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Contract Nonr-1866 (50)

NR-032-485

THE EFFECT OF HIGH PRESSURE ON B_2O_3 :
CRYSTALLIZATION, DENSIFICATION AND THE
CRYSTALLIZATION ANOMALY

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By

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July 1966

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Technical Report No. 8

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The research reported in this document was made possible through support provided by the Division of Engineering and Applied Physics and the Committee on Experimental Geology and Geophysics, Harvard University the Office of Naval Research under Contract Nonr-1866(50) and the Advanced Research Projects Agency under Contract ARPA SD-88.

Division of Engineering and Applied Physics

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CRYSTALLIZATION, DENSIFICATION, AND THE
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ABSTRACT

The crystallization and densification of B_2O_3 at high pressure have been investigated using a Bridgman anvil device. Crystallization has been observed at pressures as low as 4 kilobars and at temperatures as low as $210^\circ C$. A marked effect of water in increasing the overall crystallization rate, and the increase in this rate with increasing temperature, have been demonstrated. Increases in density as large as 17 percent, and a strong effect of temperature in increasing densification, have likewise been shown.

The crystallization behavior is discussed in terms of the kinetic formalism developed previously and is related to past observations on SiO_2 at high pressure. The densification results are considered in light of the results of other workers on B_2O_3 and SiO_2 . The anomalous crystallization behavior of B_2O_3 is discussed, and a number of hypotheses are advanced to explain the observations. These hypotheses are evaluated in relation to the results of the high pressure study.

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I. INTRODUCTION

A. Atmospheric Pressure

The resistance of boron trioxide (B_2O_3) to crystallization at atmospheric pressure is well known [1, 2, 3]. Indeed, its crystallization from a dry melt at one atmosphere has never been observed. Even seeding the melt and holding it for several months at various temperatures below the melting point is not effective in producing observable crystallization [1].¹

It has long been known, however, [1, 2] that crystalline B_2O_3 can be prepared by the stepwise dehydration of orthoboric acid (H_3BO_3). It was noted then [1] that the essential feature of the dehydration process is the formation of crystals of the cubic metaboric acid (HBO_2 I), which presumably serve as nucleation agents for the formation of crystalline B_2O_3 . The other crystalline metaboric acids, monoclinic HBO_2 II and orthorhombic HBO_2 III, are never observed to act as nucleation agents for crystalline B_2O_3 .

When seeded with crystalline B_2O_3 or HBO_2 I, melts with compositions near HBO_2 are observed to crystallize rapidly while those with compositions near B_2O_3 are found to crystallize slowly if at all.

The cubic metaboric acid is characterized [1] by a density which is nearly identical with that of crystalline B_2O_3 (2.48 vs. 2.46 gm/cm³),

¹As noted by Kracek, Morey and Merwin [1], "The added crystals merely remain suspended in the softened glass in a wholly inert condition."

and is substantially higher than that of glassy B_2O_3 (1.8 gm/cm^3) or the other crystalline metaboric acids (2.04 and 1.78 gm/cm^3 , respectively, for HBO_2 II and HBO_2 III).

A recent X-ray diffraction determination [4] of the structure of cubic metaboric acid has indicated that each boron atom is bonded tetrahedrally to four oxygen atoms and each oxygen atom to two boron atoms, so as to produce a three-dimensional network of BO_4 tetrahedra. This four-fold coordination of the boron atoms had been suggested by the previous nuclear magnetic resonance studies [5, 6].

In contrast, a crystal structure determination [7] for monoclinic metaboric acid has indicated that only one-third of the boron atoms are in a tetrahedral configuration. A diffraction study of orthorhombic metaboric acid [8] suggests that all of the boron atoms in this structure are in three-fold coordination. These conclusions are again supported by nuclear magnetic resonance studies [9]. In glassy B_2O_3 , a three-fold (triangular) coordination of the boron atoms is suggested by X-ray diffraction [e. g., 10, 11], infrared absorption [e. g., 12-14] and nuclear magnetic resonance [9, 15, 16]. Hydrated B_2O_3 glasses, with water contents up to 25 mole percent or more, fail to show evidence for tetrahedrally-coordinated boron atoms, while an estimated 5 percent of the boron atoms in glasses of 35 mole percent water are found to have tetrahedral coordination [9, 16].

The only structural investigation of crystalline B_2O_3 carried out to date [17] has indicated that the structure is composed of two sets of

BO_4 tetrahedra. In both sets, the tetrahedra are highly distorted. In one, the boron-oxygen distance is reported to vary from 1.3 \AA (its value for boron in triangular coordination) to 1.9 \AA , and the oxygen-oxygen distance from 2.37 \AA to 3.06 \AA . In the other set, the configuration of oxygen atoms around the boron atoms is described as a hybrid between triangular and tetrahedral, the boron-oxygen distances being 1.48 \AA , 1.48 \AA , 1.37 \AA , and 2.14 \AA .

It should be noted, however, that this crystal structure determination is far from certain. Because of the difficulty in obtaining large crystals, the determination was carried out with powder data only. It was not possible to assign a space group, and the precise location of the boron atoms in the selected structure is open to further question (The scattering factors for the boron atoms are significantly smaller than those of the oxygen atoms).

The principal difficulty in effecting a reliable structure determination is the small size (less than 0.1 mm) of the crystals which result from the dehydration process, and the concomitant difficulty of separating individual crystals from the general crystalline mass.

B. High Pressure

Despite its resistance to crystallization at atmospheric pressure, B_2O_3 may readily be obtained in the crystalline state at high pressures. Dache and Roy [18] and Mackenzie and Claussen [3] have prepared

both the ordinary hexagonal crystals, similar to those obtained in the dehydration of H_3BO_3 ($\alpha\text{-B}_2\text{O}_3$), and a new dense monoclinic form ($\beta\text{-B}_2\text{O}_3$).

The suggested temperature-pressure equilibrium diagram, taken from the work of Mackenzie and Claussen, but summarizing all previously reported work on the material, is shown in Fig. 1. Note that for temperatures less than about 500 degrees, and pressure in excess of about 25 kilobars, the suggested stable form is the dense $\beta\text{-B}_2\text{O}_3$.

The work by Dachille and Roy was carried out in a Bridgman-anvil high pressure device, while that by Mackenzie and Claussen was conducted in a "belt" type apparatus. The divergence between the two suggested $\alpha\text{-}\beta$ equilibrium curves in the range of overlap, if it is in fact physically significant, may well be due to the difference in pressure generating equipment (and the concomitant possibility of difference in the stress state of the samples).

In the work of Dachille and Roy, a third phase was sometimes observed in the diffraction pattern of pellets compacted at temperatures below about 350°C . In concurrent studies of the infrared absorption spectra of the pellets, (OH) absorption was observed; and it was suggested that the third phase might well be a hydrated one. This suggestion was strongly supported by the work of Mackenzie and Claussen, who never observed the third phase in runs carried out with carefully dehydrated B_2O_3 , but found similar X-ray lines on compacting H_3BO_3 .

In the previous high pressure work, crystals of α - B_2O_3 have been made at pressures as low as about 13 kilobars and temperatures as low as about $300^\circ C$. In the work of Mackenzie and Claussen, the sample of B_2O_3 could be completely crystallized in times as short as two minutes (at 40 kilobars, $600^\circ C$, for example). Even at room temperature, some five or ten percent of the sample could be crystallized in one day at 40 kilobars.

By such single-step compaction, only microcrystals could be produced (of a size similar to that obtained from the dehydration of H_3BO_3). By other extraordinary techniques, however, crystals as large as 0.3 mm could be obtained. While these crystals would be adequate for a single-crystal structure determination (assuming they could be removed from the matrix), such a determination has not yet been effected.

The melting behavior at atmospheric pressure of crystals produced at high pressure was investigated by Mackenzie and Claussen. They observed that crystals of either α - B_2O_3 or β - B_2O_3 melt at temperatures between 455 and $475^\circ C$ and above, but not at lower temperatures. Although α - B_2O_3 appears to be the stable crystalline modification at atmospheric pressure, no transformation from β to α was ever observed. The melting point of α - B_2O_3 was suggested to lie in the temperature interval between 455 and $475^\circ C$. By comparison, the melting point of crystals prepared by the dehydration of H_3BO_3 was determined [1] as $450 \pm 2^\circ C$.

The fusion of β - B_2O_3 was suggested to take place by the sequence $\beta \rightarrow \alpha \rightarrow$ liquid. It should be noted, however, that this suggestion is based

on the similar temperature range where melting is first observed. Further, no conversion from β to α was ever observed, even in a period of four days at the slightly lower temperature of 445°C .

The difference between the two reported melting points of $\alpha\text{-B}_2\text{O}_3$ ($450 \pm 2^{\circ}\text{C}$ vs. $455\text{-}475^{\circ}\text{C}$) may be due to differences in water content between crystals prepared from dehydration of H_3BO_3 and those prepared at high pressure from dry B_2O_3 . In both cases, however, the melting points were determined only by observations of melting (Recall that the crystallization of dry B_2O_3 at one atmosphere has never been observed). As shown schematically in Fig. 2, such one-way determinations of equilibrium temperatures may well be subject to error. In the case of the solid-liquid transition, the errors are most likely for materials characterized by large viscosities at their melting points (and hence small transformation rates), and those which exhibit non-linear transformation kinetics. The application of these considerations to the specific case of B_2O_3 will be treated in Part IV below.

