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THE GROWTH AND PROPERTIES OF COLORED QUARTZ

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Hydrothermal crystal growth refers to the use of aqueous solvents at high temperatures and high pressures to affect the solution and recrystallization of a material which is relatively insoluble at ordinary conditions. The use of this technique as a means of obtaining large crystals of relatively pure materials is perhaps best demonstrated by its successful application in the laboratory and commercial production of quartz. (Walker and Buehler, 1950, Hale, 1950, Laudise and Sullivan, 1959, Sawyer, 1959). The fact that one can grow colorless quartz of high purity in steel vessels in a system normally considered quite corrosive is rather surprising. Most procedures for the synthesis of quartz employ a sodium hydroxide or a sodium carbonate solution as the solvent. Fortunately, under the conditions of growth the attack of the alkali on the steel vessel results in the formation of acmite (Walker and Ballman, 1954), an insoluble sodium iron silicate, which coats the interior of the vessel and limits further corrosion. The formation of acmite and the protection its coating affords is perhaps the principal reason why electronic grade quartz can be grown on a laboratory or production basis without resorting to the use of inner liners of noble metals.

Considering the number of elements present in the composition of most steels, and the fact that the formation of acmite explains why only iron does not contaminate the grown quartz, it seems clear that other ions although present in solution do not necessarily enter the quartz structure. In view of this and the interest in the effect of impurities on the electrical properties of quartz a program was undertaken to purposely introduce ions in the quartz structure. The effect of such ions on visible color might also offer a possible explanation of the mechanism of coloration as seen in some naturally occurring quartz species such as citrine or rose quartz.

EXPERIMENTAL

The crystals obtained in this study were grown in high pressure steel autoclaves using a modified Bridgman seal or welded closures. Both these designs have been previously described (Walker, 1954, Laudise and Sullivan, 1959). Nutrient quartz was placed in the bottom of the vessel and a frame holding the seed crystals whose principal surface was

(0001) was placed in the upper region. A perforated metal disc was placed between the two regions and acted as a baffle to separate the dissolving and the crystallizing zones. The action of the baffle promotes the growth of crystals of uniform dimensions throughout the entire growing region.

The autoclaves were then filled to the desired fraction of the free volume with the solvent, closed, and placed in furnaces in which the desired temperature and temperature differential were maintained with a Leeds-Northrup Micromax controller. Temperature readings were made using chromel-alumel thermocouples strapped to the exterior of the vessels and recorded daily for the duration of each experiment which lasted about 15 days.

All experiments were carried out in 1.0 molar potassium carbonate solutions at an average temperature of 370° C. and a degree of filling of the autoclave of 80 or 85% corresponding to a pressure of about 25,000 psi (Kennedy, 1950). The doping agent was put in the nutrient zone either as the metal or as the oxide. A similar technique for quartz doping has been used by other investigators (Stanley and Theokritoff, 1956, Augustine, 1957).

At the termination of a run the crystals were removed from the autoclave and their dimensions measured for growth rate calculations. The crystals were then sectioned for spectrochemical analysis, optical absorption studies and electrical measurements.

Results and Discussion

Previous quartz doping studies by the author (Walker and Ballman, 1954), and others (Thomas and Brown, 1952,* Tsinober, *et al.*, 1959) had shown a slight green coloration in quartz grown from potassium hydroxide solutions and in view of this it was decided to further study the use of potassium compounds as solvents. The first such run using potassium carbonate as the solvent in a steel autoclave produced a dark green quartz almost black in appearance. Spectrochemical analyses of this material showed iron, 0.05 wt. %, manganese, 0.01 wt. %, and beryllium 0.008 wt. %. Both manganese and beryllium are minor constituents of the steel composition. Figure 1 shows the crystals produced in this run compared to a colorless crystal grown in a steel autoclave in sodium hydroxide solution. The crystals were well formed but showed a few areas with small fractures which appear to be the result of the inclusion of the

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* In a recent publication a green and brown colored synthetic quartz was produced in steel autoclaves with a potassium carbonate solvent. Results similar to ours were obtained regarding colors produced, color zoning and optical absorption.

