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Hydrothermal Growth of Calcite Single Crystal in NaCl Solution

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The hydrothermal synthesis of calcite single crystal was studied by using a NaCl solution as a mineralizer. The solubility of calcite in a 3 mol kg^{-1} NaCl solution was measured by a weight-loss technique to be around 2 g l^{-1} at 500 °C and 100 MPa. An optically clear rhombohedral crystal of up to 1.0 mm could be grown in a hydrothermal NaCl solution. The growth of a homogeneous layer of calcite could be observed on the calcite seed at 400 °C.

A calcite single crystal called Iceland spar has been used for such optical meterials as a Nicol prism. Recently, the demand for the growth of optically clear calcite crystals has been increasing due to a depletion of natural resources.

Many artificial techniques have been employed to grow calcite single crystal.[1—3] The flux method was recognized as being acceptable for growing calcite boule. It, however, encounters some difficulties in producing a high-quality single crystal of calcite owing to CO_2 dissociation, impurity contamination and a large thermal stress.

The hydrothermal method is one of the promising techniques for growing unstable crystals such as a carbonate compound. The authors had preliminarily reported that calcite single crystals of a euhedral form, bounded by $\{10\bar{1}1\}$, could be grown spontaneously in hydrothermal NaCl and KCl solutions as the solvent; the kind of anion in the solvent was the most significant factor for controlling the coexisting phase as well as the morphology of the grown crystals.[4] Chloride solutions as a hydrothermal solvent, were first used by N. Yu. Ikornikova and have been examined by some authors.[5,6] Experimental details, however, have not been reported.

In the present work, the solubility of calcite in a 3 mol kg^{-1} hydrothermal NaCl solution was studied as a function of the temperature under 100 MPa; the most appropriate conditions for the growth of a calcite single crystal were elucidated as basic data for the large scale production of calcite single crystals.

Experimental

In this work, highly pure natural Iceland spar was used as a starting material. The hydrothermal run was carried out in a hydrothermal pressure vessel of the cold-seal type (1/4″ I. D). The temperature was controlled with a calibrated chromel-alumel thermocouple set in the pressure vessel. The pressure was measured with a calibrated Heise gauge.

The calcite solubility was determined by the weight loss method with a hermetically sealed gold capsule (5.0 mm O. D, 4.7 mm I. D, 50 mm in length) containing cleaved Iceland spar crystals of about 3 mm in size. Crystals and the 3 mol kg^{-1} NaCl solvent solution were sealed in the gold capsule by welding and then set in a pressure vessel.

Solubility measurements were carried out under various conditions for a duration of 3 d; this was previously confirmed to be sufficiently long to achieve equilibrium. After a run, the pressure vessel was quenched into cold water. A stainless filler rod was placed in the space above the capsule so as to suppress any convection and to achieve thermal uniformity along the capsule.

The experimental growth conditions are a temperature of 350—500 °C, a pressure of 100 MPa and a duration of 3—14 d. The morphologies of the grown crystals were observed by optical microscopy. The grown crystals were also characterized by infrared spectroscopy and a back-reflection Laue method.

Results and Discussion

Solubility of Calcite in 3 mol kg^{-1} Hydrothermal NaCl Solution. The solubility of calcite in a 3 mol kg^{-1} hydrothermal NaCl solution was measured as a function of the temperature at 100 MPa by the weight-loss method. The solubility in the 3 mol kg^{-1} NaCl solution increased remarkably with increasing temperature above 400 °C and amounted to 2.0 g l^{-1} at 500 °C (Fig. 1). The value of the solubility is

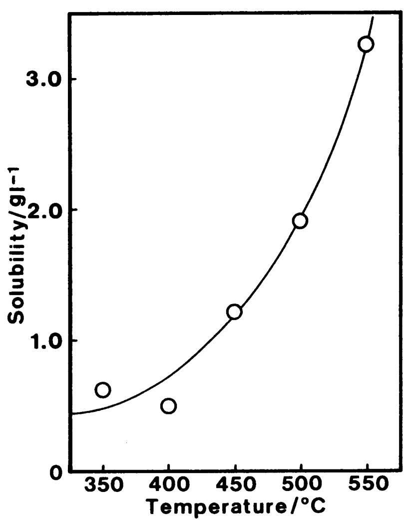

Fig. 1. Solubility of calcite in 3 mol kg^{-1} NaCl solution as a function of temperature.

