HIGH PRESSURE HYDROTHERMAL GROWTH OF BERYL SINGLE CRYSTALS

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ABSTRACT

Beryl crystals were grown under high pressure hydrothermal condition of 200 MPa and 1 GPa. Transparent and smooth crystals were grown on the seed at 550° - 700℃ from 0 - 0.3N NaOH solutions. The optimum crystal growth was observed at 600° C from 0.1N NaOH for 1GPa and from 0.025N NaOH solution for 200 MPa. Growth rates along [11$\bar{2}$0], which were considerably influenced by NaOH concentration, were 40 μ m/day for 0.025N and 25 μ m/day for 0.05N NaOH at 650℃ under 200 MPa. The beryl crystals incorporated water molecules and alkali cations in the channels of the structure. The crystals showed same refractive indices and density as those of natural emerald crystals.

INTRODUCTION

Beryl, $Be_3Al_2Si_6O_{18}$, is found with a variety of impurity cations leading to its well-known beautiful colors and its favorable use as a gem stone. The structure consists of six-membered rings of silica tetrahedra cross-linked by Be-containing tetrahedra and Al-containing octahedra to form tetrahedral frameworks with open channels that parallel the c-axis. Natural beryls commonly contain varying amounts of alkali cations, as well as water molecules in the channels. Natural beryls and synthetic ones are clearly characterized by alkali cations in the channels; cations are present in natural crystals and absent in synthetic ones(1).

The most spectacular growth of beryl was conducted by hydrothermal method(2), but there are no reports on synthesis of beryl single crystals containing alkali cations in the channels. We have already tried to establish a high pressure hydrothermal method under 1 GPa, by which we have prepared beryl single crystals which is similar to natural ones(3). In this report, properties of beryl single crystals grown under 200 MPa and 1 GPa are described in detail with the preparation method.

EXPERIMENTAL

Reagent grade $Be(OH)_2$(Kishida chemical Co., Ltd.) and $Al(OH)_3$(Wako pure chemical industries Ltd.) powders, and synthetic quartz blocks(made by Toyo communication equipment Co., Ltd.) were used as starting materials. These powders and blocks with the stoichiometric composition of beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$) were placed with 0 - 0.3N NaOH solutions in a growth chamber. An internal heating autoclave was used for the experiments under 200 MPa. A piston cylinder type vessel was also used for the experiments under 1 GPa. As a seed crystal, synthetic emerald was supported with Pt wire at an upper part of the chamber, in the middle of which a baffle plate with 20% opening space was attached to moderate thermal convection. The details of these equipments have been described by the authors(4,5).

The experiments were conducted at 500° to 700℃ under the pressure of 200 MPa and 1 GPa. After heating at the desired temperature and duration, the growth chamber was rapidly cooled to room temperature. The grown beryl crystal was cleaned with hot water. Infrared spectra were obtained in the wave number of the 4000 to 1200 cm^{-1} by using a double beam spectrometer(Japan spectroscopic Co., Ltd., A-202). Specific gravities were determined by a water displacement method. Refractive indices were also measured by an immersion method.

RESULTS AND DISCUSSION

Beryl crystal was grown on a seed crystal by dissolution-precipitation of each starting material. Table 1 shows the representative results obtained under high pressure hydrothermal conditions of 200 MPa and 1 GPa. Crystal growth of beryl was observed at 500° - 650℃ and from 0 - 0.3N NaOH solutions. At higher concentration of 0.5N NaOH solution, only albite($NaAlSi_3O_8$) was produced instead of beryl. A clear and smooth beryl crystal was grown under the optimum condition at 600℃ and from 0.1N NaOH for 1 GPa and from 0.025N solution for 200 MPa. In the experiment under 1GPa, Pt wire was included by transparent grown layer in 1 mm thick as shown in figure 1. Representative p($10\bar{1}1$) plane for hydrothermal growth was developed. The p($10\bar{1}1$) plane seems to have relatively high growth rate, compared with those of m($10\bar{1}0$) and c(0001) planes. In the experiments under 200 MPa, growth rates along [$11\bar{2}0$], which were considerably influenced by NaOH concentration, were 40 μm/day for 0.025N and 25 μm/day for 0.05N NaOH solution at 650℃ (bottom). Many pyramidal growth patterns were observed on the surfaces of the crystals grown on the seed crystals with a($11\bar{2}0$) and s($11\bar{2}1$) planes as shown in figure 2.