foreign ion since crystals grown under similar conditions without the additives are quite free of this imperfection. The next run was made in an inert system (all silver) in which the iron could be added in controlled amounts and thus offer a means of doping with particular levels of the desired impurity. The results of this run however were rather surprising in that perfectly colorless quartz was produced containing little or no iron (.001%), even though iron was available in solution at a 1% by weight concentration. It appeared then that in order to include iron in quartz a carrier ion was needed for charge balance. Beryllium was chosen over manganese since its relatively small ionic radius should permit it to be included in the quartz structure with the least difficulty. A new run was carried out again using metallic iron (1% by wt.) but this time with the addition of beryllium (0.002% by wt.) as the carrier ion and like the first run it produced a green colored quartz. The color produced however was of lower intensity than the first run and of a slightly different hue. Figure 2 shows a crystal produced in this run.

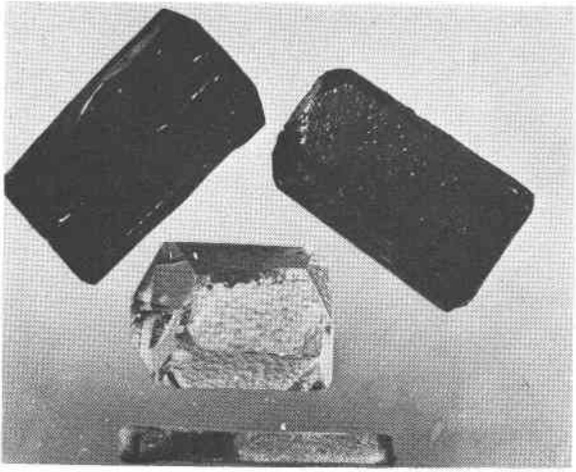


FIG. 1—Iron, manganese and beryllium doped synthetic quartz *vs.* colorless synthetic.

The color in both sets of crystals is not homogeneous but is composed of light and dark bands of green separated by zones of yellow and diminishes as the growth progresses. It was apparent from the diminishing color that the phenomenon responsible for the production of color ceased to occur after the early stages of growth. Figures 3 and 4 show the banded nature of the colored material.

Since the color produced in the grown material is composed of both green and yellow bands, both ferrous and ferric ions are presumably

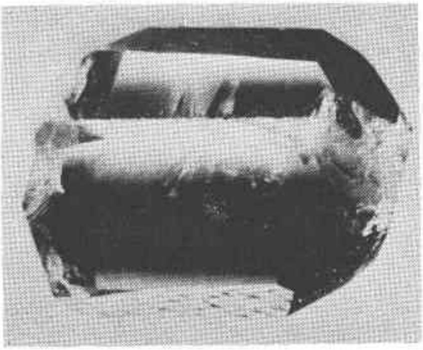


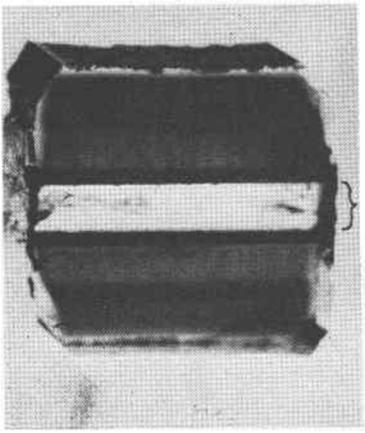
FIG. 2—Iron and beryllium doped synthetic quartz.

present in the crystal. This is not particularly surprising since recent work at the Bell Telephone Laboratories (Laudise, Crocket and Ballman, 1959) has shown magnetite to be the phase that forms under the reducing conditions in this hydrothermal system. A plausible mechanism then for the coloring effect is that of metallic iron going to ferrous and ferric ions in solution and then forming the stable magnetite phase.

