[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

Hydrothermal Synthesis of Sapphire[1]

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The corundum modification of aluminum oxide, sapphire, has for the first time been caused to deposit at an appreciable rate on a seed crystal under hydrothermal conditions. Highest growth rates were obtained by the use of Na_2CO_3 solutions as solvent. The crystallization temperature had to exceed about 395° or else diaspore was the solid phase. It was found that corundum could be doped with small quantities of chromium, *i.e.*, that synthetic ruby could be prepared, by the addition of sodium dichromate in low concentrations to the solvent.

Introduction

The techniques of hydrothermal synthesis as developed by Spezia[2] and modified by Nacken,[3] Walker[4] and others have proved quite successful in the preparation of large relatively pure samples of crystalline quartz. Aluminum oxide like SiO_2 is an amphoteric oxide virtually insoluble at room temperature but according to the studies of Laubengayer[5] and others somewhat soluble at elevated temperatures and pressures. It was felt that large crystals of sapphire, the corundum modification of Al_2O_3, prepared by the techniques of hydrothermal synthesis would be relatively strain free, since they could be prepared at moderate temperature conditions and without the excessive gradients characteristic of flame fusion and melt techniques.

Isothermal studies of the system Al_2O_3–H_2O have been carried out by several investigators, notably Laubengayer and Weitz[5] and Ervin and Osborn.[6] Laubengayer and Weitz found that corundum could be formed from diaspore, boehmite or gibbsite *in situ* at temperatures above about 450°. The pressure used ranged from about 15,000 to 30,000 p.s.i. as calculated from Kennedy's[7] *p–v–t* data for pure water and the per cent. of fill of the hydrothermal autoclave as reported by Laubengayer and Weitz. Ervin and Osborn determined the corundum–diaspore and corundum–boehmite equilibrium line as functions of pressure and temperature in pure water and found that at pressures below 2,000 p.s.i. corundum was the stable phase at temperatures above 390° while at pressures above 3,000 p.s.i. corundum was stable above about 415°. Laubengayer and Weitz found that additions of KOH lowered the corundum–diaspore transition temperature and that the presence of fluoride ion resulted in the formation of oxy-fluoride phases. No attempts to grow on a seed or to determine quantitative solubilities have been reported.

Experimental

In the methods employed in this study the required supersaturation needed to cause growth of corundum on a seed was obtained by means of a temperature differential maintained along the autoclave.

The arrangement of the furnace was similar to that employed in these laboratories for the hydrothermal synthesis of quartz as described by Walker and Buehler.[4] The hydrothermal autoclave or bomb was placed on a hot plate connected to a suitable temperature controller and surrounded by insulation. Temperatures were measured externally by strapped Chromel–Alumel thermocouples at the bottom, top and near the middle of the autoclave. Although preliminary measurements of internal temperatures in 1″ i.d. vessels have indicated that external and internal temperatures are within a few degrees of one another, it should be borne in mind that internal temperatures as here reported probably were dependent on autoclave geometry. With such an assembly it was possible by the regulation of hot plate temperatures and the depth of insulation to achieve any bottom temperatures desired up to 480° and any temperature differential (as measured between the bottom and top thermocouples) between 10 and 50°.

The autoclave assembly was found to be nearly inert under the conditions necessary for corundum crystallization. The outside member of the assembly consisted of the welded closure type autoclave previously used in these laboratories for quartz synthesis and described by Walker and Buehler.[4]

Within the cavity of this vessel was placed a silver tube closed with a threaded cap. The space between this tube and the welded closure autoclave was filled to the same fraction of its free volume as the interior. Typical dimensions were 12″ inside length and 1″ inside diameter for the autoclave and 10″ outside length and $^3/_4$″ outside diameter for the silver tube (silver tube wall thickness 0.030″). In runs where it was desired to add iron to the crystals the hydrothermal crystallization was carried out directly in the steel liner which was silver plated to prevent too much attack.

