Hydrothermal synthesis and Er$^{3+}$ ion exchange of sodium GTS-type titanosilicate

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Abstract. Powder samples of Na-GTS have been prepared using a hydrothermal method. Er$^{3+}$-exchanged Na-GTS [Na$_{4(-x)}$Er$_{(4/3)x}$Ti$_4$Si$_3$O$_{16}$·nH$_2$O] with the compositions in the range of 0.28 ≤ x ≤ 0.64 was obtained by shaking the single-phase sample of Na-GTS in the ErCl$_3$ aqueous solutions (25 mL, 0.01~0.1 M) at 25 °C for 6 hours. The chemical analyses by atomic absorption spectrometry (AAS) show that the maximum allowance of Er$^{3+}$ incorporated into Na-GTS is x = 0.64. TG-DTA measurements show that the incorporation of Er$^{3+}$ slightly decreases the water contents and the dehydration temperatures. The powder X-ray diffraction (XRD) patterns indicate that the diffraction-peak intensities vary systematically with increasing the Er$^{3+}$ composition (x). The simulation of XRD patterns suggests the cation-distribution model that Er$^{3+}$ and Na$^+$ ions preferentially occupy the 4e and 6g sites, respectively.

1. Introduction

Grace titanosilicates (GTS), represented by pharmacosiderite, have three dimensional tunnel-type structures. Na-GTS (Na$_4$Ti$_4$Si$_3$O$_{16}$·6H$_2$O) crystallizes as a rhombohedral phase (space group R3m; a = 7.812 Å, α = 88.79° [1]) close to cubic system. Other forms such as K-GTS (K$_3$HTi$_4$Si$_3$O$_{16}$·4H$_2$O) show the cubic P4/m symmetry (a ≈ 7.8 Å). In GTS-type structures (Fig. 1), four TiO$_6$ octahedra linked by edge-sharing form a Ti$_4$O$_4$ cubic cluster; the clusters are linked through SiO$_4$ 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 ion-exchange properties of GTS for Cs$^+$ or divalent cations (Co$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, etc.) have been investigated for the application to the radioactive waste treatments [2–4]. However, the ion-exchange properties of GTS for trivalent cations have not yet been reported, although the optical and catalytic properties of trivalent-cation-exchanged forms are interesting. In the present study, Er$^{3+}$-exchanged forms of Na-GTS are investigated by TG-DTA and powder XRD to examine the dehydration behavior and the occupied positions of Er$^{3+}$.

2. Experimental

2.1. Sample preparation

Sodium GTS-type titanosilicates (Na-GTS: Na$_4$Ti$_4$Si$_3$O$_{16}$·6H$_2$O) were prepared by a hydrothermal method according to the procedure reported by the previous studies [5, 6]. The starting materials were NaOH, amorphous SiO$_2$ fine powder, TiCl$_4$ aqueous solution and HCl. The mixture with the compositional ratios of TiO$_2$/SiO$_2$ = 0.32 and Na$_2$O/TiO$_2$ = 5.62 was heat-treated at 100 °C for 24 hours in a closed pressure-resistant vessel. The obtained sample was filtered with distilled water and dried at 40 °C for 48 hours to gain a single phase of Na-GTS. The Er$^{3+}$-exchanged forms were...
obtained by shaking 0.5 g of Na-GTS in the ErCl$_3$ aqueous solutions (25 mL) at 25 °C for 24 hours. The concentrations of Er$^{3+}$ ($C_{Er}$) in the aqueous solutions were varied between 0.01 and 0.1 M, where the 25 mL of 0.036 M ErCl$_3$ aqueous solution is necessary for complete exchange of Na$^+$ in Na-GTS for Er$^{3+}$. The obtained samples were filtrated, washed and dried at 80 °C.

2.2. Characterization

The Er$^{3+}$ concentration in the supernatant solutions was analyzed with atomic absorption spectrometry (AAS) to evaluate the ion-exchange amount [x in Na$_4$(1/3$\times$Er$^{3+}$)$_{4/3}$Ti$_4$Si$_3$O$_{16}$·$n$H$_2$O]. The phase identification was performed using a Rigaku RINT2200 powder X-ray diffractometer. The dehydration process was examined by TG-DTA. The heating rate of 10 °C/min and the cooling rate of 20 °C/min were applied in the TG-DTA measurements.

3. Results and discussion

3.1. Ion-exchange amounts for Er$^{3+}$

Figure 2 shows the variation of the Er$^{3+}$ composition (x) in the Er$^{3+}$-exchanged Na-GTS [Na$_4$(1/3$\times$Er$^{3+}$)$_{4/3}$Ti$_4$Si$_3$O$_{16}$·$n$H$_2$O] as a function of the concentration of ErCl$_3$ aqueous solution ($C_{Er}$), where the x values were evaluated from AAS for Na$^+$ in the filtrate after the ion-exchange experiments. The figure shows that the Er$^{3+}$ composition (x) increases monotonously with increasing $C_{Er}$ up to 0.05 M and then is kept constant in $C_{Er}$ ≥ 0.05 M. Thus, the x value of 0.64 obtained in $C_{Er}$ ≥ 0.05 M is the maximum allowance of the Er$^{3+}$ exchange.

