

A study of the hydrothermal growth of ruby

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Summary. Experiments have been conducted to determine the optimum conditions for the hydrothermal growth of ruby. The solubility of corundum in various solutions has been determined and compared with the respective growth obtained in each medium. The discrepancy between solubility and effective growth is discussed.

The need for a high degree of chemical purity has resulted in the development of platinum liners for the autoclaves. The effects of impurities and of other factors on the growth of ruby crystals have been studied. The crystal habit of hydrothermal ruby is also described.

CORUNDUM has frequently been noted as small crystals in hydrothermal studies (Morey and Ingerson, 1937), but only in recent years have attempts been made to prepare large crystals by this technique. An initial study of the $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ system was made by Laubengayer and Weitz (1943). They converted hydrated forms of alumina (gibbsite, boehmite, and diaspore) into corundum under isothermal conditions. Ervin and Osborn studied the system further and determined the corundum-boehmite and corundum-diaspore equilibrium lines as functions of temperature and pressure.

The controlled growth of corundum on a seed crystal was first achieved by Laudise and Ballman (1958), using one-inch bore steel autoclaves. They confirmed part of Ervin and Osborn's phase data for the $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ system and also investigated the $\text{NaOH-Al}_2\text{O}_3\text{-H}_2\text{O}$ and $\text{Na}_2\text{CO}_3\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ systems. Using gibbsite as the source material growth upon a seed crystal was obtained in both systems when a temperature gradient of about 30°C existed between the source material and the seed, and the crystallization temperature was above 395°C . The pressure in these experiments was estimated at 2000 atmospheres. Growth from sodium hydroxide solution was found to be initially very rapid but later stopped, while with sodium carbonate the growth rate was much slower but continued as long as there was any source material present. This was

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explained on the basis that the solubility versus temperature curve for corundum in sodium carbonate solution was much steeper than that for corundum in sodium hydroxide over the temperature range investigated. Hence for a given temperature gradient the degree of supersaturation would be much greater in sodium carbonate than in sodium hydroxide. The authors furthermore suggested that growth in sodium hydroxide solution took place because of the differing solubilities of gibbsite and corundum, and that when the more soluble gibbsite had been converted into corundum after one or two days, the difference in solubilities was eliminated and growth stopped.

A further publication by Laudise and Nielsen (1961) has compared the hydrothermal growth of corundum to that of quartz (Brown *et al.*, 1952). They found that increased temperature and pressure gave rise to increased solubility in both systems but that the effect of temperature was far more pronounced in the case of sodium carbonate solution. Working in the corundum-stable region of temperature and pressure they reported growth at rates of up to 0.25 mm per day on the (0001) face, and crystals were grown with up to 200 % weight increase on the original seed. The autoclaves were fitted with silver liners to prevent iron contamination by corrosion of the autoclave walls. The addition of a small amount of sodium dichromate to the growth medium produced chromium-doped corundum, i.e. ruby.

The aim of the present work has been to establish the optimum conditions under which the hydrothermal growth of single crystals of ruby may be achieved. Attention has been given to the various factors that may influence the growth rate and the quality of the crystals produced.

Experimental

The general procedure adopted was essentially the same as that developed in these laboratories for the growth of quartz crystals (Brown *et al.*, 1952). The autoclave was placed on a hot-plate and the assembly thermally insulated with vermiculite. In this way a temperature gradient was set up along the length of the autoclave, which provided the necessary conditions for growth. Temperatures were monitored by chromel-alumel thermocouples, and the hot-plate temperatures were controlled by Ether 'Transitrol' controllers.

The autoclaves were constructed from EN58G stainless steel and had an internal diameter of $\frac{7}{8}$ inch with a total internal volume of about 90 cm³. A conventional 'lens ring' type of seal was incorporated. In order to overcome the considerable iron contamination that occurs in

stainless steel autoclaves at temperatures above about 500° C, platinum linings were fitted.