C. Kinetics

Expressions have been derived in a previous paper [19] for the effect of pressure on the rates of nucleation and growth. These expressions indicate that the application of pressure may significantly increase the rate of nucleation of crystals in a less dense liquid. The effect of pressure on the rate of crystal growth, on the other hand, may in some cases at

moderate pressures be an enhancing one, but should in all cases at sufficiently high pressures be a retarding influence.

The steady-state rate of homogeneous nucleation per unit volume, I_v , may be expressed [19, 20]:

$$I_v \sim \frac{N_v^0 D'}{a_0^2} \exp(-W^*/kT) \quad (1)$$

where N_v^0 is the number of molecules per unit volume, D' is the diffusion coefficient for molecular transport across the nucleus-matrix interface, a_0 is an intermolecular diameter, and W^* is the work of forming the critical nucleus.

For a nucleus which is spherical in shape, W^* may be expressed:

$$W^* = \frac{16}{3} \frac{\sigma^3}{(\Delta G_v)^2} \quad (2)$$

Here σ is the nucleus-matrix specific surface free energy and ΔG_v is the difference in Gibbs free energy per unit volume between nucleus and matrix (referred to bulk phases). Use of ΔG_v in this expression is strictly correct only when the nucleus material is incompressible; when both nucleus and matrix are fluid phases, it should be replaced by ΔP , the pressure difference across the nucleus-matrix interface.

In evaluating the effect of pressure on nucleation rate, it was indicated [19] that the principal effect should be the variation of W^* with

pressure. Using a number of plausible assumptions,² it was possible to express this variation:

$$(\partial W^*/\partial P)_T = -W^*[3\Gamma V^\alpha \sigma + 2(V^\alpha - V^\beta)/V^\beta \Delta G_V] \quad (3)$$

Here Γ is the surface excess mass [21], V^α is the molar volume of the matrix and V^β is the molar volume of the nucleus.

Applying this to the case of B_2O_3 , we may use:

$V^\alpha - V^\beta/V^\beta = 0.3$ and $V^\alpha = 40 \text{ cm}^3/\text{mole}$ [1, 3]. Using the value of Southard [22] for the latent heat of fusion, and estimating the temperature of homogeneous nucleation, ΔT^* , from the results of Turnbull [23] on other systems ($\Delta T^*/T_M = 0.2$), we may take ΔG_V as about 10^9 ergs/cm^3 . The crystal-liquid surface energy may be estimated from the finding of Turnbull [23] that for many other materials the surface energy per atom is about one-half the latent heat of fusion per atom. For B_2O_3 , this becomes $\sigma \sim 100 \text{ ergs/cm}^2$.

With these values for the respective parameters, a knowledge of Γ , the surface excess mass, is the only additional information needed to evaluate $\partial W^*/\partial P$. Unfortunately, in the case of the solid-liquid transition even the sign of Γ cannot a priori be known with any certainty.

²The specific assumptions used in the derivation of eq. (1) were the following:

- (1) The critical nucleus is spherical in shape.
- (2) The nucleus is incompressible. This is equivalent to assuming that the densities of internal energy and entropy of the nucleus are independent of curvature, and permits use of ΔG_V in the expression for W^* .
- (3) The term representing the pressure dependence of the equilibrium temperature in $(\partial \sigma/\partial P)$ may be neglected in comparison with the variation of chemical potential with pressure (the Γ term).

Useful estimates of $\partial W^*/\partial P$ may, however, be made by using some reasonable assumptions about Γ . First, let us take $\Gamma = 0$ (equivalent to assuming that the surface energy is independent of pressure). Then:

$$(\partial W^*/\partial P)_T \sim -.0006 W^*/\text{BAR} \quad (4)$$

This represents an extremely rapid decrease of W^* with pressure, and indicates, subject to the approximations employed, that the rate of crystal nucleation should be strongly enhanced by the application of pressure.

The size of the contribution of the Γ term to the variation of W^* with pressure may be estimated by taking $\Gamma = 10^{14}$ molecules/cm² (1.6×10^{-10} mol/cm²). Then:

$$(\partial W^*/\partial P)_T \sim .0002 W^*/\text{BAR} \quad (5)$$

Γ Term

The sign of this contribution is negative for a surface excess (Γ positive) and positive for a surface deficit (Γ negative). For the assumed Γ , the magnitude of the contribution is quite large (comparable with the previous value).

Thus, when Γ is zero or positive, or when it is negative but of magnitude less than $2\sigma(V^\alpha - V^\beta)/3V^\alpha V^\beta(\Delta G_v)$, the work of forming the critical nucleus should decrease rapidly with increasing pressure.

This effect of pressure on W^* (which acts to increase the nucleation rate) is expected generally to outweigh its effect on the

diffusion coefficient for molecular transport across the nucleus-matrix interface (which acts to decrease the nucleation rate). The latter effect may perhaps be estimated from the variation of viscosity with pressure. From the work of Dane and Birch [24], the viscosity of B_2O_3 at 1 kilobar is higher than its value at atmospheric pressure by a factor of 4.5 at $359^\circ C$, and by a factor of 1.5 at $516^\circ C$.

The effect of pressure on growth rate may be seen by considering the standard expression for the rate of advance of a solid-liquid interface, per unit cross section of the interface [19, 25]:

$$u = (f D'' / a_0) [1 - \exp(-V\Delta G_v / RT)] \quad (6)$$

Here u is the growth rate in cm/sec; D'' is the diffusion coefficient for molecular transport across the crystal-liquid interface; a_0 is the jump distance; and f is the fraction of sites at the interface where atoms can preferentially be added or removed.

The application of pressure is expected to decrease D'' , and for the growth of a more dense phase, to increase $[1 - \exp(-V\Delta G_v / RT)]$ by increasing the motivating potential, ΔG_v . The magnitude of the former effect may perhaps be estimated from the variation of viscosity with pressure, while the latter should be most significant at temperatures near the equilibrium temperature at one atmosphere, but not very important at large departures from equilibrium.³

³The reader is referred to Reference 19 for more detailed treatment of these considerations.

The application of pressure to a material such as B_2O_3 , in which defects are expected [19, 26] to have a sizable effect on growth, should serve to increase the fraction, f , of preferred growth sites—again because of the increase in motivating potential which accompanies the increase in melting point with pressure.⁴

At sufficiently high pressures, the effect of pressure on D^n should predominate, and the growth rate is expected to decrease with increasing pressure. At lower pressures, the growth rate may increase with increasing pressure (if the effect on D^n is outweighed by the effect on $[1 - \exp(-V\Delta G_v/RT)]$ and f). Under such circumstances, a maximum in the isothermal growth rate-pressure relation should be observed.⁵

It should be noted, of course, that the experimentally-determined quantities in studies at high pressure are often not the individual rates of nucleation and growth, but rather their combination in the volume fraction, X , transformed in a given time, t . For a constant nucleation rate per unit volume, I_v , this last quantity may be expressed [27]:

$$X = 1 - \exp(-\pi I_v u^3 t^4/3) \quad (7)$$

⁴The reader is referred to Reference 19 for more detailed treatment of these considerations.

⁵Alternatively, if the temperature at which a given extent of growth is obtained in a given time is plotted as a function of pressure, a minimum in the curve should be observed.

D. Densification of Glass

It is well established [28-32] that glass-forming materials can undergo a "permanent" densification when subjected to high pressures. The densification is observed to be appreciably larger when compaction is carried out above the glass transition temperature than when it is carried out in the glassy state, and can be observed to anneal out at atmospheric pressure at temperatures below the glass transition temperature [29, 30, 33].

The densification of SiO_2 in the glassy state was extensively investigated by Mackenzie [28], who reported that increases in density of 15 percent or more could be obtained (by compaction at 75 kilobars, 300°C , for example). The densification was shown [28, 31] to increase with increasing temperature and pressure of compaction.

The data for B_2O_3 compressed in the glassy state, not nearly so extensive as those for SiO_2 , are summarized in Fig. 3. As shown there, this densification also seems to increase with increasing temperature and pressure. There are, however, significant differences among the results obtained by the different investigators at the common temperature of 25°C . In contrast with the results on SiO_2 , the data in Fig. 3 seem to indicate an increase in densification with decreasing shear component of the pressure (the Cohen and Roy study was carried out in a Bridgman anvil device, in which high shear stresses are

anticipated, while the Mackenzie study was conducted in a "belt" apparatus, in which the shear component should be appreciably smaller).

For B_2O_3 compressed in the glassy state, the largest reported densification was about 5 percent. When the compaction was carried out in the "belt" apparatus above the glass transition temperature, however, increases in density of more than 7 percent were observed [29].

E. Crystallization Anomaly

The observations cited above of the crystallization and melting behavior of B_2O_3 at atmospheric pressure seem to present an interesting problem, which may appropriately be termed the " B_2O_3 crystallization anomaly".

By the principle of microscopic reversibility, if molecules are added to and taken from similar sites (in freezing and melting respectively), then the curves of growth rate and melting rate vs. motivating potential (undercooling or superheat) should be continuous with the same slope through the equilibrium temperature (see Fig. 4).

