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HYDROTHERMAL CRYSTAL GROWTH OF CALCITE IN NaCl AND KCl SOLUTIONS

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Hydrothermal growth of calcite single crystal was studied by using NaCl and KCl solutions which have been considered to be naturally existing as the saline mineralizer. Both of NaCl and KCl solutions were found to be the effective mineralizer for the growth of calcite crystal of optical grade. Optically clear single crystals of calcite could be grown from each chloride solution.

Calcite ($CaCO_3$) has been used as an optical material in microscopes and has been recently watched with keen interest for the application to laser devices. The high quality single crystal of calcite for optical use, however, has been parched in nature. So, it becomes urgent to grow the optical grade of calcite single crystals.

Many artificial methods were attempted to grow the single crystal of calcite.[1,2] The decomposition of calcite at high temperature makes it difficult to grow the high quality crystals. The hydrothermal growth method is one of the attractive techniques to suppress the dissociation of CO_2 and to lower the strain induced by the thermal stress if the inclusion of the solution is avoided.

In the system of hydrothermal synthesis, the rule to select the solvent has not been defined. In the first place, it is necessary to examine whether single crystals can be grown without any formation of second phase or compound. Some solutions containing Na^+ or K^+ were employed as the solvent to elucidate the effect of the mineralizer. All runs were carried out in a sealed gold capsule (5 mm O.D, 70 mm in length) set in a cone-in-cone type of the hydrothermal

reaction vessel.

The crystallized product at 500 °C under 100 MPa with 3 mol kg^{-1} Na_2CO_3 solution was not calcite but unknown compound. Its XRD datum does not agree with those of pirssonite and gaylussite, which were confirmed by Balascio et al.[3]

The second item to be considered is the morphology and perfection of the crystals grown under the hydrothermal condition. In contrast to Na_2CO_3 solution, the experimental run in NaOH or KOH hydrothermal solution did not give any other phase except calcite. The grown crystals, however, showed dendritic form (Fig. 1), which were not acceptable for the optical application.

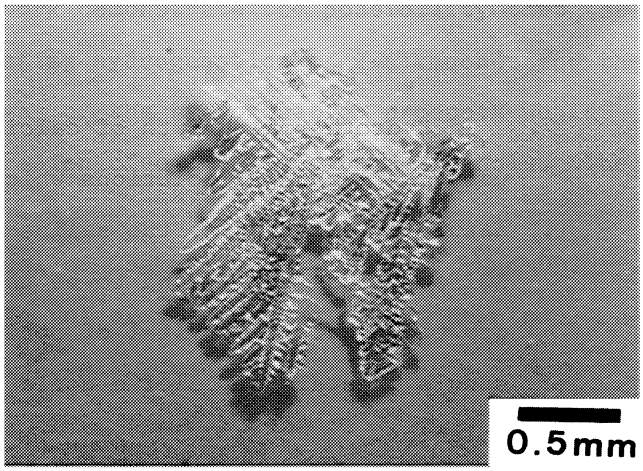


Fig. 1. Photomicrograph of calcite crystal grown from 2 mol kg^{-1} NaOH sol.

As stated above, it turns out from these data that the attention has to be paid for anion species as well as the cation species. The kinds of ions in solvent are the strong influencing factors for the stable phase formation, growth rate and the morphology of the grown crystal.

NaCl and KCl aqueous solutions have been well known as the main component of the naturally existing mineralizer. The NaCl solution must play an important role for the growth of natural calcite single crystals as well known natural saline mineralizer.[4]

The solubility dependence of $CaCO_3$ on the concentration of some hydrothermal chloride solutions were reported by N.Yu. Ikornikova.[5] He reported that the solubility in NaCl solution is much smaller than those in other chloride solutions such as $CaCl_2$ and LiCl.

Ikornikova tried to grow calcite crystals with seed, but did not report the experimental details and results.[6] In the present work, we focused on the elucidation of the NaCl solution as the mineralizer for the growth of calcite single crystal. KCl solution was also employed as the hydrothermal solution for the growth of calcite crystals and evaluation of the calcite stability in the solution.