Equation 1 shows this over-all reaction and equations 2, 3, and 4 show a possible stepwise formation of ferrous and ferric ions leading to the production of magnetite.

$$3Fe^\circ + 4H_2O \leftrightarrows Fe_3O_4 + 4H_2\uparrow \qquad \text{Eq. 1.}$$

$$\begin{aligned} Fe^\circ + 2H_2O &\leftrightarrows Fe(OH)_2 + H_2\uparrow \\ Fe(OH)_2 &\leftrightarrows Fe^{++} + 2OH^- \end{aligned} \qquad \text{Eq. 2.}$$



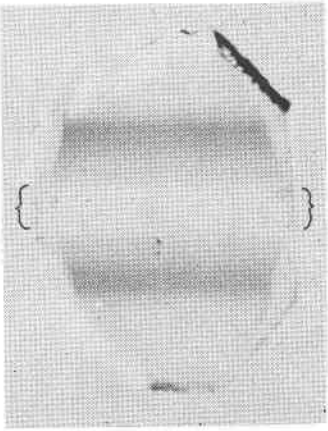


FIG. 3 (left)—Cross section cut parallel to *c* axis of iron, manganese and beryllium doped sample showing seed area marked by brackets and zonal distribution of color.

FIG. 4 (right)—Cross section cut parallel to *c* axis of iron and beryllium doped sample showing seed area and zonal distribution of color.

$$Fe(OH)_2 + 2H_2O \leftrightarrows Fe(OH_3) + H_2\uparrow$$

$$Fe(OH)_3 \leftrightarrows Fe^{+++} + 3OH^- \qquad \text{Eq. 3.}$$

$$Fe(OH)_2 + 2Fe(OH)_3 \rightleftarrows Fe_3O_4 + 4H_2O \qquad \text{Eq. 4.}$$

Coloration takes place only while there is a high concentration of ferrous and ferric ions in solution as the metallic iron is being oxidized. Once the metallic iron surface is all converted to magnetite the concentration of ferrous and ferric ions now in solution in equilibrium with the stable magnetite phase is too low for iron to be included in the crystal in any quantity and color ceases to be produced.

A run was made to test this hypothesis and powdered crystalline magnetite (1% by wt.) was used as the source of iron along with beryllium ions (BeO, 0.02% by wt.) as the carrier. This run produced perfectly colorless quartz and appears to bear out the proposed mechanism.

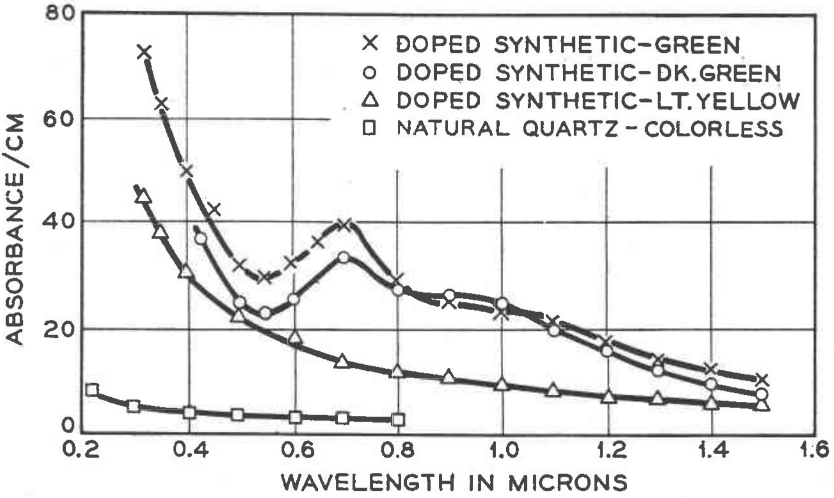


FIG. 5—Absorbance/cm. vs wavelength for synthetic and natural quartz samples.

Table 1 shows that impurity levels found in the colored samples as well as in naturally occurring quartz. The doped samples are in general an order of magnitude greater in impurity concentration.

Figure 6 shows a plot of the optical absorbance/cm. at 0.7 micron versus wavelength for the colored samples and a representative natural quartz sample. As can be seen there are two areas of high absorption one peak occurring about 0.7 micron and another in the ultraviolet region of the spectrum. The high absorption in the ultraviolet region is characteristic of ferric ions in quartz as well as in other materials. Less is known about where ferrous ions in quartz would show an absorption

TABLE 1. IMPURITY CONCENTRATION (WEIGHT PER CENT) FOUND IN NATURAL AND SYNTHETIC QUARTZ SAMPLES

Impurity	Natural Quartz			Doped Synthetic	
	(Colorless)	Rose (Pink)	Citrine (Yellow)	Green (Zone)	Yellow (Zone)
Fe	<0.001	—	0.001^+	0.026	0.015
Ti	—	0.005	—	—	—
Mn	—	—	—	0.016	0.005
Be	—	0.001	—	0.03	0.008

peak. However, ferrous ion generally shows an absorption peak at about 0.9–1.0 micron (Holmes and McClure, 1957) and since the conditions of the experiment indicate both ferrous and ferric ions to be present the consistent peak at 0.7 micron is most likely due to the ferrous ions.