Although there is a paucity of relevant experimental data—just as there is a paucity of reliable kinetic data on crystal growth from the melt generally [26]—curves of this form have been observed by Swift [34] on the crystallization and melting of devitrite ($Na_2O \cdot 3 CaO \cdot 6 SiO_2$) in a soda-lime glass, and by Cormia, Mackenzie and Turnbull [35] on the crystallization and melting of P_2O_5 . Further, while a detailed study of the crystallization and melting kinetics of cristobalite has yet

to be carried out in the vicinity of the melting point, the crystals have been observed to melt and grow at small departures from the equilibrium temperature [36, 37].

Far otherwise is the experience with B_2O_3 . As we have seen, crystals prepared by the dehydration of H_3BO_3 have been observed to melt at temperatures exceeding $450^\circ C$, while those prepared at high pressure are observed to melt at temperatures of $455-475^\circ C$ or higher. In both studies, crystallization of a dry melt, even one seeded with crystals, could not be observed.

A number of hypotheses may be used to explain this anomaly. These will be discussed in Part IV below.

In the present paper, we shall report some observations on the effect of high pressure on B_2O_3 , particularly the effect of high pressure on its crystallization and densification behavior; discuss these observations in terms of the kinetic treatment outlined above; and utilize these and other observations in attempting to elucidate the problem of the crystallization anomaly.

II. EXPERIMENTAL TECHNIQUE

Samples of B_2O_3 , prepared under a number of conditions, were held at temperature and pressure in a Bridgman-anvil or "squeezer" high pressure device. At the end of a desired period, the samples were quenched by first lowering the temperature to ambient and then removing the pressure. Subsequent examination by X-ray diffraction, and in most cases by optical microscopy as well, was used to detect crystallization. Measurements of density were also carried out to investigate the crystallization and evaluate the effect of pressure on the residual glass.

The B_2O_3 starting material used in this study was a special high purity grade furnished through the courtesy of the U. S. Borax Corporation.⁶ As supplied, the material was in the form of irregular flakes, typically about 50 mm x 75 mm x 2 mm in size. Despite the nominally sealed containers used in shipment, the surface layer had hydrated to crystalline orthoboric acid, resulting in an overall translucent appearance.

In some runs, designated as air loading, this material was directly crushed in a Plattner-type steel mortar in the ambient atmosphere of the laboratory. The forming of a sample pellet from the crushed powder

⁶U. S. Borax Corp., Rockefeller Center, New York City, New York.

(typical particle size, approximately 20 microns) and transfer of the loaded anvils to the high pressure device were likewise carried out in the ambient atmosphere.

To investigate the effects of water, several runs were made in which a drop of water was added to the crushed powder before forming the sample pellet. These runs, with other conditions similar to those for air loading, will be designated as wet loading.

To study the effect of pressure on "dry" B_2O_3 , a different preparation and loading procedure was adopted. This will be termed dry loading. In this case, flakes of the starting material were broken into a few pieces, placed in clean uncovered platinum boats, and held at about $1300^{\circ}C$ for periods of 16-20 hours. The boats were removed rapidly from the furnace, and transferred directly to a newly designed glove box [38]. This glove box, containing Plattner mortar, Petri dishes, bottles of phosphorus pentoxide powder, hammer, anvils, clamps, transfer boxes, etc., could be closed and evacuation begun within about 20 seconds after placing the sample inside. In this way, the sample was provided with dry environment by the time it cooled to the temperature range where hydration effects are most severe.

Following evacuation into the range of 10^{-5} torr, the glove box was back-filled with dry nitrogen gas (dew point less than $-110^{\circ}F$). Open Petri dishes in the glove box were filled with phosphorus pentoxide powder; manipulation, crushing of the samples, and loading of the anvils were carried out under a positive pressure of the dry gas. The box was

opened to the ambient atmosphere only after the loaded anvils had been placed in O-ring sealed brass containers (which also contained phosphorus pentoxide powder).

The loaded anvils were transferred to the "squeezer" area in these sealed containers; the containers were opened; the anvils were rapidly placed in the "squeezer"; and the pressure was quickly applied. The estimated time of exposure to the atmosphere in this operation was about 10 seconds, during which time the anvil holder was tightly clamped around the anvils.

The high pressure device was shear "squeezer" of a type described previously [39, 40] and shown schematically in Ref. 19. The anvils were made of Vasco Supreme Steel,⁷ heat treated to a hardness of Rockwell C-68-69. The sample diameter regularly used was 0.225 inches; the sample height was determined by a steel or aluminum spacer-retaining ring, 0.010 inches thick.

The pressures to be reported in this paper are the nominal pressures obtained from a Heise gauge in the hydraulic system. Previous calibrations of the present apparatus have indicated close correspondence between nominal pressure and true pressure (determined for the bismuth and quartz-coesite transitions). In any case, for purposes of the present work, the exact magnitude of the pressure will not be important.

⁷Obtained from Vanadium Alloys Steel Co., Boston, Mass.

The temperature of each run was measured with a chromel-alumel thermocouple located at the anvil base, and was controlled with a Honeywell controller.

The presence of crystallization was generally determined by means of X-ray diffraction. Because of the severe hydration problem, the sample pellets were usually removed from the squeezer as soon as the pressure was released, and were immediately placed on a glass slide and run on a Norelco diffractometer.

In some cases, however, the pellets were examined optically, and measurements of refractive index and density made, in lieu of or prior to the diffraction work. The density measurements were carried out using a Berman balance,⁸ with which the weight in air and weight in toluene of the sample could readily be compared. The optical examination and measurements of the index of refraction were carried out with a Zeiss polarizing microscope and standard index oils. In some instances, particularly with those samples which had first been X-rayed, it was necessary to fracture the sample under the index oil to obtain a reliable determination, since hydration of the surface to H_3BO_3 prevented direct measurements.

⁸Obtained from Bethlehem Instrument Co., Bethlehem, Pennsylvania.

III. RESULTS

The most striking feature of the present work was the observation of copious crystallization at high pressures, even in the temperature interval of the glass transition at one atmosphere. Under dry loading conditions, crystals were obtained at pressures as low as 4 kilobars (at 250°C) and at temperatures as low as 210°C (at pressures of 10-30 kilobars).

When the lowest temperature at which crystallization can be observed in a given time (arbitrarily chosen as several hundred hours) is plotted as a function of pressure, the results presented in Fig. 5 are obtained (the data obtained for dry loading conditions). As shown there, a broad minimum in temperature is observed, at about 200-210°C, extending from about 10 kilobars to about 30 kilobars. Outside this pressure interval, the lowest temperature for crystallization seems to be appreciably higher than 200-210°C. It should be noted that the results shown in Fig. 5 represent only a small fraction of the total data obtained in the investigation. The points shown were chosen to delineate the region of observable crystallization.

In the region of temperature and pressure where crystallization could be observed, the extent of crystallization (measured semi-quantitatively by the relative integrated intensity in the $d = 2.78 \text{ \AA}$, $\alpha\text{-B}_2\text{O}_3$ diffraction peak) was found to increase, and the half-width of the diffraction peak to decrease, with increasing duration of the run. For runs of a given length at a given

pressure, the extent of crystallization was observed to increase with increasing temperature.

In contrast with the results of Mackenzie and Claussen, who observed crystallization in a day at room temperature and a pressure of 40 kilobars, we were unable under dry loading conditions to observe crystallization at 40 kilobars in 311 hours, even at the appreciably higher temperature of 240°C. At the somewhat lower temperature and pressure of 145°C, 20 kilobars, a run as long as 517 hours failed to produce observable crystallization. As we shall see in Part IV below, our results are in much better agreement with kinetic expectations than are those of the previous workers.

A pronounced effect of water in enhancing crystallization kinetics was observed in runs carried out under different loading conditions at a particular temperature and pressure. For runs of a given time, the extent of crystallization (measured semi-quantitatively by the relative integrated intensity in the $d=2.78 \text{ \AA}$, $\alpha\text{-B}_2\text{O}_3$ diffraction peak) was found to increase in the order: dry loading < air loading < wet loading. Correspondingly, exposure to water was found to result in observable crystallization at temperatures well below the minimum temperature for crystallization under dry conditions. For example, at 20 kilobars, crystallization was observed with air loading at 130°C in 70 hours, while with dry loading no crystallization was detected at 195°C in runs as long as 239 hours. Significant variability in the extent of crystallization in a given time was noted in the results obtained with air loaded runs, presumably due to variations in the exposure to atmospheric water.

With samples prepared under conditions of air loading or wet loading, the H_3BO_3 peak at $d = 3.18 \text{ \AA}$ ($2\theta = 28.3^\circ$, $\text{CuK}\alpha$) was almost always present. It was found that the presence of this main H_3BO_3 diffraction peak could provide a fairly useful indication of hydration in our samples. In evaluating this possibility, "cry" B_2O_3 was crushed in a Plattner mortar, and the resulting powder placed on a beam balance. The increase in weight with time of exposure to laboratory air was measured, and was compared with the time required for a similar powder sample, placed on a diffractometer, to show the definite appearance of the H_3BO_3 diffraction peak. In this way, it was found that increases in weight as small as 0.5 percent could readily be detected.

No traces of H_3BO_3 could be found in the diffraction patterns of dry-loaded starting materials. For samples which were X-rayed immediately upon removal from the Bridgman anvils, a similar absence of the hydrous phase was noted. This was true even for runs of several hundred hours at low temperatures, and provides evidence against the pick-up of atmospheric water while the samples were under pressure.