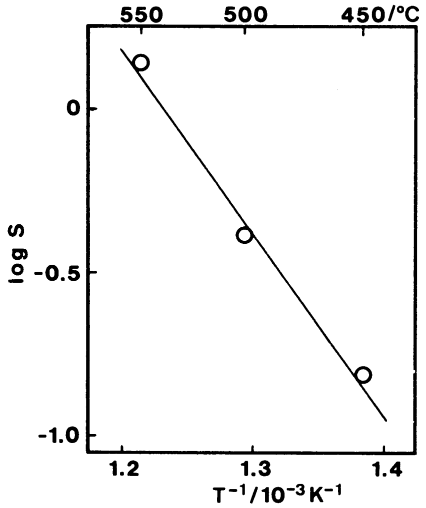

Fig. 2. Log S (solubility) of $CaCO_3$ as a function of $1/T$ in 3 mol kg^{-1} NaCl.

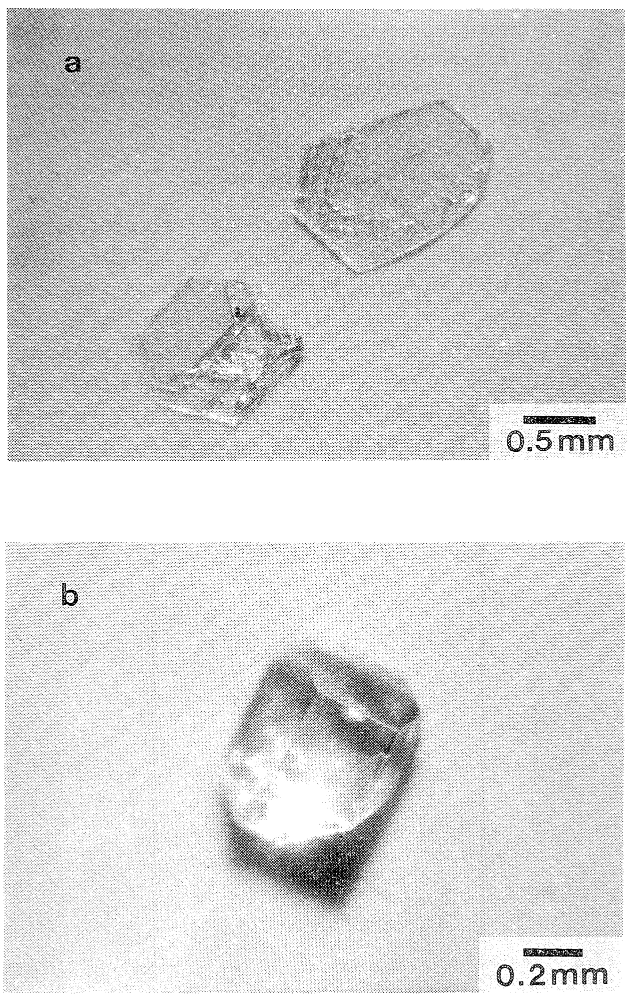

Fig. 3. Photomicrographs of calcite crystals grown in 3 mol kg^{-1} NaCl solution at 500 °C and 100 MPa for 10 d.

acceptable eventually for hydrothermal growth. Thus, all the growth experiments were carried out above 400 °C.

Figure 2 shows a plot of log S (Solubility) vs. $1/T$ in order to investigate the dissolution behavior of calcite in a 3 mol kg^{-1} NaCl solution at 100 MPa. The van't Hoff relation was confirmed to hold. The enthalpy of the solution, ΔH, was calculated to be about 46 kJ mol^{-1}, much larger than $\Delta H°=-12$ kJ mol^{-1} in a $CaCO_3$-H_2O system under ordinal conditions.[7] This fact indicated that the state of dissolved species under hydrothermal conditions was quite different from that under ordinary conditions at atmospheric pressure.