Figure 7 shows the optical absorbance/cm versus the impurity concentration for areas of different color intensity within the same crystal. It is clearly indicated that the absorption at 0.7 micron is proportional to both the Be and the Mn concentration but not to the total iron concentration, thus it is apparently only the ferrous portion of the total iron concentration which is causing this peak.

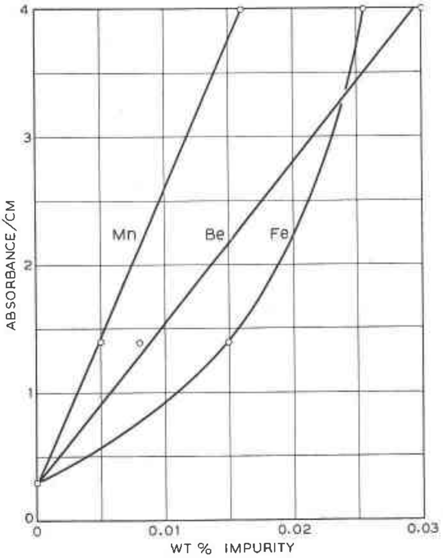


FIG. 6—Absorbance/cm. vs. impurity concentration for doped synthetic quartz.

It appears that when ferrous iron is included in the quartz it not only carries along a beryllium or manganese ion as a charge balancer but seems to permit an additional number of these ions proportional to the ferrous iron included to enter at the same time. This would explain why manganese and beryllium appear to obey the Beer Lambert law as shown in the plot.

It is difficult to explain why such a high concentration of beryllium is found in iron doped quartz when runs doped with beryllium alone do not include beryllium in amounts greater than about 10 ppm.

CONCLUSIONS

The formation of acmite, an insoluble sodium iron silicate, prevents the inclusion of iron in quartz crystals grown from sodium hydroxide or carbonate solutions. Potassium carbonate solutions do not form an analogous compound and can be used when quartz is to be iron doped. In other alkali carbonate or hydroxide solutions quartz is either not the stable phase under experimental conditions or growth rates are too low to be of use.

In order for ferrous or ferric ions to be included in the quartz structure a carrier ion* must be used for charge balance. Manganese and beryllium work well with beryllium preferred due to its smaller ionic size which permits its inclusion with the least strain.

The inclusion of iron in quartz appears to be due to a high concentration of ferrous and ferric ions put in solution as metallic iron is oxidized by the alkaline solution and forms the stable magnetite phase.

The high optical absorption of the colored material in the ultraviolet region of the spectrum is characteristic of ferric ion compounds, and the peak at about 0.7 micron is most likely due to ferrous ion.

The presence of both green and yellow bands in the grown quartz further indicates the presence of both ferrous and ferric ions within the same crystal, the green and yellow being characteristic of ferrous and ferric ions respectively.

ACKNOWLEDGMENT

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* A carrier ion is any ion other than the substituting ion which must also be included (presumably interstitially) to balance charges.

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COMMENT ON "GROWTH AND PROPERTIES OF COLORED QUARTZ"

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The interesting results of Ballman (preceding article) on the differences in concentration of various ions in the different crystallographic zones suggest the following explanations which supplement or modify the author's conclusions.

(1) Keith and Tuttle (*Am. J. Sci.*, **Bowen Volume**, 1952, p. 203) found a similar zoning of alternate "segments" of different color in natural quartz (after irradiation). It is interesting to note that such crystals as well as those grown by Ballman provide examples of the chemical inhomogeneity of a "single phase" which still qualifies as a phase in the context of the Phase Rule.

(2) Ballman suggests that a "carrier ion must be used for charge balance" in order for ferrous or ferric ion to be included in the quartz structure. Since their valence is also lower than Si^{4+}, it is obvious that the elements suggested (Be^{2+}, Mn^{2+}) cannot form half-breed derivatives