

Thermodynamic stability of norsethite $\text{BaMg}(\text{CO}_3)_2$ under hydrothermal conditions

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Norsesite $\text{BaMg}(\text{CO}_3)_2$ has piezoelectric properties, and shows a birefringence (0.175) higher than conventional piezoelectric crystals. Hence, it is expected that norsethite is a new-generation material of an acousto-optic device or wavelength conversion element. To reveal the characteristics of the norsethite, it is necessary to grow a crystal of several mm. Under atmospheric pressure, the solubility of norsethite is extremely low, and the growth rate is quite slow (several nm/min). Therefore, the hydrothermal synthesis method is useful as well as the conventional carbonate growth. However, since the hydrothermal synthesis needs a pressure- and heat-resistant container, the crystallization process under hydrothermal conditions is invisible. Recently, we have succeeded in fabricating the chamber that allows the in-situ observation under hydrothermal conditions. As a result, we, for the first time, succeeded in in-situ observing the solution-mediated transition of norsethite under hydrothermal conditions. In this study, we investigated the thermodynamic stability of norsethite under hydrothermal conditions by measuring the solubility to quantitatively understand the solution-mediated transition mechanism of norsethite under hydrothermal conditions.

Pure water at room temperature was circulated by a pump into the in-situ observation chamber under hydrothermal condition containing powdered norsethite for several hours. The pH of the solutions returned to atmospheric pressure from the chamber was measured at 3MPa and individual temperature T . The dissolution equilibrium was confirmed from the change in pH. Ba^{2+} , Mg^{2+} , and CO_3^{2-} concentrations in saturated solutions of norsethite were measured by ICP (Inductively coupled plasma) atomic emission spectrometry and total organic carbon measurement.

Fig.1 shows the temperature dependence of the solubility product K of norsethite under hydrothermal conditions and atmospheric pressure. The curves correspond to the result fitted by the revised van't Hoff equation. At 3 MPa, the solubility product of norsethite increased from room temperature to around 40°C, and then decreased with increasing temperature as well as atmospheric pressure². In contrast, the solubility product of norsethite under hydrothermal conditions was ca. 5 units lower than that under atmospheric pressure.

To further understand the thermodynamic stability of norsethite, the dissolution enthalpy dH and the dissolution entropy dS under hydrothermal conditions and atmospheric pressure were determined from the fitting parameters. The dissolution enthalpies $dH_{298.15}$ of norsethite and barium carbonate at 30°C were 78.45 (kJ/mol) and -57.61 (J/mol/K), respectively, and these dissolution entropies $dS_{298.15}$ were 19.88 (kJ/mol) and -126.8 (J/mol/K), respectively. Also, the dissolution enthalpies $dH_{363.15}$ of norsethite and barium carbonate at 90°C were -125.5 (kJ/mol) and -763.5 (J/mol/K), respectively, and dissolution entropies $dS_{363.15}$ were -221.2 (kJ/mol) and -856.3 (J/mol/K), respectively. The dissolution enthalpy and dissolution entropy of norsethite and barium carbonate under hydrothermal conditions decreased with increasing temperature. Using these results, we calculated the difference of the chemical potential between norsethite and barium carbonate. As a result, we revealed that norsethite relatively easily crystallizes under hydrothermal conditions.

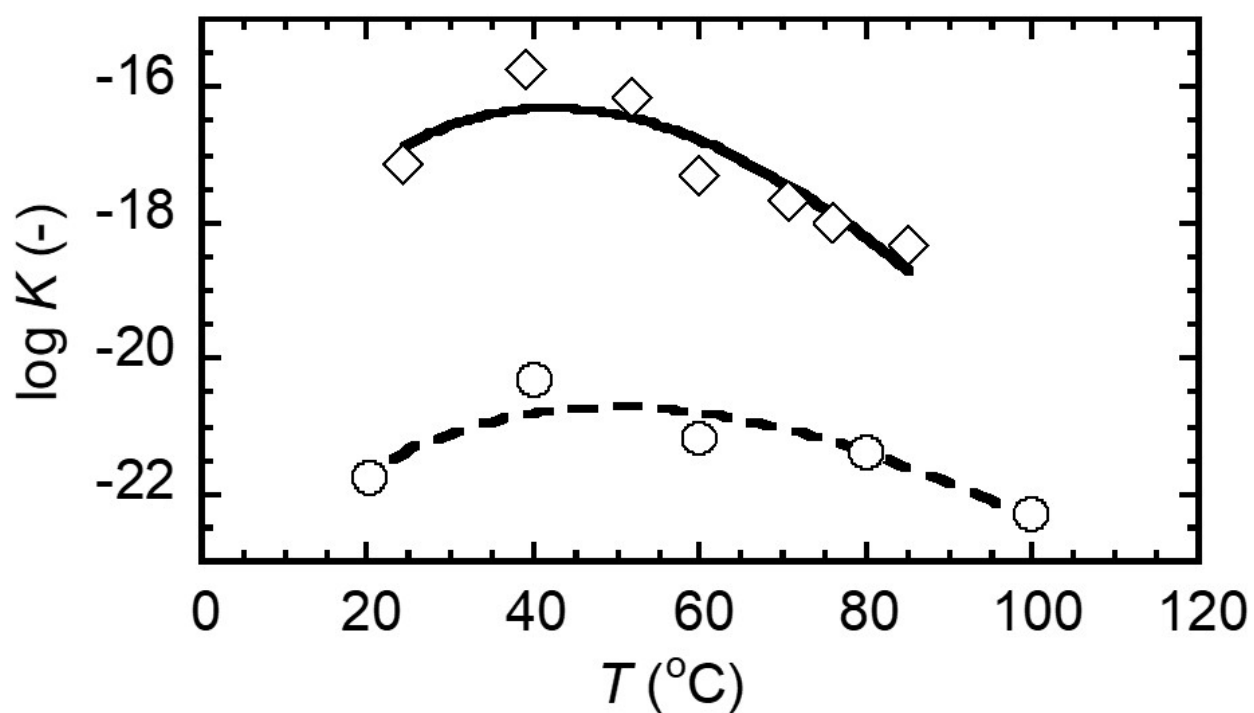


Fig.1 The temperature dependence of the solubility product K of norsethite under hydrothermal conditions (: \circ) and atmospheric pressure (: \diamond)