The most successful design of liner is shown in fig. 1. It consisted of a close fitting sheath for the body of the autoclave, having a rim fitting flush to the sealing flange. An internal platinum ring was sweated inside the lens ring, and projected slightly above and below the ring. When the liner and lens ring assembly were in position the top of the lens ring was covered with a piece of platinum foil, 0.001 inch thick, before securing the lid. In this way a platinum-to-platinum seal was effected both at the top and the bottom of the lens ring. These autoclaves, with liners, were used at base temperatures of up to 650° C and pressures of 1000 atmospheres.

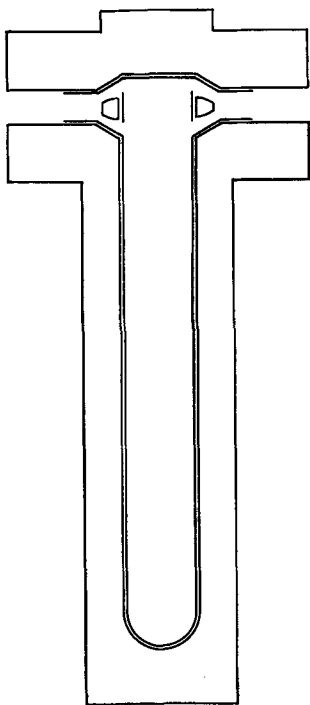


FIG. 1. Stainless steel autoclave with platinum liner.

To increase the temperature gradient inside the autoclave a platinum baffle was employed. The size of the baffle hole was varied between $\frac{1}{8}$ inch and $\frac{3}{8}$ inch without any marked effect on growth rates, and a $\frac{1}{4}$ inch was chosen as a convenient size for subsequent experiments.

Small pieces of corundum crystal, grown by the Verneuil process, were used as the alumina source in the early experiments, but were later replaced by sintered blocks, pressed from British Drug Houses Ltd. A.R. calcined alumina and fired at 1500° C. The latter material was found to give more reproducible results. Each block weighed about 7 g and two were used for each run. The seed crystals were cut from single crystal boules of Verneuil corundum. Where possible A.R. grade chemicals were used in all experiments.

Results and Discussion

Solubility experiments. A preliminary series of some eighty experiments was made to determine the solubility of corundum under hydrothermal

conditions. The effect of concentration of sodium hydroxide solution was studied under different conditions of pressure and temperature using mild steel autoclaves under isothermal conditions. Pressures were estimated from the published data for water (Holser and Kennedy, 1959), and the solubility determined from the loss in weight of a seed crystal suspended in the solution. The majority of the runs were confirmatory experiments designed to check the reproducibility of the results. From those results presented in table I it may be seen that the effect of both temperature and pressure is negligible compared with the dependence on the alkali concentration over the range of conditions used.

TABLE I. Solubility measurements in sodium hydroxide solutions

Temperature	Estimated pressure	Concentration of sodium hydroxide	Duration of run	Solubility
400° C	150 atm	1.0 N	15 hr	0.75 g/100 ml
400	450	1.0	15	4.1
400	1200	1.0	15	4.1
400	450	1.0	60	3.8
400	450	0.1	200	0
420	450	1.0	60	4.0
440	600	1.0	160	4.8
440	450	2.0	140	8.8

The experience with the growth of quartz in solvents of different alkalinity suggested that it would be of interest to try a similar series for corundum. The solubility was, therefore, determined in a variety of solvents under standard conditions of temperature, pressure, and solvent concentration. These results are shown in table II; an appreciable solubility was found in all instances.