Reagent $Al(OH)_3$ (poorly crystallized finely powdered Gibbsite) or reagent Al_2O_3 (poorly crystallized corundum, particle size about 100 mesh) was placed in the bottom of the silver tube, and seed crystals of the desired orientation were suspended on a silver frame in the upper portion of the autoclave. In the runs where the silver tube was used, all parts in the tube interior were silver; in the runs with the welded closure autoclave alone the steel liner and all parts in its interior were silver plated.

The seeds consisted of pieces of the desired orientation cut from corundum rod prepared by the Verneuil process and purchased from the Linde Air Products Co., New York. Between the nutrient and the seeds there was placed a perforated metal disc or baffle. The fraction of the area of this baffle left open varied between 0.10 and 0.05. The baffle served to cause most of the temperature differential to occur over the baffle region as evidenced by the fact that with lower fractions of the area of the baffle left open the difference in growth rates between bottom and top seed crystal decreased. In runs where the silver tube was used an auxiliary baffle made of wire screen was placed between the tube and the autoclave wall to aid in further localizing the temperature differential in the baffle region.

The silver tube was filled to the required fraction of its free volume with the appropriate solvent and closed; the space between tube and autoclave was filled to the same fraction of its free volume and the bomb was closed. The silver tube then supported no pressure but satisfactorily provided an inert container for the crystallization.

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[1] Presented in part before the Physical and Inorganic Chemistry Division of the American Chemical Society Meeting, New York, September, 1957.

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[3] R. Nacken, Captured German Report RDRDC/13/18, February 28, 1946.

[4] A. C. Walker and E. Buehler, *Sci. Monthly*, **69**, 148 (1949).

[5] A. W. Laubengayer and R. S. Weitz, THIS JOURNAL, **65**, 250 (1943).

[6] Guy Ervin and E. F. Osborn, *J. Geol.*, **59**, No. 4, 387 (1951).

[7] G. C. Kennedy, *Amer. J. Sci.*, **248**, 540 (1950).

Results and Discussion

The systems NaOH–H_2O–Al_2O_3 and Na_2CO_3–H_2O–Al_2O_3 were investigated in a search for conditions where crystals could be grown. It was found that for concentrations of Na_2CO_3 or of NaOH between one and two molar and for degrees of fill between 0.70 and 0.85 diaspore was the thermodynamically stable phase as determined by *in situ* conversion or deposition on a seed at all temperatures investigated below about 395°. However, above about 395° corundum was the stable phase as found by *in situ* conversions of Gibbsite. Corundum and diaspore were identified by optical examination, wet analysis and from their X-ray powder patterns. It might be noted that even in the case of *in situ* conversion particle size of the corundum was appreciable. The hydrothermal preparation of diaspore from Gibbsite without seeding is also notable since previous investigators[6] have reported that seeds were always required.

In the corundum stability region striking differences in behavior were found between Na_2CO_3 and NaOH as solvents. In NaOH larger growth rates were observed when $Al(OH)_3$ was used as the nutrient. This growth was rapid in the first few days of the run but rapidly fell thereafter. It was observed that in both NaOH and Na_2CO_3 the nutrient was almost entirely converted *in situ* to corundum after a few days. However, in Na_2CO_3 growth was observed to continue as long as nutrient remained and the rate with Al_2O_3 as nutrient was nearly equal to that found with $Al(OH)_3$. The postulated explanation is that in NaOH growth is mainly due to supersaturation with respect to corundum caused by the difference in solubility between Al_2O_3 and the more soluble metastable Gibbsite, boehmite and diaspore.