In natural emeralds(4), water molecules and alkali cations are incorporated in the open channels as shown in figure 3. According to Wood(5), in the absence of alkali cations, water molecules are oriented in type I configuration. If alkali cations are also present in the

TABLE 1
Representative results by high pressure hydrothermal growth under 200 MPa and 1 GPa

NaOH (N)	Pressure (MPa)	Temperature (℃)	Durations (days)	Products
Water	1000	500	3	Be, Qu
Water	1000	650	3	Be
0.1	1000	600	6	Be
0.1	1000	700	5	Be, Ph
0.2	1000	600	5	Be, Ab
0.2	1000	650	4	Ab, Be
0.3	1000	600	4	Ab, Be
0.025	200	630	4	Cb, Ph*
0.025	200	700	3	Cb, Be
0.05	200	540	2	Cb, Be
0.05	200	650	4	Cb, Be
0.1	200	700	2	–

Be:Beryl($Be_3Al_2Si_6O_{18}$), Ab:Albite($NaAlSi_3O_8$), Qu:Quartz
Cb:Chrysoberyl($BeAl_2O_4$), Ph:Phenacite(Be_2SiO_4), *:trace

channels, its electrostatic attraction rotates the adjacent water molecules in type II configuration. These two types of water molecules can be distinguished the origin of beryl by IR spectra. There are large differences between IR spectra of synthetic hydrothermal emerald and that by the authors. Synthetic hydrothermal emeralds show only one absorption at 3690 cm^{-1}(7). In the beryl crystals obtained from 0.1 - 0.3N

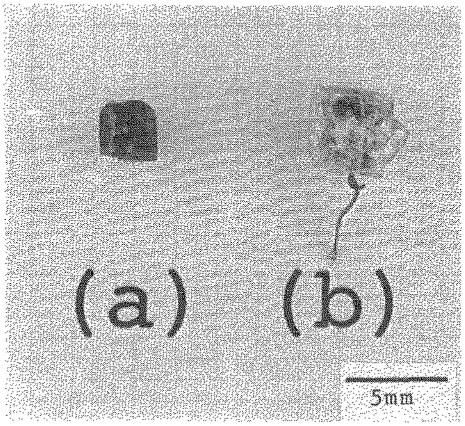

FIGURE 1. Flux grown seed(a) and beryl crystal(b) grown at 600°C under 1 GPa from 0.1N NaOH solution

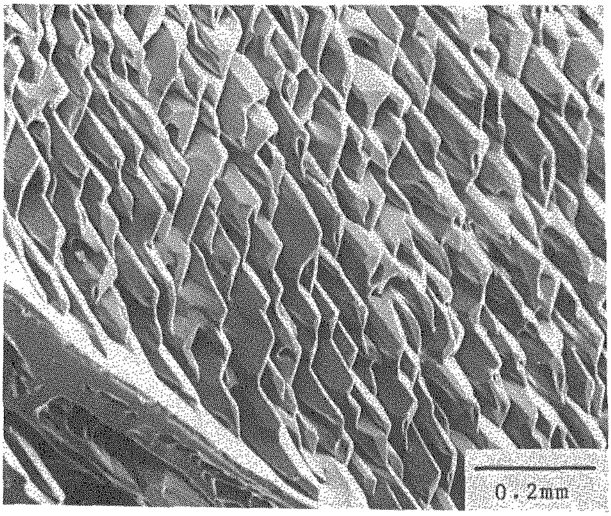

FIGURE 2. Scanning electron micrograph of the crystal grown on s($11\bar{2}1$) under 200 MPa from 0.025N NaOH solution for 4 days

NaOH solutions under high pressure hydrothermal conditions, two sharp absorption spectra corresponding to O-H vibration were observed at 3690 cm^{-1} (type I) and 3590 cm^{-1} (type II). The absorption belong to 3590 cm^{-1} was deeper with increasing the concentration of NaOH solution as shown in figure 4. Accordingly, the present beryl crystal (0.3N NaOH solution) was identical with natural Colombian emeralds in IR spectra(6).

The presence of alkali cations in the channels was also recognized from line analysis of seed and growth region in the crystal by EPMA(JEOL, JSCM-733) as shown in figure 5. The channels were also somewhat large for the direction of a-axis in the present beryl, compared with emerald grown by flux method due to the presence of alkali cations and water molecules.

As indicated in table 2, there are so many different type emerald distinguishing physical properties. The refractive indices were determined as ω =1.5880 and ε =1.5790. These values were intermediate between Linde hydrothermal beryls (ω =1.570-1.580 ε =1.562-1.572) and natural emeralds (ω =1.565-1.602, ε =1.558-1.596)(5). The density, 2.68 gcm^{-3}, was also identical with that of natural emeralds (2.67-2.70 gcm^{-3}).