TABLE II. Solubility of corundum in various solutions. Base temperature: 500° C; pressure ~ 500 atm; 14 days' duration

Solution	Solubility	Solution	Solubility
1 N KOH	18 ± 1.0 g/100 ml	1 N K ₂ CO ₃	2.3 ± 0.1 g/100 ml
1 N NaOH	8.5 ± 0.5	1 N NaF	3.0 ± 0.5
1 N LiOH	5.5 ± 0.5	1 N KF	2.7 ± 0.1
1 N Na ₂ CO ₃	1.2 ± 0.1	1 N NaF/NaOH	4.8 ± 1.0

Growth of corundum on seed crystals. A series of experiments designed to give growth on a seed crystal was then carried out in stainless steel autoclaves under a standard set of conditions, which were set by the maximum safe working limits of the autoclaves: base temperature 650° C, top temperature 450° C, estimated pressure 750 atm.

A baffle was incorporated between the source corundum and the seed, and the latter was suspended by means of a fine platinum wire. In this

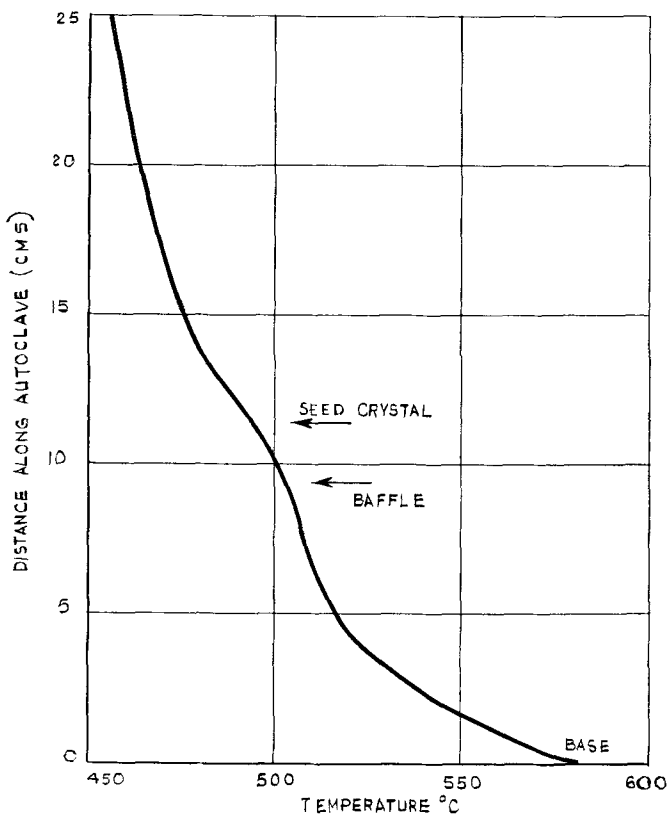


FIG. 2. Temperature gradient along autoclave wall.

type of experiment, an accurate measurement of the pressure cannot be made, partly because of lack of knowledge of actual solution temperatures and partly because of the lack of p , v , t data for such solutions. The temperature at points along the outside of the autoclave was measured in one instance; the values are shown plotted in fig. 2. It may be deduced that the temperature difference between the source corundum and the seed crystal was about 40° C.

The results given in table III show that growth has occurred only in potassium carbonate, rubidium carbonate, and caesium carbonate solutions. In most of the other solvents there was a slight loss in weight of

TABLE III. Growth on seed crystals in various solutions

Solution	% weight gain	Solution	% weight gain	Solution	% weight gain
1 N KOH	none	2 N KF	none	2 N KBO ₃	none
1 N NaOH	none	2 N K ₂ SiO ₄	none	1 N Rb ₂ CO ₃	205
1 N Na ₂ CO ₃	none	2 N KCl	none	2 N Cs ₂ CO ₃	140
1.5 N K ₂ CO ₃	110				

the seed crystal. Only the alkali metal carbonates show appreciable variation of solubility with temperature over the range investigated. The absence of growth with sodium carbonate solution was surprising in view of the work of Laudise and Ballman (1958) but some growth was observed in a later experiment using a platinum liner.

Further experiments using potassium carbonate solution as the solvent for corundum growth are listed in table IV. The growth rates show a marked dependence upon the carbonate concentration, and in the last three of the runs listed a considerable number of spontaneously nucleated crystals were produced.

