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BLUE SYNTHETIC QUARTZ

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Many reports have been made concerning the intentional introduction of impurity atoms into α -quartz during hydrothermal synthesis (Brown and Thomas, 1955; Chi *et al.*, 1955; Stanley and Theokritoff, 1956; Cohen and Hodge, 1958; Brown *et al.*, 1960; King *et al.*, 1962). Only iron has been previously incorporated in sufficient concentration to cause visible coloration of the crystal (Tsinober and Chentsova, 1958; Tsinober *et al.*, 1958; Ballman, 1961) without additional treatment such as x-irradiation (Augustine and Hale, 1958). However, recently it has been found that cobalt can be added during growth and a blue-colored crystal can be produced (Sawyer, 1964). This report concerns observations made on a crystal from Western Electric run # X-126, and an unmarked Y-bar material from Sawyer Research Products. Growth conditions for the Western Electric crystal X-126 were as follows:

solvent	-1.0 molar NaOH
degree of fill	-82%
pressure	-1600 bars
crystallization temperature	-390° C.
dissolving temperature	-345° C.
total growth along (0001) face	-1.7 mm/day

No data were available on the Sawyer Research Products crystal but it is presumably grown in a sodium carbonate solution at lower temperatures and pressures and correspondingly lower growth rate.

The amount of cobalt in the final product depends not only on the concentration of that ion in the solution around the growing crystal, but it also depends on the aluminum concentration as well. A solution containing 0.025 molar Co^{2+} , 0.05 molar Al^{3+} and 1.0 molar NaOH introduced about twice the intensity of coloration produced with a similar solution containing no Al^{3+} but having the same Co^{2+} concentration. The function of the Al is not known.

The absorption spectrum of the blue quartz is shown in Fig. 1, and the values of

$$A \equiv \frac{1}{t} \log_{10} \frac{I_0}{I}$$

where t = sample thickness in cm, and I_0 and I are the usual incident and transmitted intensities indicate how pale the color has been in crystals so far produced. There is only very weak dichroism for light polarized

parallel and perpendicular to (0001). The three absorption peaks are characteristic of Co^{2+} in a tetrahedral site (Ballhausen and Jørgensen, 1955; Cotton *et al.*, 1961; Pappalardo *et al.*, 1961; Ferguson, 1960) which may be presumed to be the Si^{4+} site of the SiO_4 tetrahedron. The absorption corresponds to the transition: ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ which has relatively great intensity because of the lack of a center of symmetry in the T_d coordination configuration of the cobalt ion (Ballhausen and Liehr, 1958).

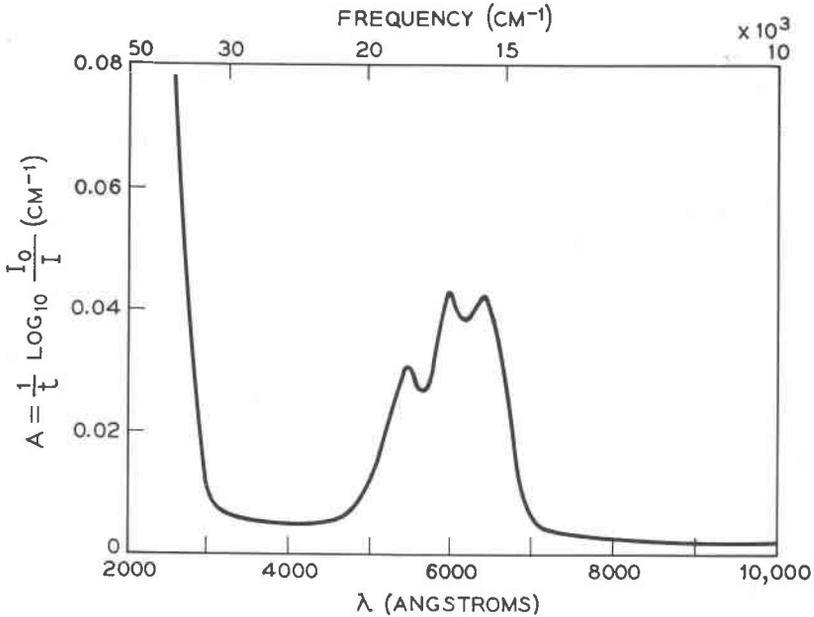


FIG. 1. Absorption curve for blue synthetic quartz (WEC0 X126) containing 5.8 ppm (by wt.) of Co^{2+} in tetrahedral sites.

The three components of the absorption band near $16,000 \text{ cm}^{-1}$ (6000 \AA) arise from the spin-orbit splitting of the ${}^4\text{T}_1({}^4\text{P})$ level and the admixture of various doublet and quartet states lying very close together in this region (Liehr, 1963).

