

HYDROTHERMAL GROWTH OF CALCITE SINGLE CRYSTAL IN $\text{Ca}(\text{NO}_3)_2$ AND NH_4NO_3 SOLUTIONS

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Received 25 January 1988; manuscript received in final form 3 October 1988

Two kinds of solvents, $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 solutions, were found to be very effective for growing calcite single crystals without contamination of metal ions such as Na^+ and K^+ . Spontaneously grown crystals with high transparency had a rhombohedral form bounded by $(10\bar{1}1)$ faces. NH_4NO_3 solvent gives great advantage in reducing the growth temperature below 200°C . The character of crystals grown in $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 solutions were compared with natural calcite crystals using FT-IR spectroscopy.

1. Introduction

Calcite is one of the common minerals in nature and its transparent crystals are known as Iceland spar. Recently the demand for calcite and rutile single crystals with a large birefringence has been increasing because of application for polarized devices in optical communications. Because of the depletion of the high quality natural crystals, much work concerning the artificial growth of calcite has been done using the high temperature flux method. Czochralski and travelling solvent zone melting methods produce a calcite boule from a $\text{CaCO}_3\text{--Li}_2\text{CO}_3$ melt at $700\text{--}800^\circ\text{C}$ [1–3]. However large thermal gradients and alkali carbonate flux inclusions cause serious defects and contaminations by metal ions.

Natural calcite crystals are thought to be grown hydrothermally [4]. The hydrothermal technique generally offers several advantages: suppressing the dissociation of CO_2 and producing high quality crystals in a homogeneous solution. Ikornikova firstly investigated chloride solutions, but did not mention the details of crystal growth and the quality of the grown calcite crystals [5,6]. Balascio et al. and Kinloch et al. reported that K_2CO_3 solution was an effective solvent to grow calcite crystals on a cleaved seed [7,8]. In order to protect the reaction vessel from corrosion by alkali solvents, silver was used as a liner.

The authors already revealed that alkali chlorides and the alkali nitrate solutions were also useful mineralizers the same as alkali carbonate solution [9,10]. In the present work, $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 were found as more effective solvents for calcite growth avoiding the contamination of alkali metal inclusions and allowing lower growth conditions.

2. Experimental

The solubility of calcite in the solution was determined by the weight loss method. Solvent solution and cleaved calcite grains were sealed in a gold capsule (5.0 mm OD, 4.7 mm ID and 50 mm in length). The capsule was set in a Tuttle-type cold-seal vessel [11] and then maintained at each condition for a time to achieve the equilibrium. The inner temperature of the vessel was measured beforehand with a sheathed thermocouple set inside the vessel and calibrated against a thermocouple held on the outer wall of the vessel. Following a run, the reaction vessel was quenched in cold water.

Quartz glass capsules were also used to study growth conditions, because the system was superior for observing growth phenomena.

The experimental conditions were as follows; temperature of $100\text{--}500^\circ\text{C}$, pressure of 0.1–100

MPa, concentration of 0.1m–4.5m and duration of 3–10 days. Grown single crystals were evaluated by XRD, optical microscopy and FT-IR.

3. Results and discussion

3.1. Solubility of calcite

The solubility of calcite in 1.5m $\text{Ca}(\text{NO}_3)_2$ and 3m NH_4NO_3 solutions was determined as a function of temperature at 100 MPa to elucidate the effect of solvent as shown in figs. 1 and 2. The solubility in 1.5m $\text{Ca}(\text{NO}_3)_2$ solution increased with increasing temperature and the solubility is about twice as much as that for 3m NaCl in this temperature range. The results indicate that $\text{Ca}(\text{NO}_3)_2$ is more effective than in the NaCl or KCl solutions previously reported [10]. The solubility curve of calcite in 3m NH_4NO_3 at 100 MPa (fig 2) shows that NH_4NO_3 solution is the most effective solvent even at temperatures below 200 °C. The solubility at 200 °C was 8.1 g/l. This solution, however, could not serve as a solvent at temperatures above 300 °C, due to the instability of NH_4NO_3 .