TABLE IV. Growth of corundum from potassium carbonate solution

Concentration	Duration	% weight gain of seed
1.0 N	14 days	46
2.0	14	115
2.0	28	157
3.0	14	195

Growth of chromium doped corundum. All of the crystals grown in these experiments using unlined autoclaves were coloured green, presumably due to iron contamination, and contained numerous inclusions. Consequently, in experiments designed to achieve chromium doping it was often difficult to decide from the colour whether any doping had taken place. In order to eliminate iron the majority of the ruby growth runs were performed using platinum liners, but until they became available a series of doping runs was carried out in unlined autoclaves in order to determine the most promising method.

The attempts at chromium doping are summarized in table V from which the only positive doping agent appeared to be potassium dichromate. It was significant that the chromate or dichromate ion had a strongly inhibiting effect upon the growth rate, although this was not apparent when ammonium dichromate was used due to its tendency to decompose leaving a residue of chromic oxide. Since boule ruby was

almost insoluble under the conditions investigated it would appear that the inhibiting effect might be due to the adsorption of chromate ions on the corundum surfaces. Using 3N potassium carbonate solution, addition of 0.5 g and 1 g of potassium dichromate reduced the respective growth rates to $\frac{1}{3}$ and $\frac{1}{20}$ of the value for the pure solvent.

TABLE V. Incorporation of chromium in corundum crystals

Nutrient material	Solution	% weight gain of seed	Observations
Flame-fusion ruby	2 N K_2CO_3	none	—
Flame-fusion ruby	2 N Rb_2CO_3	none	—
Corundum + $(NH_4)_2Cr_2O_7$	2 N K_2CO_3	110	No appreciable doping*
Corundum + $K_2Cr_2O_7$	2 N K_2CO_3	42	Reasonable Cr doping†
Corundum + Cr_2O_3	3 N K_2CO_3	73	No appreciable doping
Corundum + Cr_2O_3	1 N Rb_2CO_3	112	No appreciable doping
Boehmite + $K_2Cr_2O_7$	3 N K_2CO_3	37	No appreciable doping
Boehmite + Cr_2O_3 }	1 N Rb_2CO_3	500	No appreciable doping
Fired at $1480^\circ C$ }	1 N K_2CO_3	111	No appreciable doping

* Iron contamination in some experiments obscured visible evidence of doping.

† Repeated in several experiments.

Experiments using platinum lined autoclaves. From the results of the previous experiments it was decided to confine work to solutions of potassium and rubidium carbonates as there appeared to be little advantage in the use of the caesium compound. Since the maximum temperature and pressure safely attainable with the stainless steel autoclaves lay only just inside the region for corundum stability, these conditions were adopted for the remaining experiments. Maintaining a hot plate temperature of $650^\circ C$ and a reciprocal degree of filling of 3.0, the top temperatures reached by the autoclaves were in the range 450° – $470^\circ C$ and the corresponding pressures estimated at 750 atmospheres. Raising the pressure to an estimated 1000 atmospheres produced no measurable alteration in either the quality or quantity of growth when all other conditions were unaltered.

Chromium doping. The dependence of the growth rate upon the concentration of potassium dichromate was confirmed using platinum liners. It was apparent that for a given degree of chromium doping (potassium dichromate concentration) a definite solvent concentration would be preferred. Since the presence of 1.0 g potassium dichromate resulted in a satisfactory degree of doping, i.e. the formation of deep pink ruby with a chromium content of about 0.1 %, this concentration

was adopted for subsequent experiments to determine the appropriate optimum growth conditions.