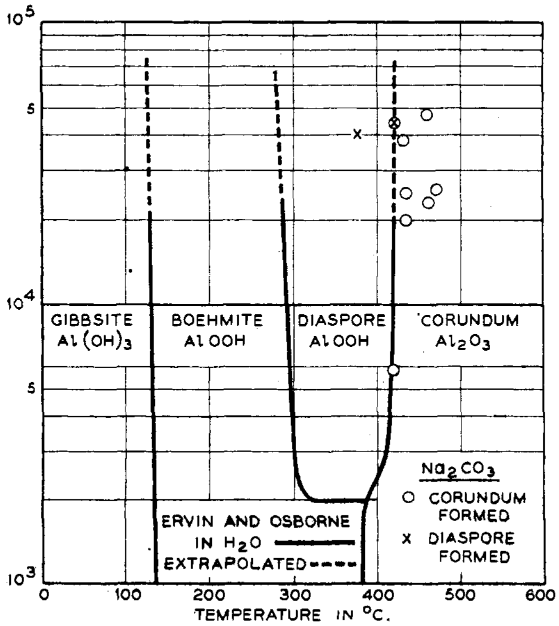

Fig. 1.—Phase relations in Al_2O_3 systems.

This was borne out by the fact that in hydroxide solutions with Gibbsite as nutrient once the Gibbsite was converted *in situ* in the bottom of the autoclave growth of corundum on a seed drops off. It might be noted that $CO_3^=$ or $(OH)^-$ evidently lowers the temperature of the diaspore–corundum transition about 50° as reported in the literature. A possible explanation of the apparent lowering of the transition temperature is that the reported diaspore–corundum transition temperature was high by about 50°. Diaspore and boehmite may actually have been metastable in several regions where they have been reported to be stable. In basic solutions one would expect that reaction rates for phase transitions would be faster and that true equilibrium would be achieved more easily. The fact that good crystalline diaspore can be formed without seeds is also probably due to the relative ease of achieving equilibrium in basic solutions.

Runs were made in Na_2CO_3 at the pressure and temperature conditions shown in Fig. 1. In general pressures in excess of 30,000 p.s.i. were required for reasonable growth rates. The pressures shown correspond to fills of from about 0.70 to 0.85 of the free volume as calculated from Kennedy's[7] data. On this figure is superimposed the phase diagram for Al_2O_3–H_2O as found by Ervin and Osborn. It might be noted that according to Ervin and Osborn's data all the hydrothermal crystallizations made in this study in $CO_3^=$ where corundum was formed lie within the stability region for corundum even in pure water. The points found in our study seem to be little dependent on the concentration of Na_2CO_3 between one and two molar. Preliminary solubility measurements indicate that at 0.80 of the free volume and 420° the solubility of corundum in 1 *M* Na_2CO_3 is as large as that of quartz in 0.5 *M* NaOH at 0.80 of the free volume and at 400°. This makes it seem likely that with proper choice of conditions it might eventually be possible to grow corundum at rates as high as quartz. Data for NaOH are lacking but the temperature coefficient of solubility probably is less than in Na_2CO_3 where the temperature dependent $(CO_3)^=$–CO_2 equilibrium will certainly affect the solubility of Al_2O_3. Consequently with a given temperature differential Al_2O_3 has a higher supersaturation and therefore a larger growth rate in Na_2CO_3 than in NaOH where growth, as was stated above, seems only to occur due to the supersaturation of metastable phases.

Temperature differentials of about 30° in Na_2CO_3 were employed. Higher differentials caused considerable self-nucleation and lower differentials slowed the rate. In NaOH, as was stated above, with differentials of about 30° growth was apparently mainly due to the supersaturation with respect to corundum caused by the higher solubility of metastable phases. With lower temperature differentials the rate fell off slightly and was again probably due only to the presence of metastable phases. Higher differentials currently are being investigated where the possibility exists that growth may take place without the presence of metastable phases.

All growth rates were determined by the measurement of the thickness of seed plates before and after growth. Rates from 0.002 to 0.010 in./day were found. The growing face principally investigated was that perpendicular to the crystallographic *c*-axis (0001). While this face does appear in some natural crystals, it is not predominant in natural corundum and might therefore be expected to be fast growing. However, under hydrothermal conditions it has been found to be quite persistent, (0001) seeds kept that face even when grown to considerable thickness. Microscopic examination of spontaneously nucleated hydrothermal corundum crystals showed them to be hexagonal platelets whose (0001) faces persisted even when quite thick. These spontaneously nucleated crystals were bounded almost always by (0001) and $(11\bar{2}0)$ with only the occasional appearance of other faces. One might therefore deduce that under hydrothermal conditions (0001) is not an especially fast-growing face. Indeed preliminary indications are that several other faces are faster growing. When cylindrical plates whose ends were (0001) were used as seeds, $(11\bar{2}0)$ faces were formed quickly but (0001) persisted.