Arrhenius plots were made from the solubility measurements, as shown in figs. 3 and 4. It was

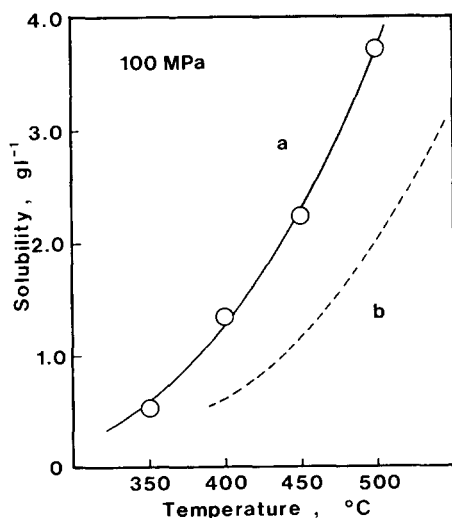


Fig. 1. Solubility of calcite in 1.5m $\text{Ca}(\text{NO}_3)_2$ and 3m NaCl solutions as a function of temperature: (a) in 1.5m $\text{Ca}(\text{NO}_3)_2$ solution; (b) in 3m NaCl solution.

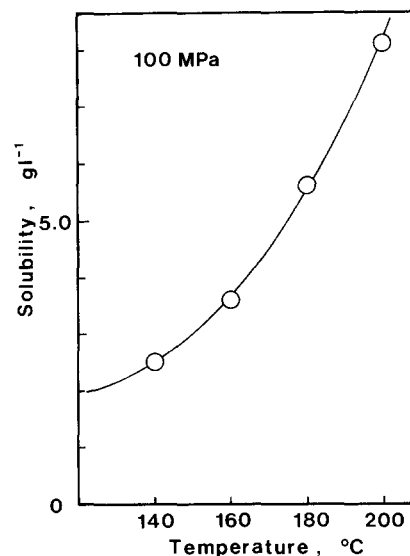


Fig. 2. Solubility of calcite in 3m NH_4NO_3 solution as a function of temperature.

clearly confirmed that the Van 't Hoff relation held in all these system. Table 1 summarizes the enthalpy of dissolution calculated from figs. 3 and 4. The enthalpy value in NH_4NO_3 , which is smaller than those in the other solutions, suggests that the chemical species dissolved in NH_4NO_3 solution had a stronger chemical bonding.

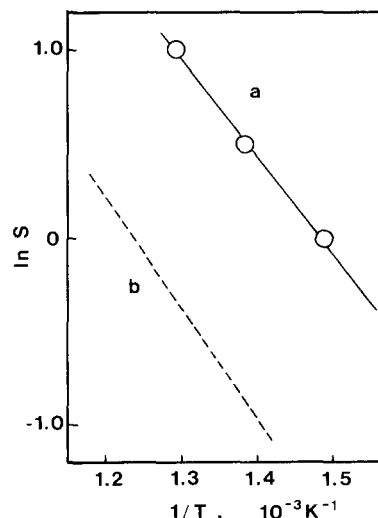


Fig. 3. Log S (solubility) of CaCO_3 as a function of $1/T$: (a) 1.5m $\text{Ca}(\text{NO}_3)_2$; (b) 3m NaCl.

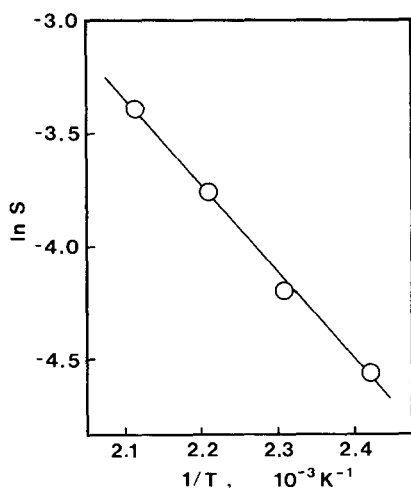


Fig. 4. Log S (solubility) of CaCO_3 as a function of $1/T$ in $3\text{m NH}_4\text{NO}_3$.