Although most of the runs were carried out in the reported stability field of the high density crystalline form, $\beta\text{-B}_2\text{O}_3$ (see Fig. 1), this form was observed in only a single case (at 32 kilobars, 268°C). In all other runs where crystallization was observed, the crystals were of the lower density, $\alpha\text{-B}_2\text{O}_3$, form. Even in the run where crystals of $\beta\text{-B}_2\text{O}_3$ were produced, crystals of $\alpha\text{-B}_2\text{O}_3$ were observed as well.

The crystals of $\alpha\text{-B}_2\text{O}_3$ were observed to hydrate to H_3BO_3 on extended exposure to the atmosphere of the laboratory. The rate of

this hydration was, however, appreciably lower than that observed for glassy B_2O_3 , even for glassy material densified at high pressure.

While no systematic study was made of the densification of B_2O_3 under pressure, the density was determined for a number of samples which gave amorphous diffraction patterns after compaction. In all cases, the densification was carried out in the glassy state (the glass transition temperature at atmospheric pressure is about $230^\circ C$, and rises at least initially by more than $20^\circ C$ per kilobar [41]).

Densities as high as 2.17 gm/cm^3 and refractive indices as large as 1.532 were observed in the densified glasses (for comparison, the density of ordinary B_2O_3 glass is about 1.83 gm/cm^3 , and its refractive index is about 1.457). In many cases, sizable variations in density and refractive index were observed across the sample pellet. The central region was generally found to be more dense and have a higher refractive index than the peripheral regions. These variations very likely reflect the non-uniformity of pressure across the sample pellet, as previously observed by other workers [e. g., 42-44].

For the range measured, the relation between density and refractive index was found to depart from a straight-line interpolation between the values for ordinary glass and α -crystals. In particular, the density for a given refractive index was generally higher than would be expected from such an interpolation. The largest positive deviation from the interpolation on a ρ - n plot was about 0.15 gm/cm^3 , while the largest negative deviation was about 0.08 gm/cm^3 .

While the effect of pressure on densification could not be specifically evaluated from our data, increases in temperature at a given pressure were found to result in substantial increases in density. At 20 kilobars, for example, compaction at 250°C resulted in a density increase of about 17 percent, while compaction at 150°C increased the density by only about 10 percent. While there are no other data on densification at such temperatures, it should be noted that both these values exceed those found by Mackenzie in compaction above the glass transition temperature in a "belt" apparatus. For compaction carried out at room temperature, the densifications observed in the present study exceed those reported previously. At 40 kilobars, for example, increases in density of 4 to 6 percent were observed, compared with the value of 2 to 3 percent noted by Bridgman and Simon (see Fig. 3 above).

IV. DISCUSSION

From the kinetic treatment outlined in Part I above, the expected rates of nucleation and growth may readily be estimated. Assuming a Stokes-Einstein relation between the bulk viscosity and the diffusion coefficient for transport across the nucleus-matrix interface, taking the viscosity data of Parks and Spaght [45], using the model of Hoffman [46] to estimate the difference in Gibbs free energy between crystalline and amorphous B_2O_3 , and taking $W^*/kT \sim 50$ at a relative undercooling ($\Delta T/T_E$) of 0.2, in consonance with results on other materials, [20, 47] the nucleation rate per unit volume is estimated from Eq. (1) to be approximately $1 \text{ cm}^{-3} \text{ sec}^{-1}$ at 240°C .⁹ This value is near the lower limit of observability.

The growth rate may conveniently be estimated from Eq. (6) by using a number of rather simple assumptions. According to the criterion of Jackson [48, 49], B_2O_3 is expected to have a smooth interface in growth from the melt, and the growth may then be expected to take place at steps provided by screw dislocations or nuclei formed on the interface. If growth is assumed to take place by a surface nucleation mechanism, and the standard model for such growth [25] is used to evaluate f , and if a Stokes-Einstein relation is employed to evaluate D'' from η ,¹⁰ the

⁹See Reference 19 for details of this evaluation.

¹⁰It has been suggested [50], however, that D'' may exceed the diffusion coefficient for transport in bulk liquid by a factor of 10 or 100.

growth rate is expected to vary with temperature as shown in Fig. 6 .

As indicated there, the expected growth rate at 240°C is only about $2 \times 10^{-6} \text{ \AA}/\text{sec}$. For most experimental conditions, such a growth rate would be unobservably low.

For studies carried out at high pressure, the discussion of Part I has indicated that the rate of nucleation may be appreciably higher than its value at atmospheric pressure. This enhanced rate may even be sufficiently large that the nucleation step is not the limiting factor in the transformation. The effect of pressure on the growth rate of B_2O_3 was likewise considered in Part I. As indicated there, the application of pressure is expected to increase $[1 - \exp(-V\Delta G_v/RT)]$ and f , while decreasing D'' , and could result in a maximum in the isothermal growth rate versus pressure relation.

Since the observation of crystallization requires growth of nuclei to a detectable size, it might seem plausible to interpret the minimum in the temperature-pressure relation of Fig. 5 in terms of the competition between these effects of pressure on growth rate. Such an interpretation does not, however, seem worthy of merit, and the observed minimum is not satisfactorily understood at the present time. For although the effect of pressure on f and $[1 - \exp(-V\Delta G_v/RT)]$ may be important at temperatures near the melting point at one atmosphere, its effect at large undercoolings should be quite small and should be far outweighed by the effect of pressure in decreasing D'' .

Although no direct measurements of growth rate were made in the present study, it does seem possible to derive a useful estimate of this quantity from the X-ray diffraction data. At 20 kilobars, 250°C, for example, the integrated intensity was found to increase and the half-width of the diffraction peak to decrease, between runs of 16 and 25 hours. Although the individual crystals could not be resolved optically, particle-size broadening should be appreciable only for particle sizes below about 1000 Å, and since the diffraction pattern from the 16 hour run showed significant broadening, while that from the 25 hour run showed only little broadening, we may roughly estimate the growth rate to be about 500 Å in about 10 hours, or about 10^{-2} Å/sec. This estimate may well be good to order-of-magnitude accuracy.

The growth rate predicted from Eq. (6) for this temperature at atmospheric pressure is about 10^{-5} Å/sec, or about three orders of magnitude lower than the estimated observed rate at 20 kilobars. The growth rate expected from Eq. (6) at 20 kilobars cannot presently be predicted, because of the uncertainty in specifying the viscosity at this pressure. The growth rate is, however, expected to be much smaller than its value at atmospheric pressure, thus resulting in a greater discrepancy between the predicted and the estimated-observed rates.

It is true, of course, that the rates observed in studies at atmospheric pressure often exceed those calculated from Eq. (6) by a factor

of 10 or 100 or so [26, 36]; but the difference estimated in the present study considerably exceeds this factor.

In this light, the crystallization reported by Mackenzie and Claussen at room temperature, 40 kilobars in 24 hours, is even more difficult to understand. Our own failure to detect crystallization at this pressure, even in a run of 311 hours at the higher temperature of 240°C, suggests that catalysis by impurities (most likely, water) may have been operative in the previous study.

A similarly large divergence between expectation and observation was, however, found by the present authors in a parallel study of SiO₂ under high pressure [19]. In that investigation, crystallization was observed at high pressures (30 kb, for example) at temperatures (500°C, for example) hundreds of degrees below the glass transition at one atmosphere.

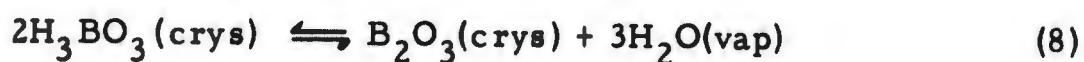
A number of models were discussed [19] to account for this unexpected observation of crystallization. The most plausible of these models was based upon the catalytic effect of water, and the possible existence of a water-rich region in the vicinity of the interface. It was expected that these effects would be enhanced by the application of pressure, both because pressure should increase the solubility of water in the amorphous phase, and because water should be retained in the sample to higher temperatures at high confining pressures.

In any case, a marked effect of even trace amounts of water in increasing crystallization kinetics has now been demonstrated in both SiO_2 and B_2O_3 under high pressure. Generalizing as before from these two classic network systems, one might well expect even small amounts of water to have a profound effect on the crystallization kinetics of other network materials, an effect which will be more pronounced at high pressure than at one atmosphere.

The increase in the overall crystallization rate with increasing temperature, observed here for B_2O_3 was also noted in the study of SiO_2 . It is very likely related to the general increase in molecular mobility which accompanies increases in temperature.

The observations on hydration may well be viewed in terms of known thermochemical data on the system $\text{B}_2\text{O}_3\text{-H}_2\text{O}$. The relevant data, taken from the JANAF Tables [51], are summarized in Table I. From this data, the free energy change on hydration and the vacuum needed to avoid hydration may readily be estimated.