Crystals generally were grown on wafers with either the *c*-axis normal or inclined 60° to the plane of the wafer. Increases in dimensions of about 0.25 in. in the *c* and 0.30 in. in the *a* direction have been achieved. Crystals with natural faces formed as large as $^3/_4''$ in the *a* and 0.40 in. in the *c* direction have been prepared. Increases in weight of over 200% have been achieved.

Green crystals containing iron have been grown by carrying on the crystallization in the welded liner directly and colorless crystals which were essentially pure have been prepared by the use of the silver tube.

Crystals doped with chromium (synthetic ruby) have been prepared. Concentrations of $Na_2Cr_2O_7 \cdot 3H_2O$ of about 0.10 g./l. caused about 1% chromium by weight to be included in the crystal. The resultant crystals were blood red in color.

Further studies of the conditions for crystallization, the solubility and phase equilibria relationships, and the properties of the grown sapphire are in progress.

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[CONTRIBUTION FROM MERCK SHARP & DOHME RESEARCH LABORATORIES DIVISION, MERCK & CO., INC.]

Synthesis of Selenides and Tellurides. I. The Reduction of Selenites by Hydrazine

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Aqueous hydrazine of strength sufficient to dissolve selenium reduces metallic selenites to selenides, provided that the product is insoluble in the reaction medium. The selenides of cadmium, copper(I), copper(II), lead(II), mercury(II) and zinc have been produced in excellent yields *via* this reaction. In the cases of zinc and cadmium, isolable hydrazino selenide complexes of formula $MSe \cdot N_2H_4$ are formed as intermediates.

The high interest in the semi-conducting properties of selenides and tellurides has made desirable the development of safe and efficient methods for their production. In particular, such methods should be capable of yielding high-purity products, both as regards compositional ratio and trace contaminants without recourse to lengthy and cumbersome procedures; further, in view of the serious health hazard involved in the handling of selenium and tellurium compounds, the processes should preferably avoid the use of volatile materials. It is the purpose of this and subsequent papers to describe processes designed to meet these conditions.

Previously described methods for preparing selenides comprise: (1) union of the elements at elevated temperature; (2) reduction of selenites and selenates by hydrogen or ammonia at elevated temperature; (3) metathesis of metal salts with hydrogen, ammonium or alkali selenides; (4) reduction of selenium in alkaline solution or selenosulfate by means of dithionite[1,2]; (5) and in the special case of cadmium selenide, by decomposition of selenosulfate ion in presence of cadmium ion.[3]

Hovorka[4] studied the reduction of alkali selenites by means of aqueous hydrazine as being of possible analytical interest, but found that the product is a mixture of selenide and selenium (*i.e.*, polyselenide). This proves likewise to be the case when a water-insoluble selenite is digested with dilute hydrazine: selenium is precipitated and reduction ceases at that point. On the other hand, the solubility of selenium increases with hydrazine concentration by way of the equilibrium[5]

$$6N_2H_4 + 3H_2O + (2x + 1)Se \rightleftharpoons 6N_2H_5^+ + 2Se_x^= + SeO_3^=$$

and use can be made of this property to bring about complete reduction.

Addition of solid zinc selenite to a 4–10 fold excess of commercial hydrazine hydrate pre-heated to about 80°, results in a vigorous evolution of nitrogen and heat, and formation of a white to peach-colored insoluble solid. This substance was identified as the novel complex hydrazinozinc selenide, $ZnSe \cdot N_2H_4$

$$2ZnSeO_3 + 5N_2H_4 \longrightarrow 2ZnSe \cdot N_2H_4 + 6H_2O + 3N_2$$

It forms dense, acicular crystals which are stable

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