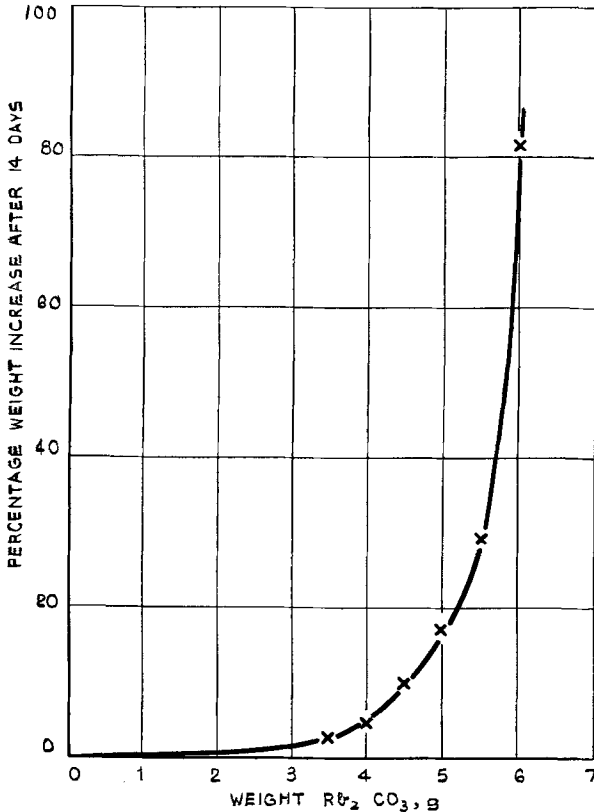


FIG. 3. Growth of corundum on seeds from rubidium carbonate solutions.

It was also noted that the growth of undoped corundum proceeded at a faster rate in platinum lined autoclaves than in unlined ones for given conditions. Presumably the iron 'doping' also had an inhibiting effect upon the growth rate.

Solvent concentration. The concentration of the solvent was found to be the most important factor affecting growth. For a given amount of growth the quality appeared to be better when rubidium carbonate was used as a solvent than with potassium carbonate solution. For this reason the majority of the work was carried out using rubidium carbonate and a plot of growth rate against concentration is given in fig. 3.

The rubidium carbonate concentration is given as the weight of solid used in each run, since the normality should be related to the total volume of the autoclave, and not to the volume of liquid.

It was found that too small a concentration resulted in a very slow growth rate, while too large a concentration produced poor quality growth and excessive spontaneous nucleation. Under the stated experimental conditions the best results were obtained when 4.5 g rubidium carbonate were used with 30 cm³ water.

Crystal orientation. The crystals produced showed well-developed basal planes, with little tendency to grow along the triad axis. In most experiments the seed crystals were cut with dimensions 2.5 cm × 0.4 × 0.1 cm, the *c*-axis being parallel to the longest dimension.

In many cases the quality of the growth was poor, consisting of parallel stacking of crystallites rather than a homogeneous single crystal. This may have been due in part to the generally rather poor crystallographic quality of flame-fusion ruby seed crystals, although in several cases some good quality growth was obtained. In addition, some crystals were grown on seeds cut from ruby produced by the fluxed melt technique (White, 1961), and where the growth rates were moderately slow some good quality crystals resulted. Using seeds with the stated orientation, the (11 $\bar{2}$ 0) prism faces developed completely if the run was left on for sufficiently long duration. After capping had taken place the growth rate was appreciably retarded (see fig. 4), but the quality of the subsequent growth was usually much improved.

In order to determine which crystal faces would predominate under hydrothermal conditions a growth run was attempted using a small ruby sphere as the seed crystal. The following faces, formed after 14 days of growth, were identified: {001}, {11 $\bar{2}$ 0}, {10 $\bar{1}$ 1}, {22 $\bar{4}$ 3}, and {10 $\bar{1}$ 4}. The first four have all been found in naturally occurring ruby but {10 $\bar{1}$ 4} has not. It was, however, quite well developed on the hydrothermal specimen.

Specimens of hydrothermally grown corundum and ruby crystals are shown in fig. 5. Those shown include dark, heavily iron-contaminated crystals; iron-free crystals grown rapidly and showing parallel sheet growth; and chromium-doped crystals of higher quality.