Morphology of Grown Calcite Single Crystal. A few growth runs were carried out with cleaved pure Iceland spar as a starting material of nutrient. Calcite single crystals of sizes up to 1.0 mm were grown spontaneously on the inner wall of the capsule at 500 °C under 100 MPa for 10 d. There were two kinds of crystal habits (Fig. 3). The morphologies of grown crystals were found to be strongly influenced by the growth temperature. Plate-like calcite crystals bounded by well developed {0001} faces could be formed mainly at elevated temperatures (above 500 °C). Associated with the crystals (Fig. 3a), a few polyhedral crystal were grown as shown in Fig. 3b. An identification of the plane is now in progress. The variation of crystal habits showed a good agreement with the occurence of Iceland spar in nature.[8] Euhedral crystals bounded by $\{10\bar{1}1\}$ faces were also prepared at 450 °C and 100 MPa for 10 d (Fig. 4). This fact suggests that the Iceland spar in nature might occur in a hydrothermal solution at a relatively lower temperature.

Figure 5 shows the characteristic IR spectra of a

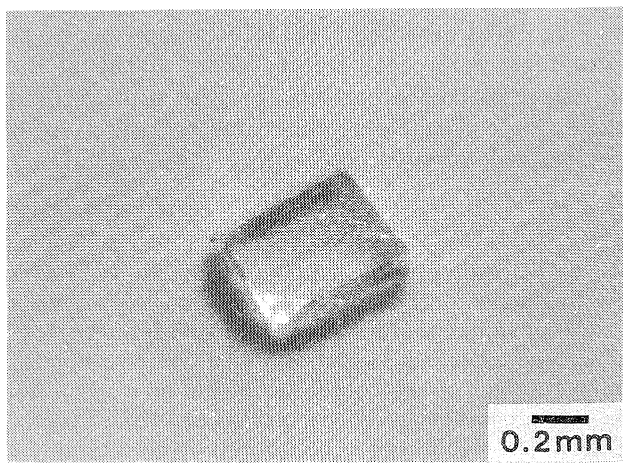

Fig. 4. Photomicrograph of calcite crystal grown in 3 mol kg^{-1} NaCl solution at 450 °C and 100 MPa for 10 d.

grown single crystal of calcite; it is identical to a high-quality natural calcite crystal, even though the crystal includes a stretching vibration due to OH^- around $3500\ cm^{-1}$. It ensures that the uptake of OH^- in this crystal is comparable to that in a well qualified optical grade of Iceland spar that is used for optical devices.

Growth Experiment with Seed Crystal. On the basis of the preliminary experiments, further growth runs with seed crystals were attempted by using a large pressure vessel (1/2″ I. D) in order to investigate the effect of seed orientation. A gold specimen container was prepared with a lid (10 mm O. D, 9.7 mm I. D, 17 cm in length) instead of a gold capsule. A short stainless filler rod was also placed above a gold container in order to adjust the thermal gradient.

Both spherical and rhombohedral seeds were suspended in the upper portion of the container. The pressure vessel was filled with a $3\ mol\ kg^{-1}$ NaCl solution, brought up to 400 °C and 100 MPa and maintained for 2 weeks. After a run, it was cooled at a constant rate of 25 °C/hr.

The thickness of the rhombohedral seed increased by 0.087 mm while keeping its appearance. On the other hand, spherical seeds were observed to be completely covered with flat smooth surfaces and the steps of a grown calcite crystal (Fig. 6). The flat plane was identified to be $(10\bar{1}1)$ faces, of which symmetry was confirmed to be two fold by back-reflection Laue photographs. This result revealed that it would be possible to accelerate the growth rate on the seed by a proper selection of the seed orientation, such as $(11\bar{2}0)$.

