[EJ] Evening Poster | M (Multidisciplinary and Interdisciplinary) | M-IS Intersection

[M-IS07]Interface- and nano-phenomena on crystal growth and dissolution

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Recent developments of observations in nano-scale opened a detail discussion concerning mechanisms of crystal growth and dissolution based on interface phenomena including dynamics. In this session, growth and dissolution mechanisms of crystals will be discussed focusing on interface phenomena of minerals in the fields of biological origin, global environment, planets and space in addition to general minerals.

[MIS07-P03]Crystal Growth of Norsethite $BaMg(CO_3)_2$ from aqueous solution

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Norsethite $BaMg(CO_3)_2$ has the space group of R32 (space group of dolomite $CaMg(CO_3)_2$:R3-), and shows strong asymmetry. Hence, norsethite exhibits the high birefringence (norsethite: 0.175;quartz: 0.009), and we expect that norsethite can be utilized as piezoelectric crystals. Furthermore, although the convenient piezoelectric crystals such as $BaTiO_3$ and $Pb(Zr,Ti)O_3$ are prepared by sintering and/or melt growth, the norsethite crystals can be synthesized by aqueous solution growth. In addition, it is well-known that carbonates become relatively easily up to ca. 1mm by hydrothermal treatment.[1)] Hence, the utilization of norsethite as parts of piezoelectric devices is also promising from the viewpoint of the growth.

Hood *et al.*, for the first time, has reported the artificial synthesis of norsethite in 1973.[2)] Recently, Pina reported that norsethite appears through the below two chemical reactions:[3)]

Amorphous phase(Mg,Ba,Cl,Na,C,O)=$Na_3Mg(CO_3)_2Cl+BaCO_3$

$Na_3Mg(CO_3)_2Cl+BaCO_3=BaMg(CO_3)_2$ $3Na^+ + Cl^- + CO_3^{2-}$

Like this way, the formation of norsethite is complicated. Hence, to control the growth of norsethite, understanding of the physical factor, which governs norsethite crystallization, is essential. In this study, we directly observed the precipitations obtained from $BaCl_2$-$MgCl_2$-$NaHCO_3$ mixture solutions by optical microscopy and powder X-ray diffraction, and examined the crystallization of norsethite from aqueous solution.

0.3M $BaCl_2$•$2H_2O$, 0.3M $MgCl_2$•$6H_2O$, and 0.125M $NaHCO_3$ were dissolved to pure water (200 mL) heated at 50-90 ^oC, and the mixture solution was stirred and heated for 3 weeks. The temporal course of the precipitation was observed by optical microscopy and powder X-ray diffraction.

First, the temporal course of the precipitations obtained at 60 ^oC was observed. Just after we added the chemical regents to the pure water, $BaCO_3$ crystals with a needle shape (witherite) sedimented. In contrast, norsethite with a rhombohedral shape was obtained in 216 h. To quantify the crystallization of norsethite, we measured the longitudinal of witherite L and (104)-face diffraction intensity of norsethite I_{104}. Witherite enlarged until 48 h. However, more than 48 h, L started to become small, and witherite gradually was dissolving. In contrast, the I_{104} increased over 200 h. These results demonstrate that norsethite is formed not by solid-solid transition, but by solution-mediated transition. At the other temperatures, norsethite also appears by solution-mediated transition. By extrapolate line of I_{104}, we also revealed the induction period of norsethite obtained at 60 °C was 182 h. In this presentation, we are going to report the solution growth of norsethite at various temperature, regarding the rate-determining process.

(1) Shin-ichi Hirano and Ko-ichi Kikuta, *J. Cryst. Growth*, 351-356, 1989.
(2) Hood et al., *Am. Mineral*, 471-474, 1974.
(3) C.M.Pina and C.Pimentel, *Dolomite*, 115-139, 2017.