Figs. 5 and 6 show the effect of concentration of the solvent on the solubility. In the case of $\text{Ca}(\text{NO}_3)_2$ solvent, the solubility rises gradually up to 3.5m and then decreases slightly. The results suggest that a Ca^{2+} concentration above 3.5m suppressed the further dissolution of calcite. The solubility in NH_4NO_3 solvent increased with the concentration, and continued to increase in this concentration range. The results indicate that a rather dilute NH_4NO_3 solution is adequate to adjust the supersaturation for the growth of calcite crystals.

3.2. Growth of calcite single crystals

The crystal growth of calcite was carried out in either gold capsules (70 mm in length) or quartz glass (10 cm in length). Fig. 7 shows the photo-

Table 1
Enthalpy of dissolution calculated from the results of figs. 3 and 4

Solvent	Temperature range ($^{\circ}\text{C}$)	Enthalpy of dissolution (kJ/mol)
3m NaCl	350–500	46
$1.5\text{m Ca}(\text{NO}_3)_2$	350–500	43
$3\text{m NH}_4\text{NO}_3$	140–200	31

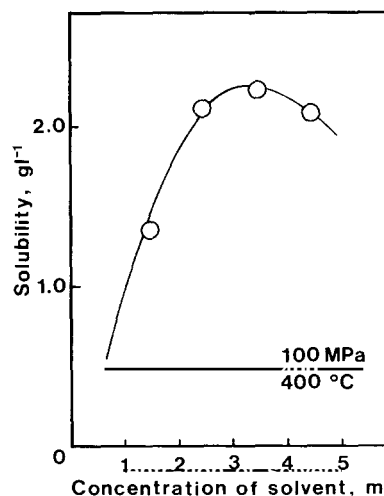


Fig. 5. Solubility of calcite as a function of concentration of $\text{Ca}(\text{NO}_3)_2$ solution at 400°C and 100 MPa .

graphs of calcite single crystals of about 0.5 mm in size grown in $1.5\text{m Ca}(\text{NO}_3)_2$ solution at 400°C , $\Delta T = 12^{\circ}\text{C}$ and 100 MPa for 10 days. Spontaneously grown crystals usually showed a rhombohedral form bounded by $(10\bar{1}1)$ faces.

Fig. 8 shows a photomicrograph of calcite crystals prepared in $3\text{m NH}_4\text{NO}_3$ at 200°C , $\Delta T = 12^{\circ}\text{C}$ and 100 MPa for 10 days. These opaque crystals were large in size, but showed a lot of growth steps on surfaces. As mentioned above, the supersaturation under this condition is too high to grow a high quality transparent calcite single

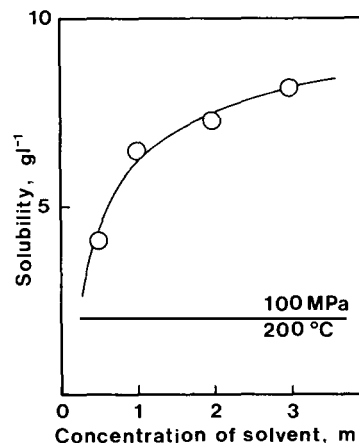


Fig. 6. Solubility of calcite as a function of concentration of NH_4NO_3 solution at 200°C and 100 MPa .