Consider, for example, the reaction:



The change in the standard Gibbs free energy in this reaction may be written

$$\begin{aligned} \Delta G_{298}^{\circ} = & \Delta G_{298}^{\circ}(\text{B}_2\text{O}_3 \text{ crys}) - 2\Delta G_{298}^{\circ}(\text{H}_3\text{BO}_3 \text{ crys}) \\ & + 3\Delta G_{298}^{\circ}(\text{H}_2\text{O vap}) \end{aligned} \quad (9)$$

TABLE I

Thermochemical Data From JANAF Tables [51]

<u>Material</u>	<u>ΔG_{298}°</u>
H ₃ BO ₃ crystal	-232.196 kcal/mol
B ₂ O ₃ crystal	-286.443
B ₂ O ₃ glass	-283.760
H ₂ O gas	-54.636

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where the free energies are referred to the standard states and a temperature of 298°K is assumed. Taking the activities of the crystalline forms as unity, the change in free energy in the reaction may be written:

$$\Delta G_{298} = \Delta G_{298}^{\circ} + RT \ln p_{\text{H}_2\text{O}}^3 \quad (10)$$

For $\Delta G_{298} > 0$, the hydration reaction will be thermodynamically favorable.

In a similar way, the conditions for hydration of the glass may be investigated by considering the reaction:



When this is done, using the data of Table I, the following results are obtained:

$$\text{B}_2\text{O}_3 \text{ crys [Eq. (8)] : } \Delta G_{298} = 14.041 + 1.776 \ln p_{\text{H}_2\text{O}} \text{ kcal/mol} \quad (12)$$

$$\text{B}_2\text{O}_3 \text{ glass [Eq. (11)] : } \Delta G_{298} = 16.724 + 1.776 \ln p_{\text{H}_2\text{O}} \text{ kcal/mol} \quad (13)$$

From this, hydration of the crystals will be thermodynamically favorable for partial pressures of water exceeding about 4×10^{-4} atm. while hydration of the glass will be favorable for partial pressures exceeding about 8×10^{-5} atm. Since the partial pressure of water in laboratory air is typically in the range about 10^{-2} atm, it should be thermodynamically favorable for both crystalline and glassy B_2O_3 to

hydrate to H_3BO_3 on exposure to such air. The hydration of the glass would be accompanied by a greater decrease in free energy, but the kinetic observation that crystals hydrate more slowly than glass may be related to kinetic factors such as the interface reaction rate rather than to the thermodynamics.

The present observations on glass densification at high pressure indicate that increases in density of 15 percent or more can be obtained by compaction at elevated temperatures (but still below the glass transition temperature). The nature of the densification process, like the subsequent annealing behavior, is not satisfactorily understood at the present time. The influence of temperature in increasing the densification at a given pressure is very likely related to an increase in molecular mobility with temperature. The exact relation between this increased mobility and the observed densification is, however, far from clear. The elucidation of this relation seems, in fact, to require a more detailed knowledge of glass structure and the processes of molecular motion than is now available.

The differences between the densifications observed at $25^\circ C$ in the present study and those reported previously seem worthy of discussion. Our results may satisfactorily be compared with those of Bridgman and Simon, but are at variance with those reported by Cohen and Roy, who noted a smaller densification than Bridgman and Simon. Our work was carried out with a powder pellet (as was Cohen and Roy's), whereas

Bridgman and Simon used a solid glass sample. As noted by Mackenzie [28], a greater degree of shear is expected when irregular small particles in contact with each other are compressed. This effect of shear, which increases densification, may be enhanced by the locally high temperatures and pressures which can be generated in the regions of contact between particles, which also increase densification. Such an increase in densification on going from solid to powder samples has been observed in studies of SiO_2 [28, 31, 32].

Our observation of a densification at 20 kilobars in the glassy state (17 percent at 250°C) which exceeds that reported by Mackenzie for compaction above the glass transition (7.5 percent at 900°C) may also be due to a similar effect. Our work was carried out with a powder sample in a Bridgman anvil device, an arrangement with a high degree of shear and a significant possibility of developing locally high temperatures and pressures at points of inter-particle contact. Mackenzie, on the other hand, used a solid sample in a "belt" apparatus, an arrangement characterized by a much smaller degree of shear and an absence of inter-particle contacts.

Turning now to the crystallization anomaly, let us consider a number of hypotheses which may be used to account for the observed behavior and discuss these hypotheses in terms of the high pressure results.

First, crystal growth might take place by a surface nucleation mechanism. In this case, the atoms would not be added to and taken from similar sites in melting and freezing, and the rates of freezing and melting would not be expected to be equal at equal motivating potentials. As noted above, B_2O_3 is expected to have a smooth interface in growth from the melt, and growth is expected to take place at steps provided by screw dislocations or nuclei formed on the interface. The principal objection to the hypothesis lies in the high crystalline perfection which it demands of the crystals used as seed material.

The application of pressure should increase the driving force for formation of the crystalline phase, and would thereby tend to increase the rate of growth. It is not clear, however, that the increase in driving force, from a value which is already large, would be sufficient to outweigh the decrease in molecular mobility with the increased pressure.

Second, the reported equilibrium temperature may be in error. As we have noted above, the melting point was determined only by observations of melting. Because of the limits of observation inherent in the experiments, the actual equilibrium temperature may lie well below the apparent equilibrium temperature (see Fig. 2). As shown in Fig. 6, the highest growth rate, of $2 \text{ \AA}/\text{sec}$, is expected at about 410°C . A lower melting point would have the effect of lowering the temperature and magnitude of the maximum and could mean that the kinetics of

crystallization would be so low as to be effectively unobservable. The merits of this suggestion may more satisfactorily be evaluated when a detailed study of the melting kinetics [52] is completed.

The application of pressure should raise the melting point, and crystallization might then take place at a higher temperature where the molecular mobility is higher. It is not clear, however, that the higher temperature will in fact correspond to a higher mobility. At the 10^{15} poise level at least, the iso-viscosity temperature seems to rise as rapidly with pressure as does the melting point. Further, the crystallization observed in the present study took place at temperatures where the fluidity is already low at one atmosphere.

Third, the growth process may be poisoned by impurities present in the material. The effects of impurities should be most severe for materials such as B_2O_3 which are expected to have smooth solid-liquid interfaces and demonstrate the features of anisotropic growth. For the case of growth from the vapor, where the interface is likewise expected to be smooth, Cabrera and Vermilyea [53] have indicated theoretically that impurity adsorption can completely impede growth up to some critical motivating potential. In the case of B_2O_3 , this critical motivating potential could represent a temperature sufficiently low that the rate of crystal growth would be negligible. In the case of melting, small amounts of impurity are not expected to have a corresponding, appreciable effect on kinetics.

It is, of course, difficult if not impossible to eliminate the possibility of impurity effects. The problem might be attempted by using B_2O_3 of higher purity, and by intentional "doping" with specified impurities; but such studies would be fruitful only if positive results were forthcoming—i. e., if impurity effects could be demonstrated.

The increase in motivating potential for crystallization with increasing pressure may provide the critical difference needed to surmount the impeding effects of impurities. The existence of such a threshold in motivating potential has not yet been demonstrated.

Fourth, the observed melting may take place by way of a metastable intermediate phase. This might occur, for example, if the boron-oxygen coordination polyhedra are different in the crystal than in the liquid. The metastable phase in this case might be an amorphous one with the same coordination polyhedra as the crystal.

Hypothetical free energy vs. temperature relations for the three phases in such a case are shown in Fig. 7. As indicated there, the equilibrium temperature between crystal and stable liquid, T_{E_2} , should be lower than that between crystal and metastable liquid, T_{E_3} . It is assumed that the transformation between crystal and stable liquid takes place at a negligible rate, because of the large change in configuration

which must take place at the interface.¹⁰ At temperatures above T_{E_3} , the crystal could melt to the metastable liquid, which then transforms to the stable liquid. On cooling, however, there is no motivation for the stable liquid to transform to the metastable liquid at temperatures above T_{E_1} , and crystallization would not be observed. It is assumed on this hypothesis that the equilibrium temperature between the two liquids, T_{E_1} , is sufficiently low that transformation from stable liquid to metastable liquid is not observed for kinetic reasons.

The application of pressure will densify the glass and may in the process effect a change in some of the coordination polyhedra to a configuration similar to that of the crystal. Mackenzie [28], however, studied the nuclear magnetic resonance absorption in a densified B_2O_3 glass ($\Delta / \sim 5$ percent), and concluded that there was no evidence for a change in the coordination of the boron atoms from 3 to 4. From his published recording, however, there did seem to be some suggestion of a resonance characteristic of 4-coordinated borons.

¹⁰The rates of melting and crystallization for the temperature range of interest, calculated from the bulk viscosity (using eq. (6) and the Stokes-Einstein relation), are quite small (e. g., see Fig. 6). It should be noted, however, that the apparent activation energy for viscous flow in B_2O_3 is unusually low (only a small fraction of the boron-oxygen bond strength); and the bulk viscosity may be inappropriate for describing the reconstruction of the network required at the interface. Indeed, considering this reconstruction, the rates of transformation between crystal and ordinary liquid may be substantially lower than would be anticipated from the bulk viscosity.

The observations of crystallization at high pressure seem, then, to favor the explanations based on impurity effects or the existence of a metastable phase. It should be noted, however, that the high pressure results may be complicated by the role of water in enhancing crystallization kinetics, and our conclusions must be regarded as tentative until the observations of crystallization are themselves more satisfactorily understood.

V. CONCLUSIONS

Experiments in a Bridgman-anvil high pressure device have demonstrated crystallization in "dry" B_2O_3 at pressures as low as 4 kilobars, and at temperatures as low as $210^\circ C$. Marked effects of even trace amounts of water in increasing the kinetics of crystallization, similar to those observed previously for SiO_2 at high pressure, have likewise been demonstrated. The densification of B_2O_3 in the glassy state has also been investigated; large increases in density as well as a strong effect of temperature in increasing densification have been observed.

