

Hydrothermal synthesis of aluminum substituted tobermorite by using various crystal phases of alumina

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Slurries of quartz and slaked lime containing various crystal phases of alumina were hydrothermally reacted to synthesize aluminum-substituted tobermorite. X-ray diffraction results confirmed the formation of aluminum-substituted tobermorite during the reaction. The aluminum species were substituted at the Q² or Q³ sites in tobermorite. The amount of aluminum substituted in the tobermorite depended on the reactivity of alumina. The tobermorite formed showed fiber- and plate-like morphologies. The reactivity of the alumina used as an additive influenced the substitution site and the amount of aluminum substituted into the tobermorite structure, resulting in controlling its morphology.

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1. Introduction

Tobermorite [$\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2) \cdot 4\text{H}_2\text{O}$] is a type of crystalline calcium silicate hydrate and it has a high potential for application in cation exchange and hazardous wastewater treatment.^{1),2)} Tobermorite comprises calcium and silicon layers and a so-called interlayer.^{3),4)} The calcium layer comprises sevenfold-coordinated calcium polyhedra, running parallel to the (001) plane; the silicate layer is formed of double chains called Dreierdoppelketten, that run parallel to the *b* axis. The interlayer region contains exchangeable cations and water molecules. Controlling the morphology of tobermorite is expected to improve its properties, such as the cation exchange ability, because the increase in the specific surface area and the exposure of the crystal plane contributes to its properties. Aluminum-substituted tobermorite synthesized using aluminum hydroxide with a 2 mol % replacement of silicate with aluminum exhibited lath-like crystallites larger than pure tobermorite without any substitution.⁵⁾ On the other hand, it has been reported that the Al/(Al + Si) ratio of aluminum-substituted tobermorite increased with decreasing crystallite size.⁶⁾ This suggests that the presence of aluminum during the reaction has an influence on the morphology of tobermorite.

It has also been reported that tobermorite is formed via a hydrothermal reaction in a $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system.^{7),8)} The hydrothermal reaction is influenced by the solubility of the materials formed because of the dissolution and deposition reactions. The presence of aluminum was suggested to decrease the solubility of silica in the CaO-SiO_2 system.⁹⁾ Alumina was used as an additive because of its almost constant solubility in the acid-to-alkaline region. Introducing additives such as various crystal phases of alumina (α - and γ -alumina) allowed us to control the supersaturation of tobermorite during the hydrothermal reaction, thereby permitting the control of the aluminum substitution in the structure of tobermorite. In the present work, mixtures of quartz, slaked lime and α - and γ -alumina were

hydrothermally reacted to clarify the influence of different additives on the morphology of tobermorite.

2. Experimental procedure

Quartz (specific surface area: 1 m²/g; Nitto Sangyo Co. Ltd.), slaked lime (specific surface area: 10 m²/g) and α -type alumina (specific surface area: 5 m²/g; Wako Pure Chemical Industries Ltd.) or γ -type alumina (specific surface area: 220 m²/g; Taimei Chemicals Co. Ltd.) were used as starting materials. Lime was prepared by calcinating calcium carbonate (Wako Pure Chemical Industries Ltd.) at 1000°C for 3 h. Slaked lime was obtained by adding distilled water to the previously prepared lime. The materials were mixed, and the mixture was then added to distilled water. The Ca/(Al + Si) molar ratio was 0.83. For the preparation of Al-substituted tobermorite, alumina was used to replace 5 mol % of SiO₂. The slurry was hydrothermally reacted at 180°C for 48 h. The hydrothermal reaction was performed with a water/solid ratio of 10. The hydrothermally reacted deposits prepared using α - and γ -alumina are referred to as samples A and B, respectively. Tobermorite synthesized without alumina was used as a control material for comparison with samples synthesized with alumina (sample C).

The crystalline phases in the samples were identified by X-ray diffraction (XRD) analysis. The morphology of the samples was observed by scanning electron microscopy (SEM). All samples were preheated at 80°C in vacuum to remove the physisorbed water. The structure of the samples was examined by Fourier transform infrared spectroscopy (FT-IR) employing the KBr method. The specimens for FT-IR were prepared by mixing 1 mg of the samples in 300 mg of KBr.