Conclusion

It is found that the solubility of calcite in a $3\ mol\ kg^{-1}$ hydrothermal NaCl solution increased remarkably upon increasing the temperature above 400 °C; the enthalpy of the solution, ΔH, was around $46\ kJ\ mol^{-1}$ at 100 MPa.

Euhedral crystals of calcite could be grown spontaneously in a $3\ mol\ kg^{-1}$ hydrothermal NaCl solution above 400 °C on the basis of solubility data.

The IR spectra of grown single crystals were found to be identical to high-quality natural Iceland spar with traces of OH^-.

Calcite single crystals could be successfully grown on seed crystals at 400 °C. This result indicates that the growth rate on the $\{10\bar{1}1\}$ plane is too slow for growing a large single crystal; thus, it is necessary to use a seed crystal with the proper orientation for a suitable facet, such as the $(11\bar{2}0)$ face.

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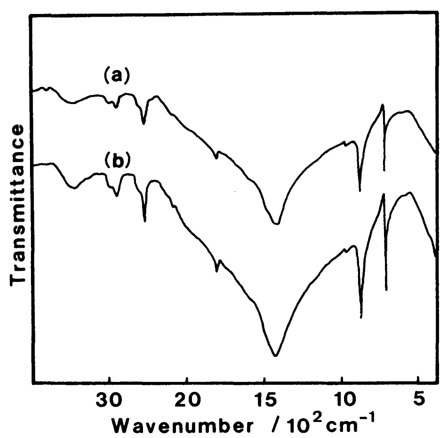

Fig. 5. IR Spectra of calcite single crystals.
(a) Hydrothermally grown crystal in NaCl solution.
(b) Natural Iceland spar crystal.

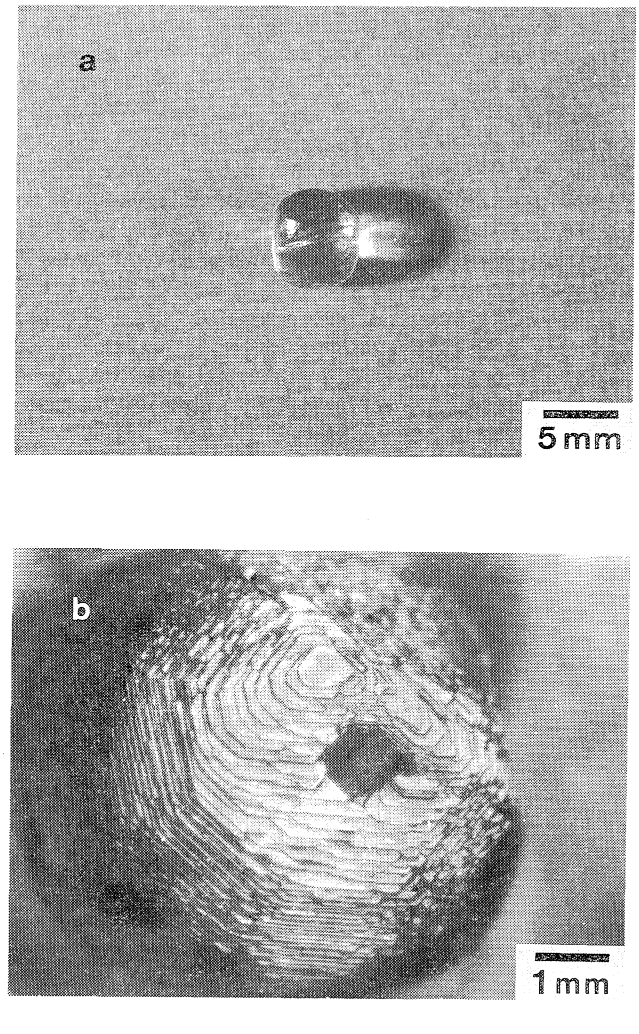

Fig. 6. (a) Spherical seed crystal. (b) Grown layer on the seed.

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