The crystallization behavior at high pressures has been discussed in terms of the kinetic formalism derived previously. The effect of pressure in enhancing the catalytic effect of water on transformation kinetics has been considered, as has the effect of shear and sample form on densification behavior.

The B_2O_3 crystallization anomaly has been considered, and a number of hypotheses have been advanced to account for the anomalous behavior. The observations of the high-pressure study have been discussed in evaluating these hypotheses.

ACKNOWLEDGMENT

One of the authors (J. F. H.) wishes to express his appreciation for support by the Society of Fellows, Harvard University.

FIGURE CAPTIONS

Fig. 1: Suggested temperature-pressure equilibrium diagram for B_2O_3 (after Mackenzie and Claussen, Ref. 3).

Δ = liquid (Ref. 3) ; \square = β - B_2O_3 (Ref. 3) ; \blacksquare = α - B_2O_3 (Ref. 3) ;
 \blacktriangle = suggested transition points (Ref. 3); \bullet = α - B_2O_3 (Ref. 18);
 \circ = β - B_2O_3 (Ref. 18).

Fig. 2: Melting rate vs. temperature schematic. T_M = thermodynamic melting point T_{MA} = apparent melting point.

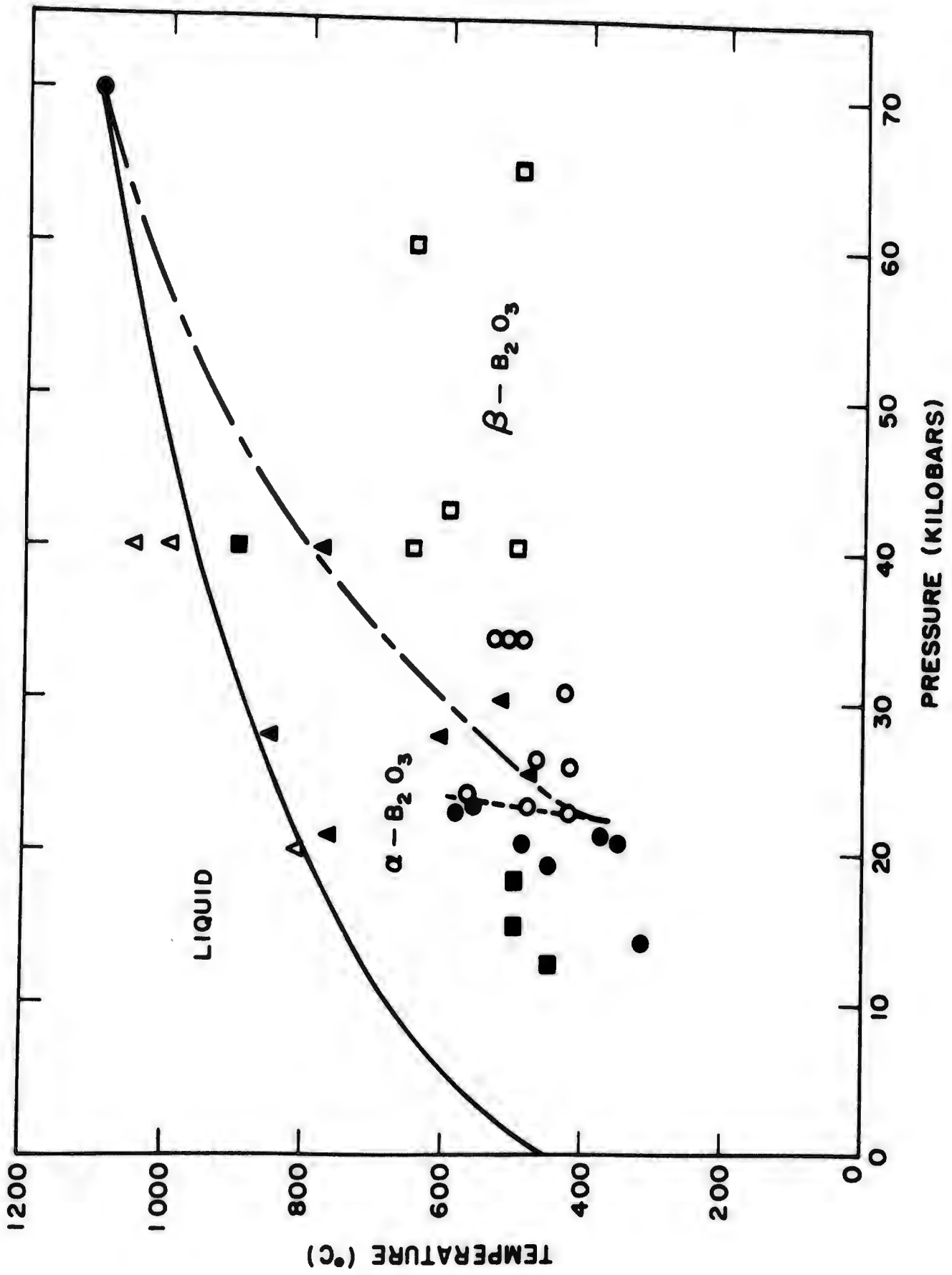
Fig. 3: Compaction data on B_2O_3 compressed in the glassy state (after Mackenzie, Ref. 28).

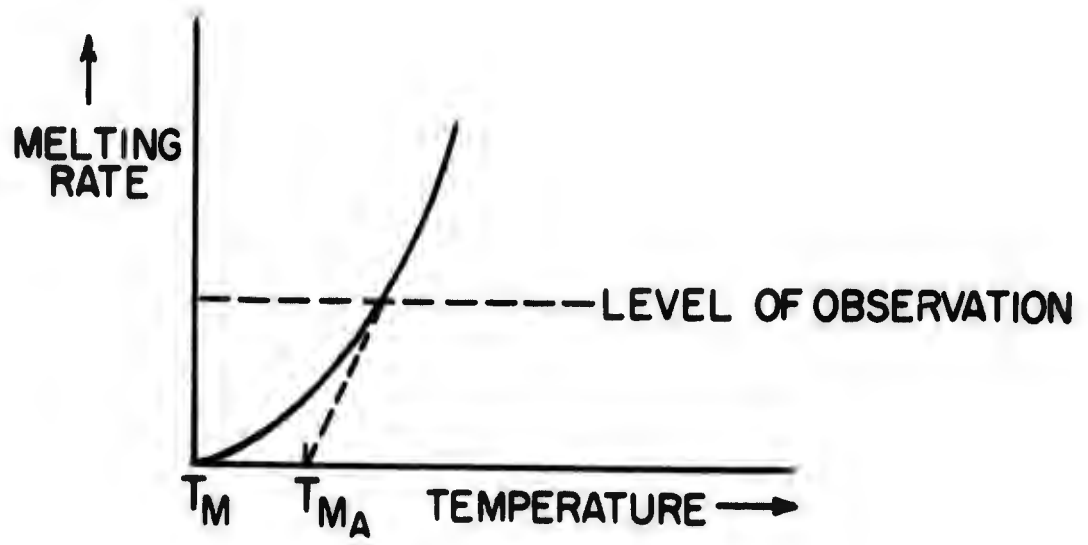
Fig. 4: Transformation rate vs. motivating potential, schematic, showing continuity through equilibrium temperature.