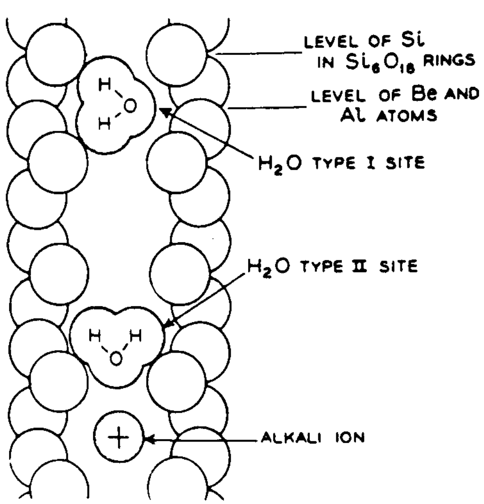

FIGURE 3. The location of water molecules and alkali cations in the channels of beryl structure

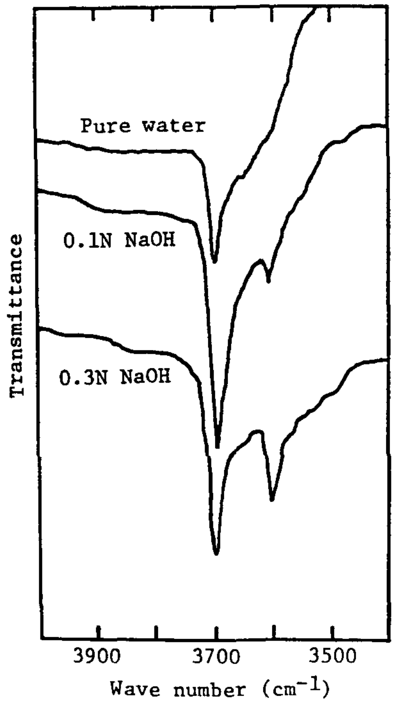

FIGURE 4. Infrared spectra of high pressure hydrothermal beryl from pure water, 0.1N NaOH and 0.3N NaOH

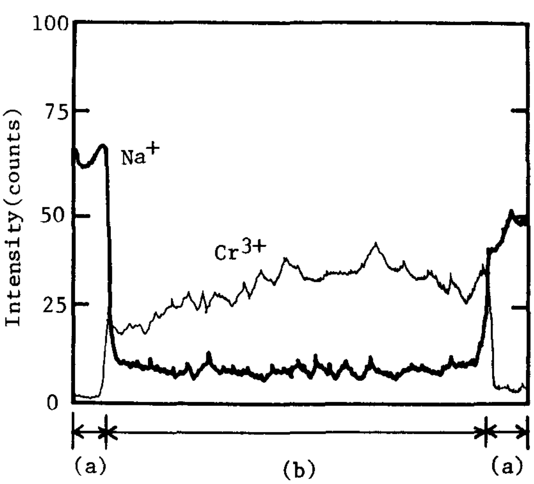

FIGURE 5. EPMA spectra for Na^+ and Cr^{3+} in the seed and growth region

TABLE 2
Properties of different types of emeralds and beryl

	High pressure hydrothrmal beryl	Flux emerald	Hydrothermal emerald	Natural emerald
Specific gravity	2.70	2.56-2.67	2.67-2.69	2.69-2.74
Refractive index ω	1.588	1.560-1.563	1.566-1.576	1.565-1.586
Refractive index ε	1.579	1.563-1.566	1.571-1.587	1.570-1.593
Types of water	I, II	-	I	I, II
Alkali present	Na	Li	-	Na, Li, Cs
Inclusions	Very few	Phenacite Pt	Phenacite	Tremolite Mica

CONCLUSION

Beryl single crystals were grown at 500° -650°C and from 0-0.3N NaOH solutions under high pressure of 200 MPa and 1 GPa. The optimum growth was observed at 600°C and from 0.1N NaOH solution. Water molecules and alkali cations were incorporated in the open channels of the beryl structure, as in natural emeralds. The refractive indices of the crystals with the density of 2.68 gcm^{-3} were ω =1.5880 and ε =1.5790.

In a survey of high pressure hydrothermal growth, though sizable crystals are not yet obtained, the beryl crystals are identical with natural ones inasmuch as they incorporated water molecules and alkali cations in the channels.

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