Conclusions

The conditions under which the best quality growth occurred were: base temperature of autoclave, 650° C; top temperature of autoclave, 475° C; reciprocal degree of filling, 3.0; weight of rubidium carbonate,

4.5 g; weight of potassium dichromate, 1.0 g; estimated pressure, 750 atm.

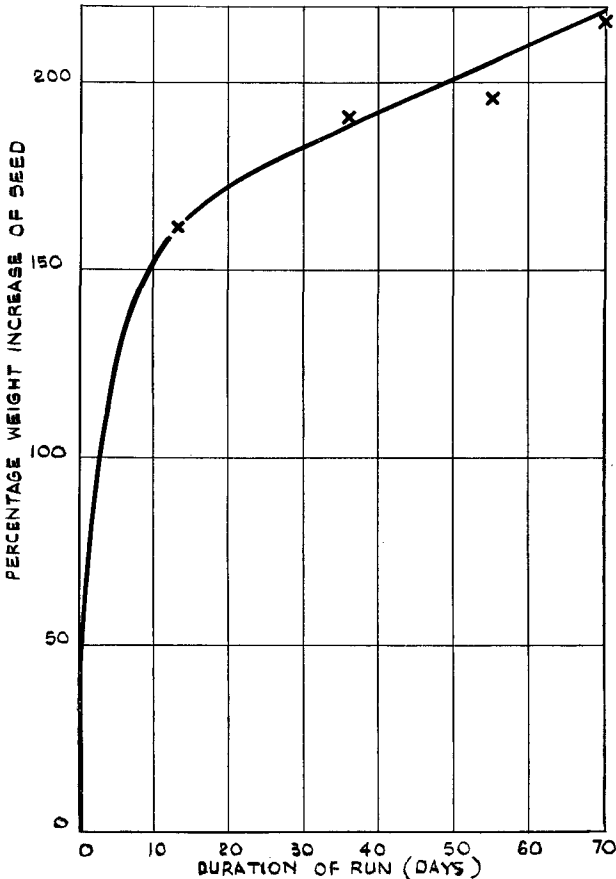


FIG. 4. The percentage weight increase of ruby grown on seed crystals plotted against duration of run.

The conditions of temperature and pressure were limited by the materials and design of the autoclaves and it was necessary to limit the growth rates to produce crystals of reasonable quality. It is quite likely that if higher working temperatures and pressures could be achieved then the growth rates and the quality of the crystals produced could be much improved. Compared with flame-fusion ruby the hydrothermal

crystals showed a more uniform distribution of chromium as opposed to the large scale inhomogeneities encountered in the former, but even the best quality hydrothermal ruby so far produced contained a large number of small inclusions, presumably of water.



FIG. 5. Specimens of ruby and corundum crystals grown on seeds.

The growth rates quoted by Laudise and Ballman, 0.25 mm per day on the (0001) face, seem remarkably rapid in view of the present work. In all of the runs performed the majority of the growth has been parallel to the (0001) face and the linear growth along the *c*-axis has rarely exceeded 1 mm over a period of 14 days.

The fact that corundum is soluble in a range of aqueous solutions of inorganic compounds but that growth only occurs in the alkali metal carbonate solutions suggests that, in most cases, it dissolves irreversibly. It is probable that in the case of hydroxide solutions the solubility of corundum is due to the formation of the corresponding aluminate, while with fluorides it is likely that an equilibrium is set up: $\text{Al}_2\text{O}_3 + 6\text{KF} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{AlF}_3 + 6\text{KOH}$; such a reaction would be expected to be dependent on pressure. The solubility of corundum in carbonate solutions would appear to depend upon the formation of some complex ion. The increase in the growth rate of corundum along the series Na_2CO_3 - K_2CO_3 - Rb_2CO_3 follows the increase in basicity of the alkali metals; the

reduced growth-rate with caesium carbonate may be due to the large size of the caesium ion.

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