3. Results and discussion

Figure 1 shows the XRD patterns of samples A, B and C. Peaks corresponding to tobermorite can be distinctly seen in each XRD pattern. The tobermorite content was determined by the quantitative XRD technique. Silicon was used as an internal standard. Samples A and B retarded the development of tobermorite crystallinity, a fact reflected by the basal spacing, which corresponded to the (002) planes around 7°. The peak

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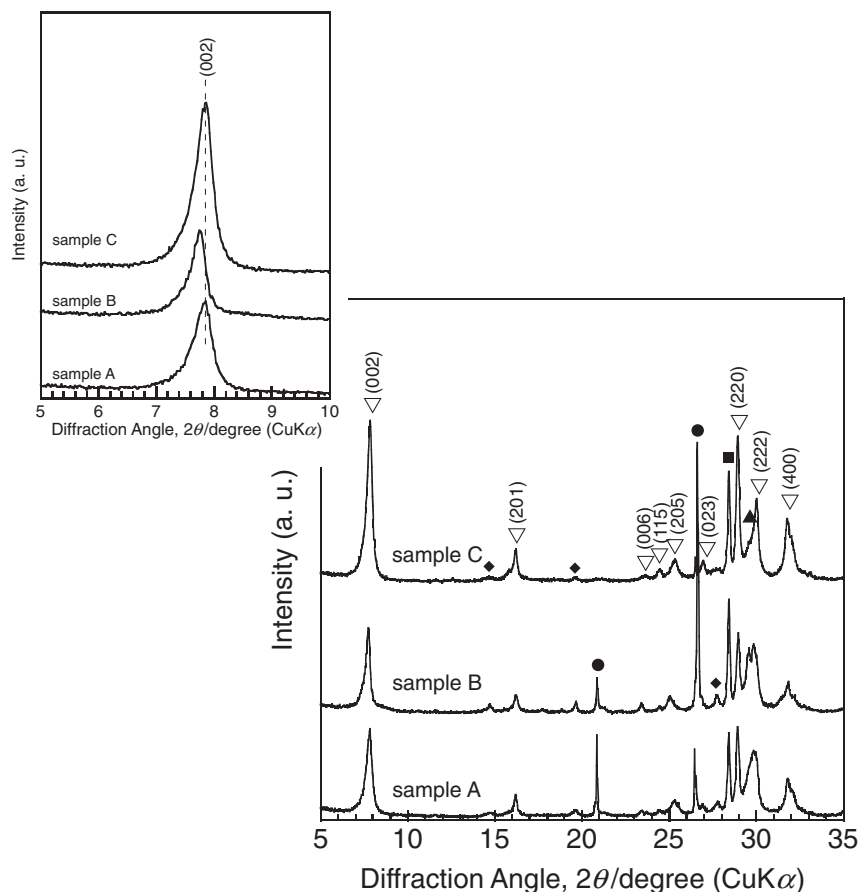


Fig. 1. XRD patterns of samples A, B and C. (▽) tobermorite (ICDD card No. 45-1475), (●) quartz, (▲) calcite and (■) silicon as an internal standard material. ◆ represents unknown peaks.

integral ratio $I_{\text{tobermorite}(002)}/I_{\text{silicon}(111)}$ of sample A was greater than that of sample B for the experimental condition. The suppression of the amount of tobermorite formation originated from the reactivity of alumina. Moreover, the peak corresponding to the (002) planes in the XRD pattern of sample B shifted to an angle lower than that of samples A and C. In a previous study, researchers reported that aluminum was incorporated into the bridging tetrahedral sites (Q^3 sites) of the tobermorite structure.⁹⁾ It is well known that aluminum is larger in size than silicon. Therefore, the aluminum substitution in the tobermorite leads to the enlargement of the basal spacing between the silicate layers along the c axis. Sample B is suggested to be substituted by aluminum into the Q^3 sites of the tobermorite structure.

Figure 2 shows the FT-IR spectra of samples A, B and C. Owing to the stretching, bending and deformation vibration modes of SiO_4 tetrahedra, in all three spectra, adsorption bands were observed at 400–600 and 900–1100 cm^{-1} . The absorption bands at 1400–1500 cm^{-1} are attributed to a carbonate ion, and those at 1630 cm^{-1} are attributed to the interlayer molecular water in each spectrum. In the spectra of samples A and B, the absorption bands at 903 cm^{-1} , which were caused by the Si–O stretching of the Q^2 sites in tobermorite,¹⁰⁾ shifted toward a wavenumber lower than that of sample C. Moreover, the absorption band in the spectrum of sample B showed a shift toward a wavenumber lower (approximately 1210 cm^{-1}) than that of samples A and C; this band was caused by the Si–O stretching of vibrations in the Q^3 sites in tobermorite.¹⁰⁾ These results imply that the different reactivity of alumina controlled the substitution sites of aluminum in tobermorite.

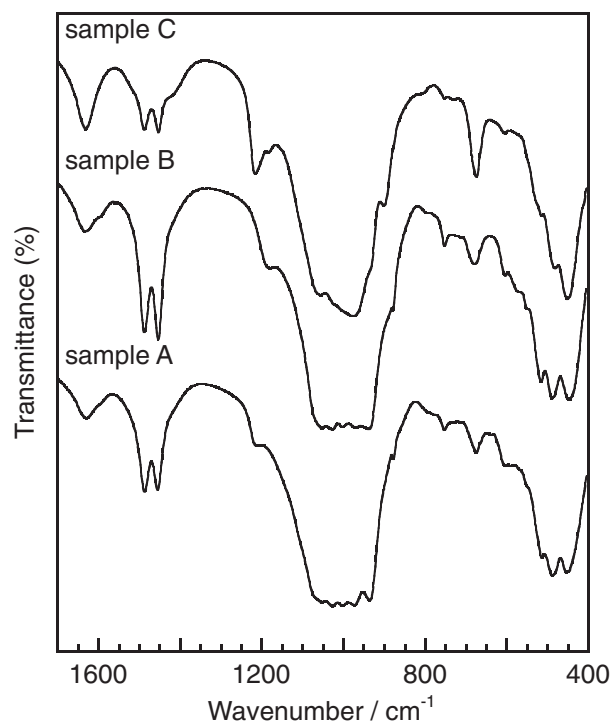


Fig. 2. FT-IR spectra of samples A, B and C.