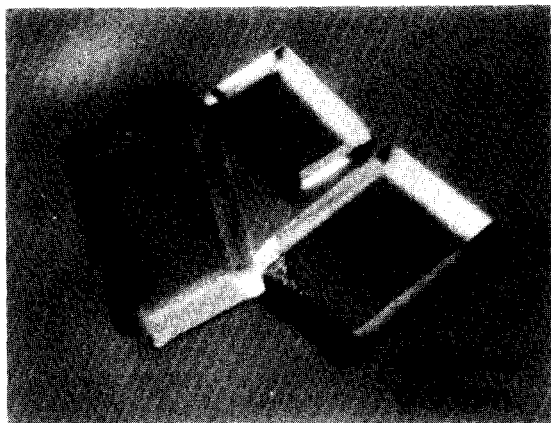


Fig. 7. Calcite single crystals grown in 1.5m $\text{Ca}(\text{NO}_3)_2$ solution at 400 °C and 100 MPa for 10 days. Marker represents 0.5 mm.

crystals, indicating that the concentration of the solvent must be lowered below 1m.

Euhedral crystals shown in fig. 9 could be actually grown in a 0.5m NH_4NO_3 solution under the same conditions. Natural calcite crystals occur in various forms, while the crystals grown in NH_4NO_3 solution below 200 °C are bounded by $(10\bar{1}1)$ faces but not by the other faces such as $\{0001\}$ in this experiment. Nutrient calcite and NH_4NO_3 solvent were also sealed in the quartz glass capsules so as to investigate the growth feature. After a run, the capsules could be directly examined by the naked eye (figs. 10a–10c). Calcite single crystals had been grown on the inner wall of the capsules even at temperatures as low as 120 °C. The pressure inside the capsule in this run was estimated to be a few MPa. These conditions were advantageous to avoid the contamination due to corrosion of the vessel and to reduce the cost of crystal growth.

3.3. FT-IR spectra of grown calcite single crystals

The FT-IR spectra of single crystals grown in $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 solutions were compared with natural calcite crystals. Fig. 11 illustrates the spectra of natural single crystals. A low quality natural calcite (a) shows the strong absorption at 2400 cm^{-1} assigned to HCO_3^- impurity. The IR spectra of single crystals grown in $\text{Ca}(\text{NO}_3)_2$ (c)

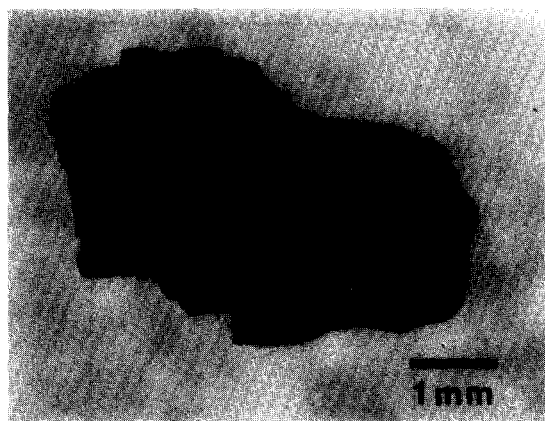


Fig. 8. Calcite single crystals grown in 3m NH_4NO_3 solution at 200 °C and 100 MPa for 10 days. Marker represents 1 mm.

and in NH_4NO_3 (d) were completely identical to those of high quality natural calcite crystals (b). The absorption due to NO_3^- also cannot be detected in these spectra. Growth runs with sealed crystals and further evaluation of optical properties are in progress in order to apply grown single crystal to optical devices.

4. Conclusion

$\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 solvents are found to be more effective solvents for calcite growth. Rhombohedral transparent calcite single crystals can be grown in $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 solvents.



Fig. 9. Calcite single crystals grown in 0.1m NH_4NO_3 solution at 200 °C and 100 MPa for 10 days. Marker represents 0.5 mm.

