
Hydrothermal Synthesis of GTS-type Sodium Titanosilicate and its Sm³⁺ Ion Exchange

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Abstract

Grace titanosilicates (GTS), represented by pharmacosiderite, have three dimensional tunnel-type structures. Na-GTS (Na₄Ti₄Si₃O₁₆·6H₂O) crystallizes as a rhombohedral phase (space group ; $a = 7.812 \text{ \AA}$, $\alpha = 88.79^\circ$) close to cubic system. In this structure, four TiO₆ octahedra linked by edge-sharing form a Ti₄O₁₆ cubic cluster; the clusters are linked through SiO₄ tetrahedra to form a three-dimensional framework with an interconnected pore system of 8-ring channels, occupied by the alkali-metal ions and adsorbed water molecules. The radioactive waste water continues to accumulate at the crippled Fukushima Daiichi Nuclear Power Plant. It is important to investigate the Sm³⁺ ion exchange properties of Na-GTS for the application of GTS to the removal of Sm radioisotopes from the radioactive waste water. In the present study, Sm³⁺-exchanged form [Na₄(1- x)Sm_{4 x /3}(Ti₄Si₃O₁₆) · n H₂O] of Na-GTS prepared hydrothermally are investigated by powder XRD to examine the occupied positions of Sm³⁺.

The starting materials for the hydrothermal synthesis were NaOH, amorphous SiO₂ fine powder and TiCl₄ aqueous solutions. For the synthesis of Na-GTS, the starting mixtures with the molar ratios of TiO₂/SiO₂ = 0.32 and Na₂O/TiO₂ = 5.62 were hydrothermally treated at 100 °C (0.23 MPa) according to the reported procedure. The Sm³⁺-exchanged forms were obtained by shaking of the synthesized Na-GTS (0.5 g) in the aqueous solution of SmCl₃ (25 mL) at 25 °C for 6 hours. The concentration of Sm³⁺ in the aqueous solution was varied in the range from 0.01 to 0.5 M. The obtained samples were filtrated, washed and dried at 80 °C, after which they were examined by powder XRD. The Sm concentrations in the supernatant solutions were analyzed with atomic absorption spectrometry to evaluate the ion-exchange amounts.

The sample with the composition $x = 0.95$ was obtained after the treatments of Na-GTS in 0.5 M SmCl₃ aqueous solutions. The increase in concentration of the SmCl₃ aqueous solution increases the exchange amount. The comparison of the observed and simulated XRD patterns suggests that Sm³⁺ ions are almost equally distributed on both 4 e and 6 g sites in the cavities of GTS framework.

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