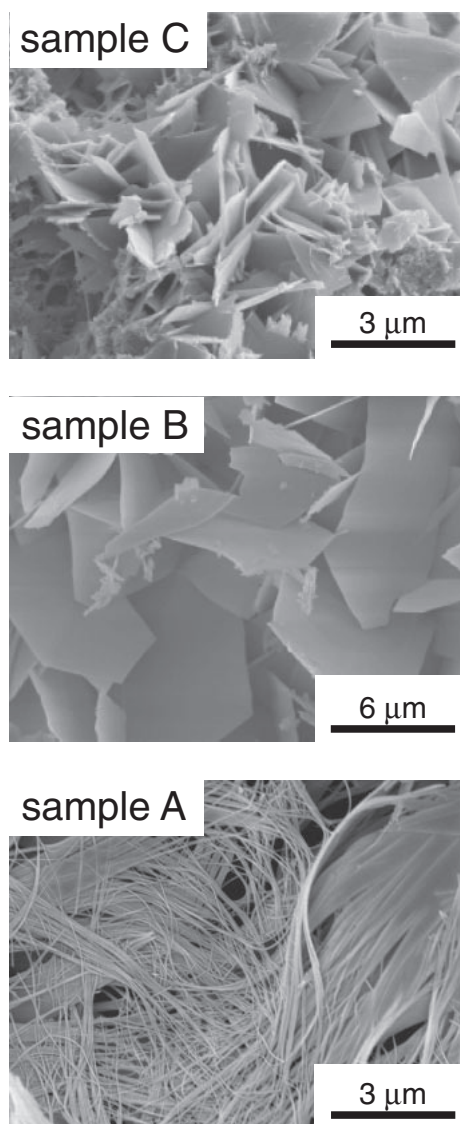


Fig. 3. SEM micrographs of samples A, B and C.

Figure 3 shows the SEM micrographs of samples A, B and C. Fiber-like deposits of a diameter of 100 nm can be observed in the SEM micrograph of sample A. The SEM micrograph of sample B shows platy deposits, which is a crystal habit of tobermorite, with a size of approximately 5 μm . Sample C shows a platy morphology; the crystals of sample C are smaller than those of sample B. The specific surface areas of samples A, B and C were measured to be 59, 46 and 50 m^2/g , respectively, by nitrogen gas sorption analysis. The amount of aluminum in samples A and B were estimated as 0.9 and 4.4 atom %, respectively, by an energy dispersive spectrometer. During a hydrothermal reaction, γ -alumina is expected to exhibit solubility higher than α -alumina because of its high specific surface

area and reactivity. It is proposed that a large amount of aluminum species exists in the reactant undergoing the hydrothermal reaction, leading to an increase in the substitution of aluminum in tobermorite.

A large amount of the aluminum substitution at the Q^2 and Q^3 sites in the tobermorite synthesized using γ -alumina led to the presence of excessive Si species dissolved from quartz in the reactant, resulting in the growth in the size because of the polymerization of the Si species. On the other hand, aluminum-substituted tobermorite synthesized using α -alumina substituted a trace amount of aluminum at the Q^2 sites only. Researchers have reported that the addition of Fe^{3+} ions during the synthesis of tobermorite formed fiber-like morphology by growth parallel to the b axis because of an increase in the silicate chain polymerization and an increase in the chain cross-linkage in tobermorite.¹¹⁾ The Q^2 sites of the aluminum substitution in tobermorite may act as a driving force to increase the silicate double chain polymerization running parallel to the b axis. As a result, the aluminum-substituted tobermorite synthesized using α -alumina exhibited fiber-like crystallites. The amount and sites of the aluminum substitution, which are influenced by the various crystal phases of alumina, in tobermorite played an important role in controlling the morphology of tobermorite.

4. Conclusion

Aluminum-substituted tobermorite was synthesized via a hydrothermal reaction by using quartz, slaked lime and α - and γ -alumina. The tobermorite synthesized using α - and γ -alumina showed fiber- and plate-like morphologies, respectively. The reactivity of alumina used as an additive influenced the amount and sites of the aluminum substitution in tobermorite. The amount and sites of the substituted aluminum in the tobermorite caused a change in the morphology of the tobermorite.

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