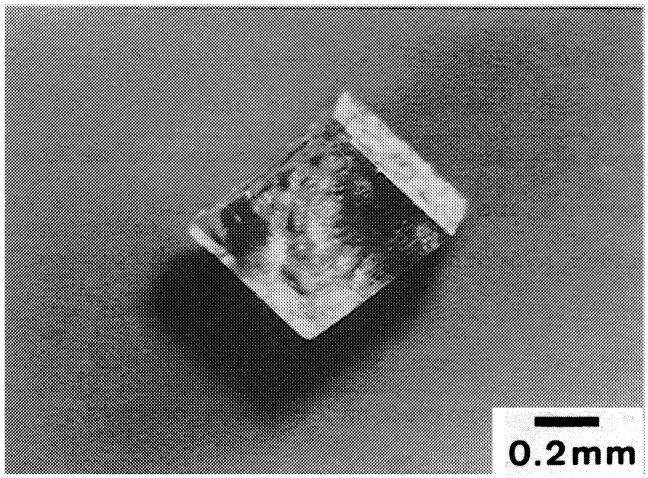
A preliminary growth run was begun with saturated NaCl solution (6.1 mol

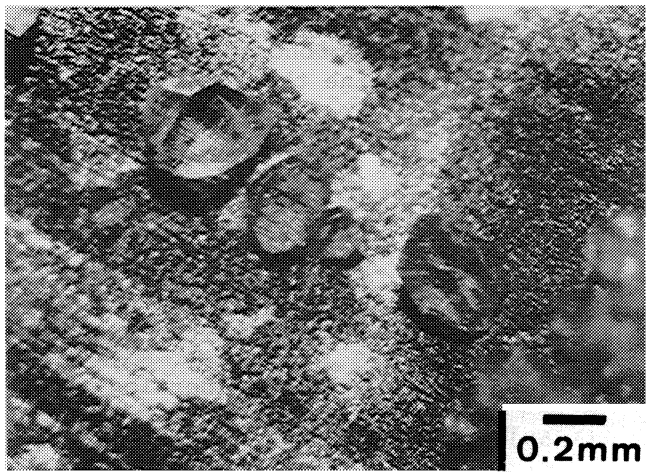
kg^{-1}) at 470 °C (nutrient temperature) under 75 MPa for 7 days.

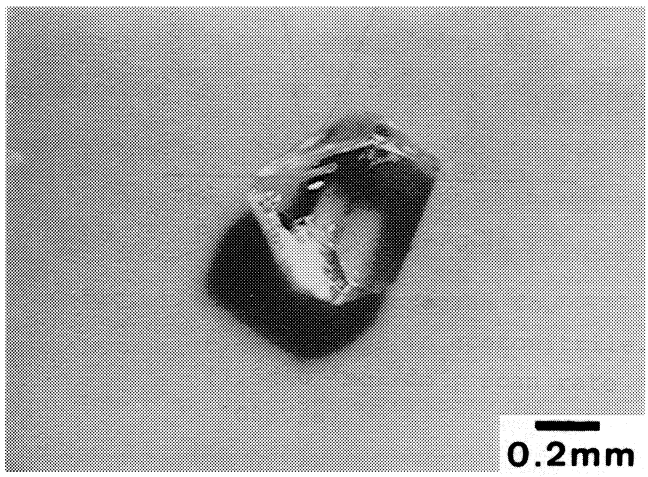
The single crystals of the size 1 mm could be grown spontaneously on the wall of the gold capsule. The grown single crystals were bounded by typical $\{10\bar{1}1\}$ rhombohedral faces, which is the characteristic morphology of calcite as shown in Fig. 2. The X-ray diffraction analysis also confirmed that these crystals were only calcite. In order to grow more perfect single crystal of calcite without any inclusion, the concentration of NaCl solution had to be lowered to 3 mol kg^{-1}. With 3 mol kg^{-1} NaCl solution, many optically clear calcite single crystal grew at the inner top of the gold capsule at 450 °C under 50 MPa for 7 days. (Fig. 3).

The growth experiment with saturated KCl solution (4.5 mol kg^{-1}) at 470 °C and 75 MPa also could give polyhedral single crystals as shown in Fig. 4. The difference of growth rate on crystallographic plane gave some suggestions when a seed crystal is cut to orient to suitable facet. $\{10\bar{1}1\}$ cleavage crystal is easy to prepare but growth rate on the plane was obviously slow.

In this work, it turned out







both NaCl and KCl solutions were employable for hydrothermal synthesis of calcite single crystals. The fact that calcite could be grown in these chloride solutions may support the occurrence of natural single crystal such as Iceland spar.[4] It is important to determine the solubility of calcite as a function of temperature in order to investigate the behavior of chemical species exsisting under hydrothermal condition and to grow large single crystals. The solubility of calcite was measured in the 3 mol kg^{-1} NaCl solution under 100 MPa. The result indicates an obvious increase in its solubility above 400 °C, and the amount of calcite dissolved under these conditions rises up to 2 g/l at 500 °C, The value of solubility at 500 °C is enough to grow calcite single crystal at the significant growth rate in the industrial scale. On the basis of Arrhenius relationship, we calcutated ΔH to be about 46 kJ/mol. Because KCl solution was found to be one of the useful hydrothermal solvents, further detailed research is also in progress to determine the solubility at various temperature.

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