2O_3, BeO, or SiO_2 capsules will be best suited for this work.

The temperature coefficient of melting with pressure can be decreased by adding water to the beryl sample. In this method, the beryl powder is mixed with water to form a thick paste. This paste is then pressed into a tungsten capsule by a pressure of 1 kbar. Under such conditions most of the water is squeezed out of the sample. There is enough left, however, to reduce the temperature coefficient to about 7°/kbar. Consequently, at 15 kbar, this technique reduces the melting point of beryl from 2000° to about 1500°C. Even at this temperature, care must be taken to prevent tungsten from diffusing through the sample. It has been found that, with the present apparatus, the heat supplied for melting can be maintained for about 2 min without appreciable diffusion of tungsten. For longer periods of heating the tungsten diffuses noticeably through the beryl, until after 7 min, it has diffused completely through the sample. In such cases, one obtains a granular mass, instead of clear single crystals.

The temperature of melting can be reduced further by using fluorine gas as a flux. This procedure has been accomplished by two methods in this Laboratory. In one experiment Teflon was used as a capsule material. At temperatures near 800°C the Teflon dissociates to give off fluorine which causes the beryl to melt in the neighborhood of 1000°C at a pressure of 20 kbar. A second method is to use CrF_3 in place of Cr_2O_3 to obtain clear green crystals of beryl. In this work, the fluorine gas is liberated at 1000°C and 20 kbar pressure, and the chromium is trapped either interstitially or substitutionally in the crystal lattice. There are undoubtedly other fluxes which would aid the synthesis. Such fluxes are not necessary, however, if the proper capsule material is selected. The capsule material must be able to withstand the high temperatures required for melting at high pressure without subsequent diffusion and chemical reaction with the molten beryl.

The beryl powder used in this work has been of two forms. The initial work was accomplished by pulverizing beryl crystals into a fine powder and adding Cr_2O_3 for color. Later experiments were accomplished by mixing BeO, SiO_2, Al_2O_3, and Cr_2O_3 in the proper proportions to obtain the sample material. This mixture melts incongruently in the absence of a flux. It is therefore advantageous to presinter the powder in an inert gas atmosphere before attempting emerald synthesis. The inclusion of Cr_2O_3 to obtain the green color necessary for emerald can be obtained by two methods. In the beryl powder obtained from pulverizing natural beryl, the Cr_2O_3 was introduced as an additive. In the samples prepared from the oxides of Be,

Al, and Si, the Cr_2O_3 was introduced, on several occasions as a substitute for part of the Al_2O_3, and at other times as an addition to the Al_2O_3 content. The outward appearance of the crystals obtained does not depend upon whether the Cr_2O_3 is introduced as an additive or by substitution. The internal properties, however, such as the electric properties and the optical properties, which determine maser and laser activities, will undoubtedly depend on the manner in which the Cr_2O_3 is incorporated in the lattice.

PHYSICAL PROPERTIES

The crystals obtained by the high-pressure method are, by outward appearance, clear crystals of beryl. Information obtained from x rays indicate that the crystals are single crystals. The addition of 1% by weight of Cr_2O_3 produces a green color identical to the color of the best natural emeralds. The density of the crystals was determined to be 2.715 ± 0.005 g/cm^3. This density was obtained by grinding a crystal into the shape of a cube $\frac{1}{8}$ in. on a side. The density was then computed from a knowledge of the mass and the volume. A rough check of the density was made by the sink–float method in dense liquids.

ACKNOWLEDGMENTS

This work was accomplished in the Physics Research Department of the Naval Ordnance Laboratory. The author would like to acknowledge the able assistance of Hubert Hall in accomplishing this work.

JOURNAL OF APPLIED PHYSICS VOLUME 36, NUMBER 1 JANUARY 1965

Epitaxial Growth on MgO of Niobium Films Investigated by Electron Microscopy

T. E. HUTCHINSON

Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota

(Received 17 June 1964)

Niobium films deposited in vacuum ($<5\times10^{-6}$ Torr) on a (100) face of cleaved MgO were found by electron microscopy to have two types of epitaxial growth, independent of the deposition rate (2 to 120 Å/min). Although the epitaxial films have a very high dislocation density for substrate temperatures below about 500°C, thin films (<250 Å) grown between 500° and 600°C have no crystalline defects observable either by direct electron microscopy or in overlapping Moiré fringe patterns. Perfect (001) epitaxy with $[100]_{Nb}//[100]_{MgO}$ occurred in these thin films for substrate temperatures from 25° to 600°C. Thicker films (>400 Å), have regions of a new orientation which enlarge as the films thicken, until only the new orientation is observed at 1000 Å and thicker. These nuclei are oriented with a {110} plane parallel to the substrate surface and a ⟨110⟩ direction along a ⟨100⟩ direction in the substrate. These nuclei grow more rapidly along their ⟨110⟩ directions. Nucleation of the new structure is discussed briefly. Calculation of the lattice misfits shows that neither of the observed orientations minimizes misfit.

I. INTRODUCTION

THE phenomenon of epitaxy, the growth of one crystal on another, has been recognized in numerous forms for more than sixty years.[1] The advent of the techniques of electron diffration and transmission electron microscopy in the last decade has enabled investigators to observe directly both the crystalline orientations and defect structures which are of major importance in providing detailed information for the understanding of this phenomenon. The majority of the data obtained in the recent years has dealt with face-centered cubic metals, and the noble metals in particular, primarily because of experimental considerations. This paper details observations of the growth of the body-centered refractory metal niobium on cleaved substrates of magnesium oxide (NaCl structure) in an environment of moderately good vacuum.

[1] F. Wallerant, Bull. Soc. Franc. Mineral 25, 180 (1902).

II. EXPERIMENTAL METHODS

High-purity niobium (99.99+%) was evaporated by electron beam heating in a vacuum of 9×10^{-7} to 5×10^{-6} Torr and condensed on a (100) cleavage face of single-crystal magnesium oxide. The deposition rate was varied between the limits of 2 and 120 Å/min. The substrate was heated to the desired temperature by a resistance heater composed entirely of high-purity sheet niobium. The temperatures recorded in this study refer to the temperature of the center of the substrate crystal of dimensions $1\times5\times1$ cm. It was initially determined by a platinum vs platinum–rhodium thermocouple and calibrated with reference to the current passing through the heater strip. The temperature was subsequently inferred from measurements of the heater current. The substrate surface temperature is likely to have been somewhat higher than that recorded as a result of absorption of radiant energy from the vapor source. The normal liquid-nitrogen cold trap located above the oil diffusion pump was supplemented with