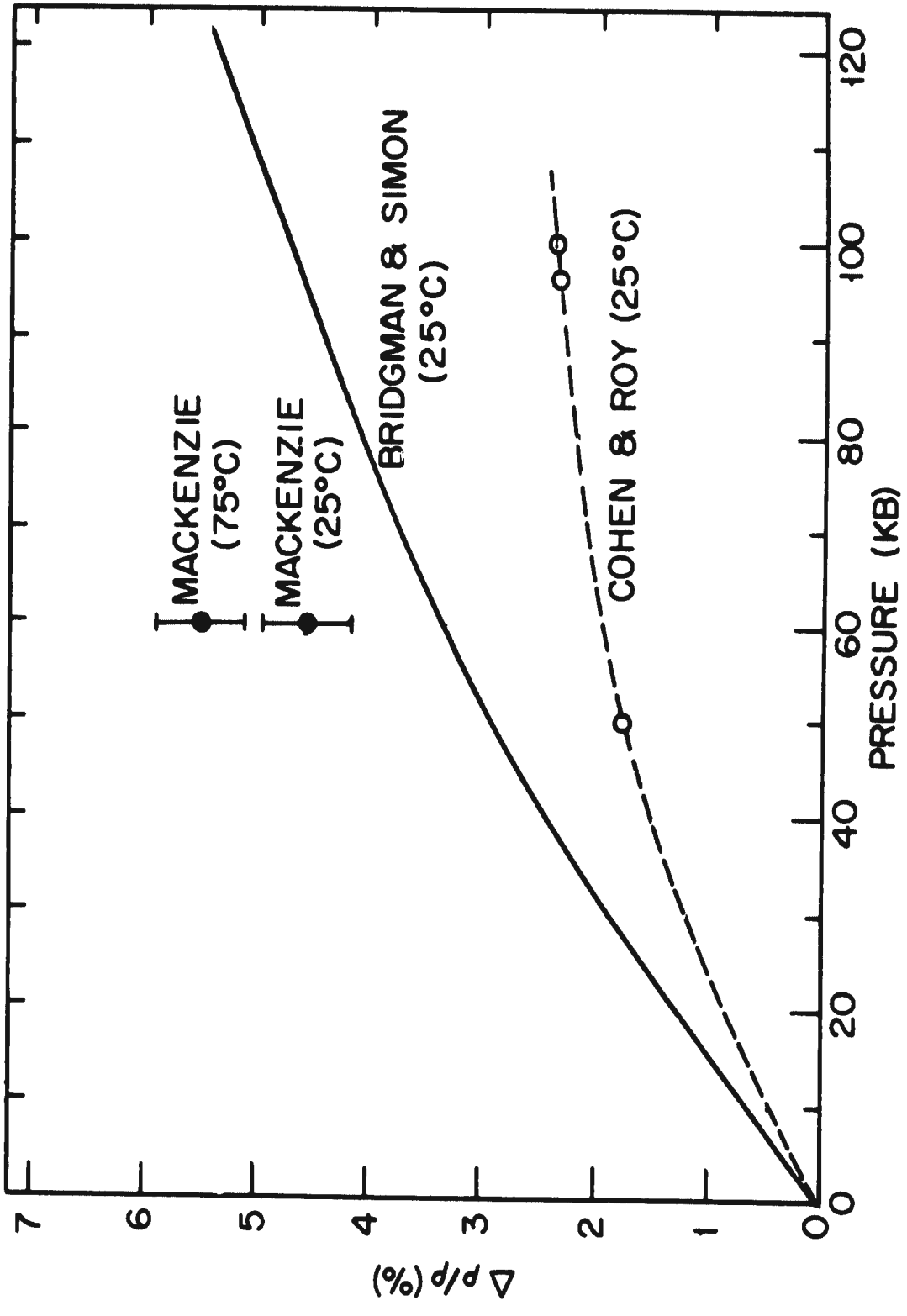
Fig. 5: Temperature vs. pressure plot, showing region where crystallization was observed \circ =no crystals; \bullet = α crystals; \blacksquare = $\alpha + \beta$ crystals. Duration of run in hours indicated adjacent to each experimental point.

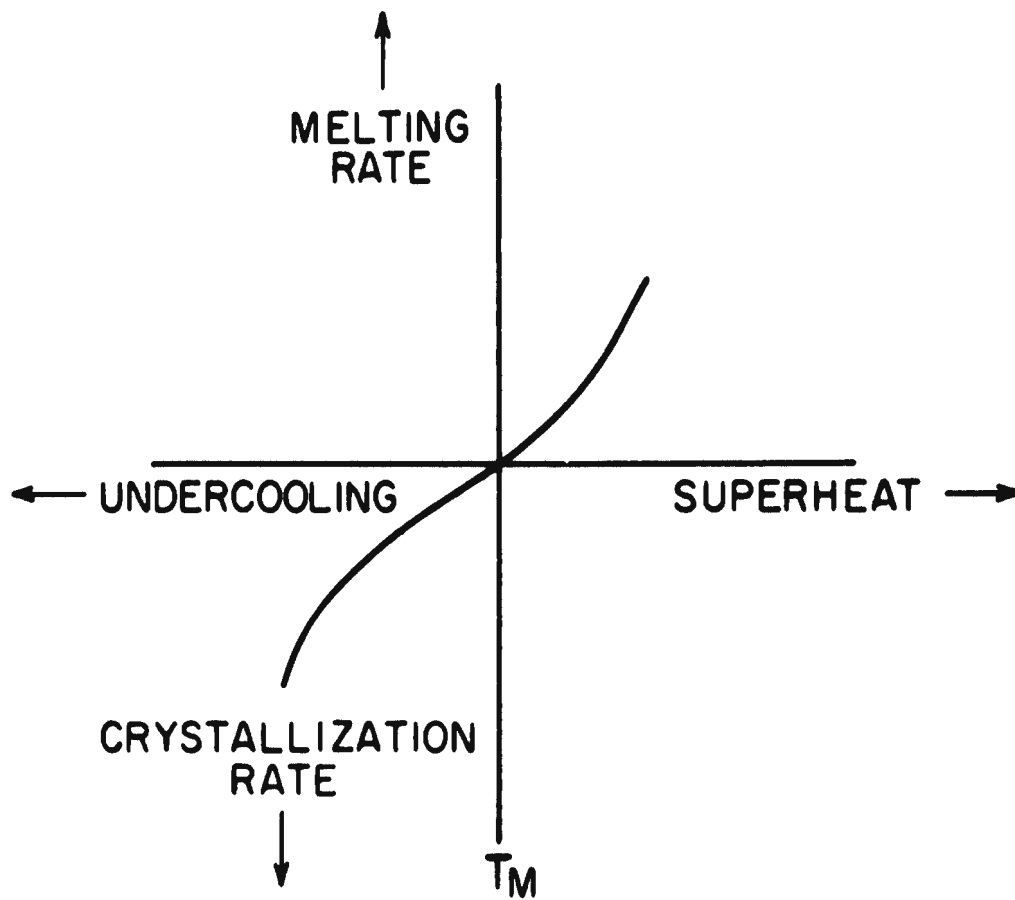
Fig. 6: Growth rate vs. temperature, theoretical for B_2O_3 crystals growing from the melt at atmospheric pressure, calculated from Eq. (6) under assumptions outlined in the text.

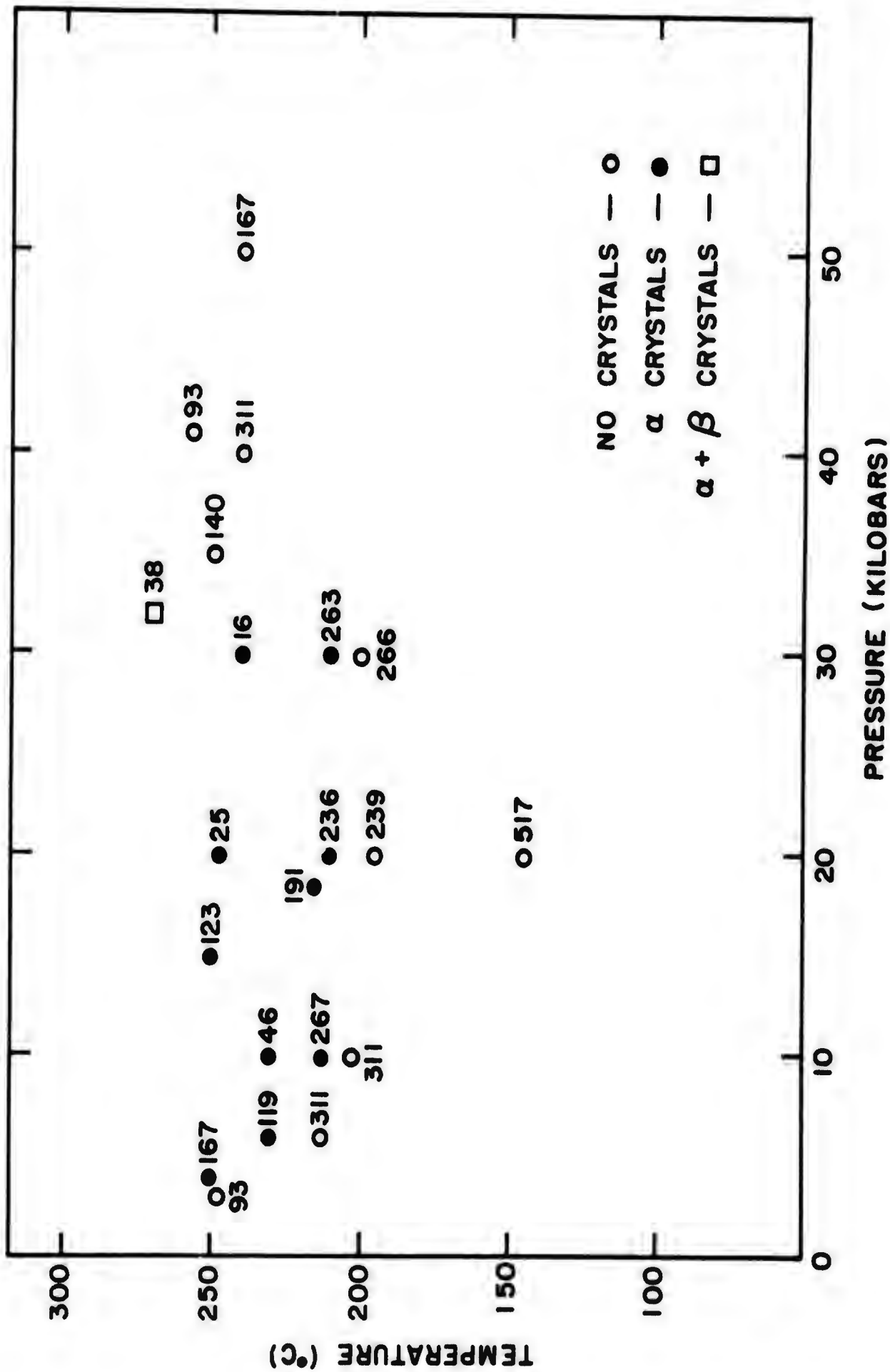
Fig. 7: Free energy vs. temperature, schematic, showing possible metastable liquid phase.