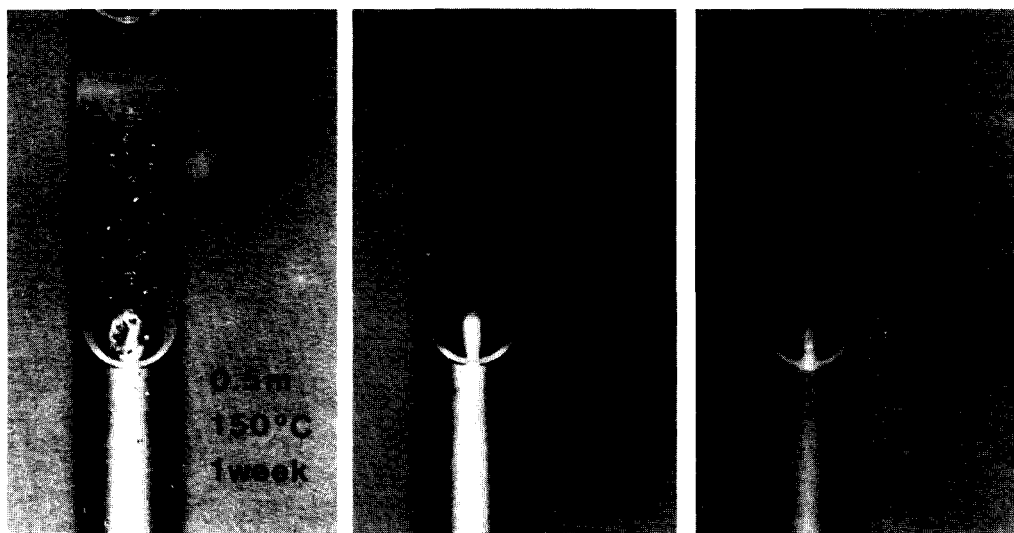


Fig. 10. Calcite single crystals grown in quartz glass capsule from NH_4NO_3 solution.

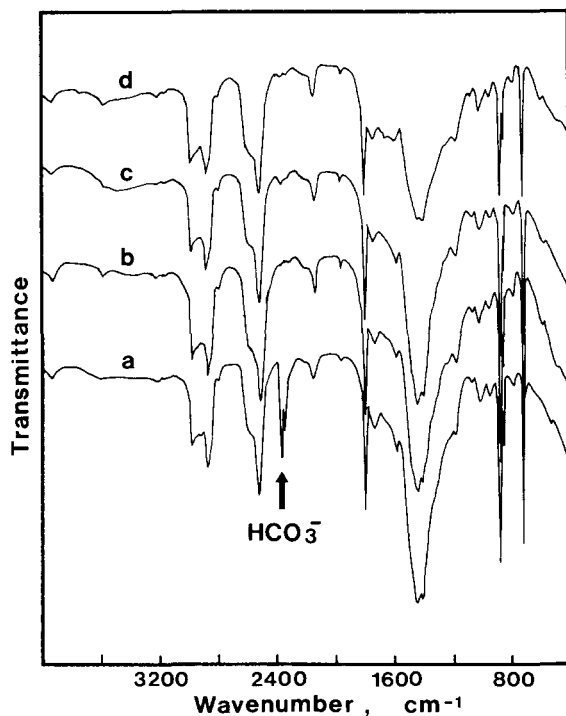


Fig. 11. FT-IR spectra of calcite single crystals: (a) natural single crystal (low quality); (b) natural single crystal (high quality); (c) artificial single crystal grown in $\text{Ca}(\text{NO}_3)_2$ solution; (d) artificial single crystal grown in NH_4NO_3 solution.

The results of this work suggest that NH_4NO_3 solvent can offer operative growth conditions to synthesize calcite single crystals at temperatures below 200°C . The application of a Teflon tube instead of a gold capsule as a container also might be possible by using NH_4NO_3 solution under such growth conditions. The FT-IR spectra of the hydrothermally grown crystals were quite identical to those of high quality natural calcite crystals. HCO_3^- and NO_3^- ions in the crystals cannot be detected as impurities. The development of NH_4NO_3 as a new solvent could give great advantage in lowering the growth conditions.

Acknowledgement

This work was partly supported by the Asahi Glass Foundation for Industrial Technology.

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