One would expect another strong quartet band about 6000 cm^{-1} (1.6μ) for tetrahedral cobalt, but the molar extinction coefficient is usually much smaller than that of the $16,000 \text{ cm}^{-1}$ (6000 \AA) band (Ferguson, 1960). Thus in the lightly doped quartz used here, the weaker band cannot be distinguished for the sample thicknesses available (5 cm). The concentration of cobalt in the samples we studied is about 5.8 parts Co per million parts of crystal by weight. This was determined in two ways:

first by emission spectrographic analysis,¹ and second by absorption spectrophotometry.

The more reliable value of 5.8 ppm is that from the emission analysis, but using the known absorption coefficient of Co^{2+} in a borate glass standard we found 10 ppm. This is a reasonably close check since the absorption coefficient may vary somewhat from one base material to another. Using the exact value to determine the absolute absorption coefficient in crystalline α -quartz, the concentration in any other α -quartz crystal can be measured spectrophotometrically through the relation:

$$\frac{1}{\alpha t} \log_{10} \frac{I_0}{I} = C$$

where I_0 is the incident radiation intensity, I is the transmitted intensity, t the sample thickness in cm, $\alpha = 8.0 \times 10^{-3}$ at $\lambda = 5940 \text{ \AA}$ and C is the concentration of Co^{2+} in parts by weight per million parts of crystal.

The inclusion of Co^{2+} ions in the lattice does not take place uniformly as the crystal grows, since bands of light and darker color appear when viewing perpendicular to the optic axis. These bands are in planes parallel with the seed plate and the spatial periodicity of color is about the same as that of the planes of varying refractive index which show in schlieren photographs of synthetic quartz (Arnold, 1957) or in irradiated samples (Arnold, 1960). Especially noticeable is a light band in crystal X-126 about 5 mm from the outside of the crystal, and this corresponds to a region of weaker absorption at 3500 cm^{-1} (2.86μ) where H_2O or H-bonded OH absorbs (Dodds and Fraser, 1965). On the other hand, there is less color near the seed in this particular crystal but the absorption at 3500 cm^{-1} continues to increase gradually from outside to seed even through the colorless region. Presumably the banding here as well as the banding seen in iron doped green quartz has something to do with variations of growth conditions, but the correlation with variations in the water absorption in the infrared is not direct.

No blue color appears in material where growth takes place along the X-direction ($11\bar{2}0$) although major rhombohedral ($10\bar{1}1$) growth is colored the same as the Z-growth material (0001). This must imply a different growth mechanism for the X and Z directions if the Co^{2+} ion is selectively excluded in one but permitted in the other. A similar effect was found for the case of iron doping (Ballman, 1961) where a blue-green color (Fe^{2+}) was present in X-growth ($11\bar{2}0$) material while a green and

¹ We are indebted to Mr. D. L. Nash for performing the quantitative emission spectrographic analysis.

yellow (Fe^{2+} and Fe^{3+}) banded coloration was present in Z-growth (0001) material.

If as the spectrum indicates the Co^{2+} replaces Si^{4+} in the tetrahedral lattice site, the charge unbalance must be compensated in some way to preserve the overall electric neutrality of the crystal. This could occur in many ways, but the most likely is that monovalent sodium ions in nearby interstitial sites may supply the extra charge required. This crystal contains about 100 parts per million of sodium by emission spectrographic analysis and this is more than enough to compensate the 6 parts per million of Co^{2+} . Other alkalis such as Li^+ as well as protons in interstitial sites could also accomplish the compensation.

From the results of doping experiments so far it seems that most ions do not fit easily into the quartz lattice, and in the case of cobalt the color is anomalous because its very highly intense absorption permits it to be seen in very low concentration.

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BLACKENING OF NATURAL QUARTZ BY γ -IRRADIATION

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INTRODUCTION

Numerous studies of color centers in natural and synthetic quartz have been made in recent years, and the general relationship of color centers in smoky quartz to chemical substitution and γ -irradiation has been established by a number of investigators: Griffiths, Owen and Ward (1954), O'Brien (1955), Cohen and Sumner (1958), Cohen (1956, 1960), Bambauer (1961), Bambauer, *et al.* (1960), and Kats (1961). The mechanism of color center development as proposed by O'Brien (1955) whereby interstitial ions are neutralized by γ -radiation is generally accepted.

Hayase (1961) qualitatively (visibly) studied the effect of gamma irradiation on natural quartz. He found that natural smoky quartz could be decolorized by heating it at 600° C. for five minutes. His samples were then irradiated by using a 2000 Curie cobalt 60 γ -ray source. Quartz from extrusive igneous rocks, formed at relatively high temperature, were darkened to a greater degree than quartz from granite and from low temperature hydrothermal veins. Quartz from gneissic and crystalline