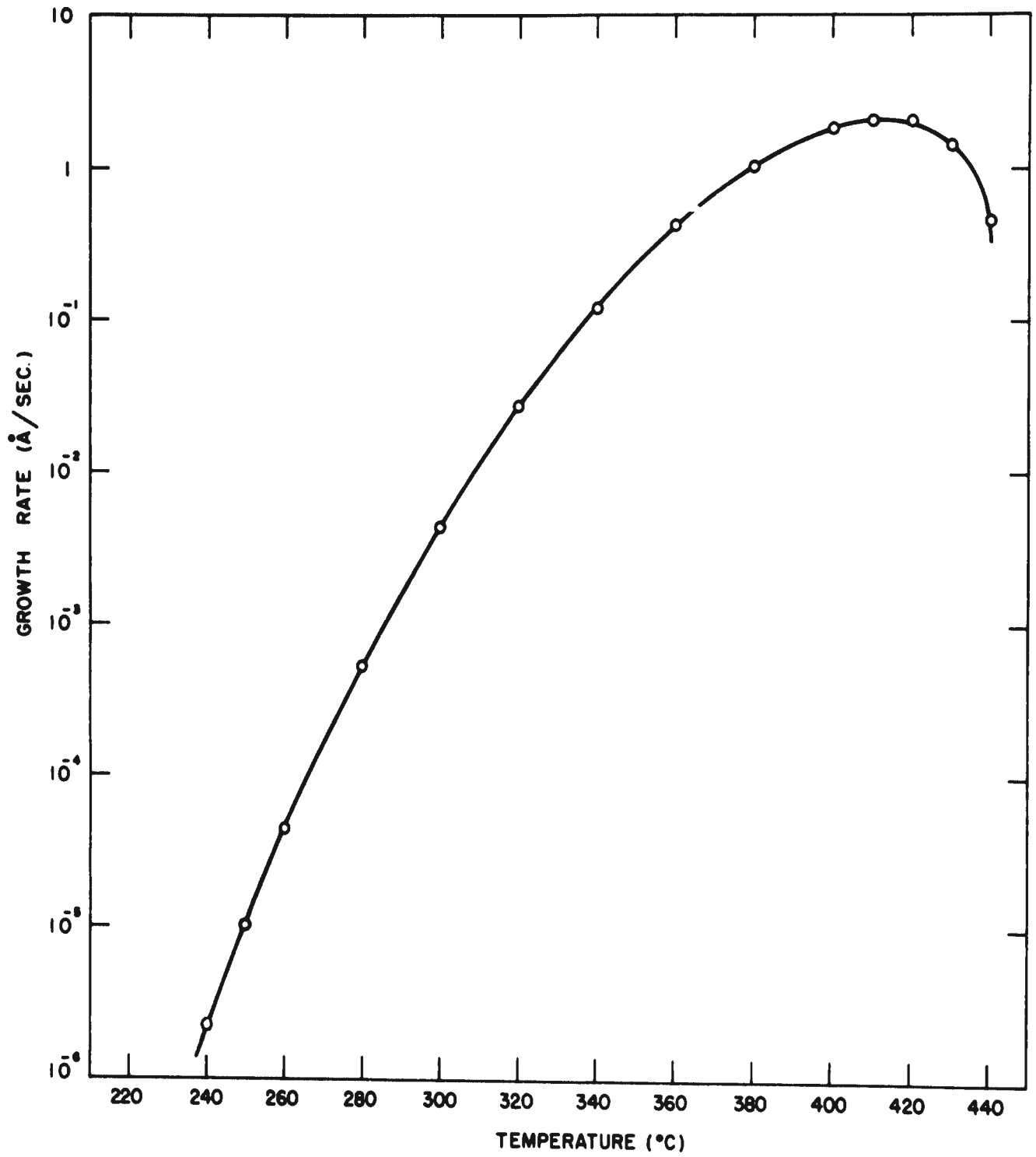


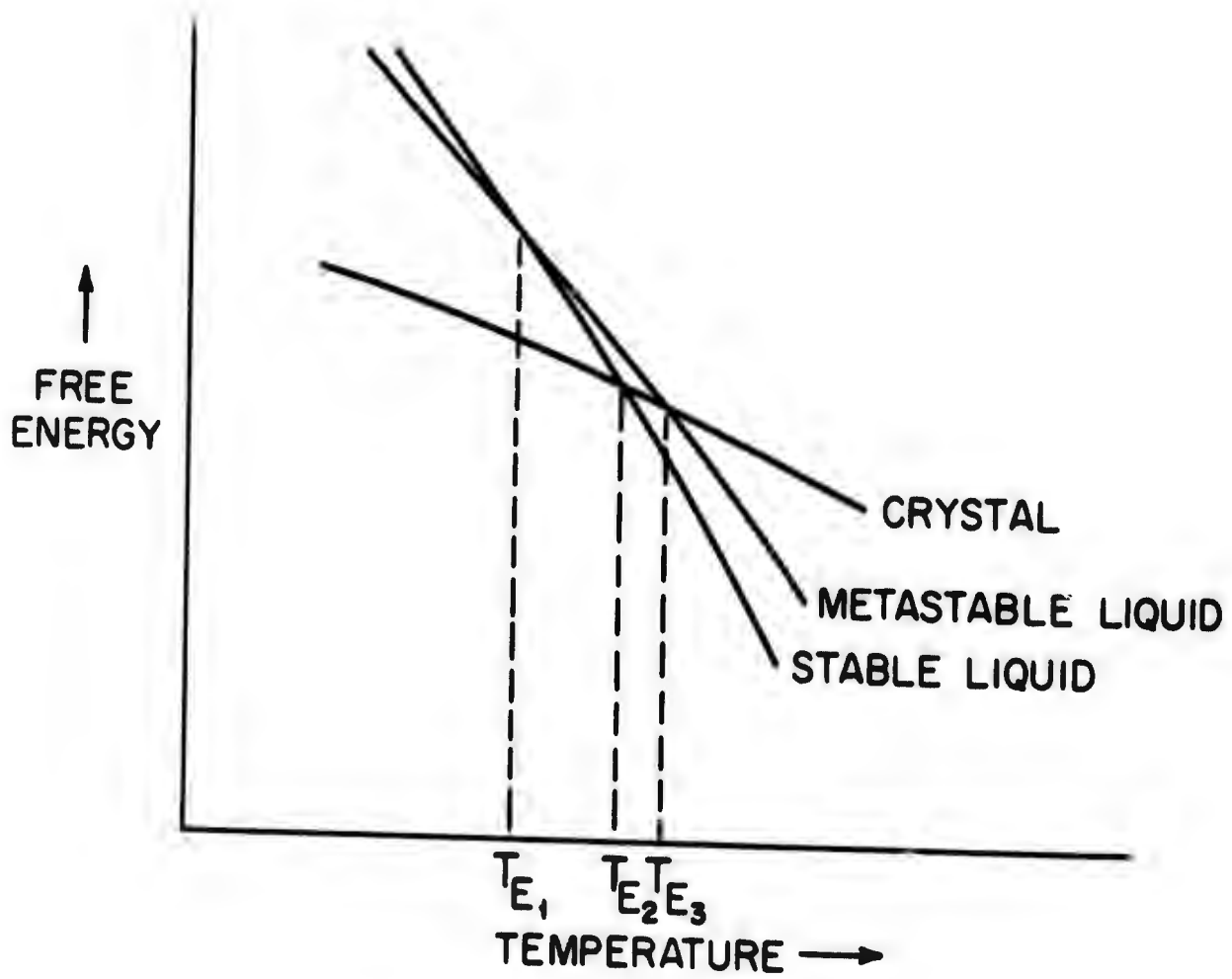












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Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Division of Engineering and Applied Physics Harvard University, Cambridge, Mass.		2a. REPORT SECURITY CLASSIFICATION unclassified	
		2b. GROUP	
3. REPORT TITLE The Effect of High Pressure on B ₂ O ₃ : Crystallization, Densification, and the Crystallization Anomaly			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Interim Report			
5. AUTHOR(S) (Last name, first name, initial) Uhlmann, D. R., Hays, J. F., and Turnbull, D.			
6. REPORT DATE July, 1966		7a. TOTAL NO. OF PAGES 41	7b. NO. OF REFS 53
8a. CONTRACT OR GRANT NO. Nonr-1866(50)		8a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 8	
b. PROJECT NO.		8b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
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13. ABSTRACT The crystallization and densification of B ₂ O ₃ at high pressure have been investigated using a Bridgman anvil device. Crystallization has been observed at pressures as low as 4 kilobars and at temperatures as low as 210° C. A marked effect of water in increasing the overall crystallization rate, and the increase in this rate with increasing temperature, have been demonstrated. Increases in density as large as 17 per cent, and a strong effect of temperature in increasing densification, have likewise been shown. The crystallization behavior is discussed in terms of the kinetic formalism developed previously and is related to past observations on SiO ₂ at high pressure. The densification results are considered in light of the results of other workers on B ₂ O ₃ and SiO ₂ . The anomalous crystallization behavior of B ₂ O ₃ is discussed, and a number of hypotheses are advanced to explain the observations. These hypotheses are evaluated in relation to the results of the high pressure study.			

14. KEY WORDS	LINK A		LINK B		LINK C	
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