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HYDROTHERMAL GROWTH OF AMETHYST AND CITRINE IN NaCl AND KCl SOLUTIONS

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Natural quartz grows from solutions containing mainly Na^+, K^+ and Cl^- ions. In this experiment, the growth of synthetic quartz under the same growth conditions as those of natural quartz was attempted using NaCl and KCl solutions as a growth solution. As a result, colored quartz equivalent in quality and color tone to natural amethyst and citrine was obtained. The quartz grown from *r*-cut and *R*-cut plate seeds with iron added to the growth solution was colorless but γ-ray irradiation produced a purplish tint. The quartz grown from *X*-cut plate and *Y*-bar seeds had a yellowish tint. Although the depth of color increased in proportion to the amount of iron, it reached close to saturation with an iron concentration of approximately 90 μg/ml solvent.

1. Introduction

Amethyst, smoky quartz, citrine, and rose quartz represent colored quartz existing in nature. Natural quartz grows in a solution containing mainly the Na^+, K^+ and Cl^- ions, and colored quartz is a product in which impurities contained in a solution were incorporated during the process of crystal growth. The coloration mechanism of colored quartz has been fairly well explicated in only relatively recent years. It is known that citrine occurs in the presence of substitutional Fe^{3+} [1], yellow quartz in the presence of interstitial Fe^{3+} [2], amethyst in the presence of interstitial and substitutional Fe^{3+} [3,4], and smoky quartz in the presence of substitutional Al^{3+} [5]. Amethyst and smoky quartz [6,7] are decolorized by heating and colored by irradiation. For artificial synthesis of colored quartz, an alkaline solution has been mainly used as a growth solution. Amethyst [8], citrine and green quartz [9] were synthesized using K_2CO_3 solution and KOH solution with added Fe. Blue quartz was obtained in NaOH solution by doping with Co^{2+} [10]. Amethyst was also obtained in NH_4F solution by doping Fe [11]. However, during the growth process using an alkaline solution, the color tone undergoes unstable changes depending on the growth conditions such as impurities used.

In this experiment, synthesis of amethyst and citrine was attempted with growth conditions as close to the growth of natural quartz as possible using NaCl and KCl solutions with iron as an impurity. Synthetic amethyst and citrine of the color tone almost equal to natural colored quartz were obtained.

2. Experimental method

The hydrothermal growth of colored quartz crystals was carried out using a platinum capsule (10 mm ID × 210 mm length) placed in an autoclave. *X*-cut $(11\bar{2}0)$, *R*-cut $(10\bar{1}1)$ and *r*-cut $(01\bar{1}1)$ plate and *Y*-bar seeds were used. Synthetic quartz crystals were used as a nutrient. Fe or α-Fe_2O_3 powder was used as an additive in concentrations of 1–1000 μg/ml solvent. As a growth solution, 10 wt% NaCl solution and 10 wt% KCl solution were used at a fill rate of 70%. The growth period was 5–20 days. The growth temperatures varied from 400 to 450°C. The temperature gradient was held at either 25 or 50°C. The crystals grown were

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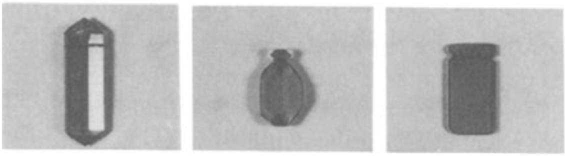

Fig. 1. Amethyst and citrine grown in NaCl solution with iron added. Left: citrine grown on *X*-cut seed. Middle: citrine grown on *Y*-bar seed. Right: amethyst grown on *r*-cut seed.

colored by irradiation with γ-rays at a dose of 2×10^6–15×10^6 roentgen using Co^{60}, and evaluated macroscopically as well as spectrophotometrically using a Shimazu spectrophotometer (Model MPS-50L).

3. Results and discussion

Under these experimental conditions, transparent high-quality crystals were obtained from the NaCl and KCl solutions containing Fe and α-Fe_2O_3. Fig. 1 shows amethyst and citrine grown in NaCl solution. The growth rates of the *X*-face, *R*-face and *r*-face were approximately 0.1, 0.01 and 0.01 mm/day, respectively. The growth characteristics such as the growth pattern obtained in this experiment were the same as previously reported [12–14]. When iron was added, the crystals grown from the *R*-cut and *r*-cut plate seeds were colorless, and the crystals grown from the *X*-cut plate and *Y*-bar seeds were yellow.

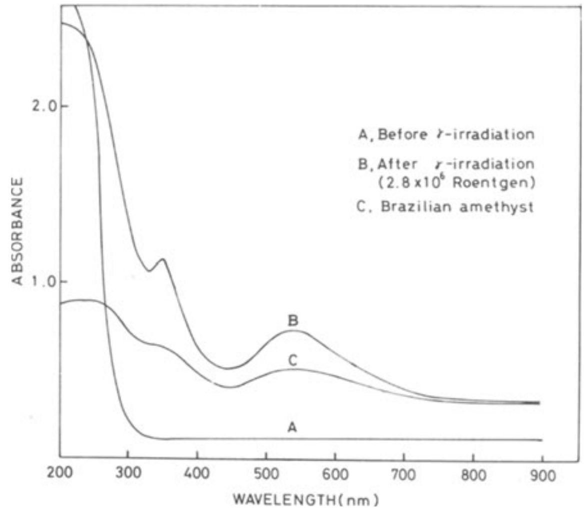

Fig. 2. Absorption spectra for synthetic and Brazilian amethyst samples.

3.1. Amethyst

The crystals grown from the *R*-cut and *r*-cut plate seeds were colorless and transparent, despite an iron content when grown. However, γ-ray irradiation changed them into amethyst of a beautiful purplish tint. Fig. 2 shows the absorption characteristics of these crystals before and after γ-irradiation in comparison with natural amethyst. Although not very distinct in the figure, the specimen before γ-ray irradiation shows a large absorp-

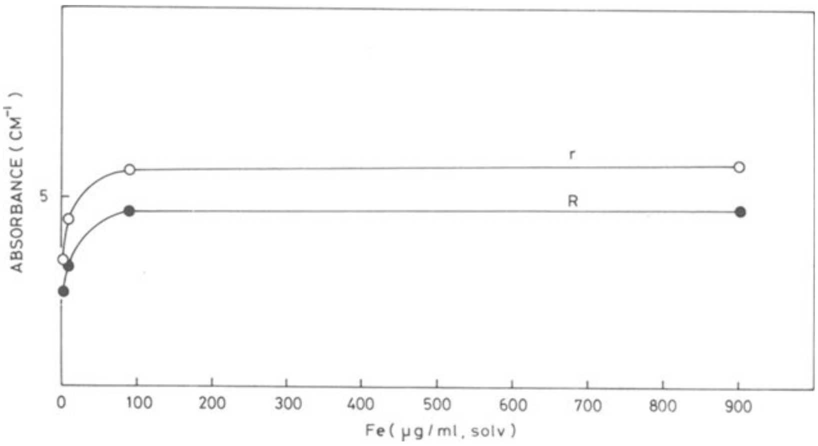

Fig. 3. Relation between the concentration of added Fe and absorbance at 545 nm.