3.2. TG-DTA

Figures 3a and 3b show TG and DTA curves of the Er$^{3+}$-exchanged samples, respectively. The TG curves show that the weights of the samples decrease steeply up to about 280 °C and then their weight losses are completed by 800 °C. The weight-loss ratios of each sample vary between 18 and 20% with heating up to 800 °C. Because the DTA curves of each sample show the endothermic peaks between 230 and 250 °C, these weight-losses can be due to dehydration from the samples. The water contents (Fig. 4a) and the DTA peak temperatures (Fig. 4b) decrease slightly with increasing $C_{Er}$ [hence, with increasing the Er$^{3+}$ composition (x)].
3.3. XRD patterns

Figure 5a shows the variation of observed XRD patterns as a function of \( C_{\text{Er}} \). We here evaluate the lattice parameters and peak intensities by a profile fitting method assuming a rhombohedral unit cell. The \( C_{\text{Er}} \) dependence of the rhombohedral lattice parameters is shown in Figure 5b. The increase in \( C_{\text{Er}} \) decreases the lattice parameter \( a \) and increases the lattice parameter \( \alpha \) to decrease the unit-cell volume \( V \). The \( \alpha \) angles range between 89.08° and 89.31°, and are very close to 90°, corresponding to cubic system, over the investigated \( C_{\text{Er}} \) range. The diffraction peaks in Figure 5a are therefore indexed as pseudo-cubic system for the sake of convenience. The \( C_{\text{Er}} \) dependence of the integrated intensities \( I(hkl) \) of pseudo-cubic \( hkl \) peaks normalized by the integrated intensity \( I(100) \) of pseudo-cubic 100 peak is shown in Figure 6. The intensity ratios \( I(hkl)/I(100) \) vary systematically with increasing \( C_{\text{Er}} \). With increasing \( C_{\text{Er}} \), the intensity ratios \( I(110)/I(100) \), \( I(111)/I(100) \), \( I(221+300)/I(100) \), \( I(310)/I(100) \) and \( I(400)/I(100) \) increase, but \( I(200)/I(100) \), \( I(211)/I(100) \), \( I(220)/I(100) \) and \( I(311)/I(100) \) decrease, where \( I(221+300) \) is the intensity of overlapped peak of 221 and 300. These observations can be attributed to the exchange of \( \text{Na}^+ \) in Na-GTS for \( \text{Er}^{3+} \).

Figure 4. Variations of (a) the weight-loss ratios in TG and (b) the endothermic-peak temperatures in DTA as a function of \( C_{\text{Er}} \). The horizontal axes in (a) and (b) are represented in a logarithmic scale.

Figure 3. (a) TG and (b) DTA curves of \( \text{Er}^{3+} \)-exchanged Na-GTS operated at a heating rate of 10 °C/min.

Figure 5. Variations of (a) observed XRD patterns of \( \text{Er}^{3+} \)-exchanged Na-GTS and (b) rhombohedral lattice parameters as a function of \( C_{\text{Er}} \). The diffraction indices in (a) are labeled as those in pseudo-cubic system. The horizontal axis in (b) is represented in a logarithmic scale.
3.4. Possible occupied site of Er$^{3+}$

The previous structural analysis of a natural sample of Sr$^{2+}$-exchanged GTS [7] showed that Sr$^{2+}$ ions occupy both 4e-site at (0.63, 0.63, 0.63) and 6g-site at (0.96, 0.5, 0.5) in the GTS cavity. On the assumption that Er$^{3+}$ in Er$^{3+}$-exchanged Na-GTS is also distributed on the same sites as the case of the Sr$^{2+}$-exchanged GTS, we here examine several cation-distribution models of Er$^{3+}$ in the present Er$^{3+}$-exchanged Na-GTS as shown in Table 1. Figure 7 shows the observed XRD pattern of the Er$^{3+}$-exchanged Na-GTS with $x = 0.64$, together with the calculated ones from each Er$^{3+}$-distribution model. The peak intensities of the observed XRD pattern are in good agreement with the calculated one from the model (A). This suggests that Er$^{3+}$ and Na$^{+}$ ions preferentially occupy the 4e and 6g sites, respectively.

**Table 1.** Cation-distribution models of Er$^{3+}$-exchanged Na-GTS based on the structural analysis of Sr$^{2+}$-exchanged GTS [7].

| Models | Site occupancy factors | Er$^{3+}$ | Na$^{+}$ |
|--------|-----------------------|----------|----------|
|        | 4e-site | 6g-site | 4e-site | 6g-site |
| A      | 0.213    | 0       | 0        | 0.240   |
| B      | 0.213    | 0       | 0.360    | 0       |
| C      | 0        | 0.142   | 0        | 0.240   |
| D      | 0        | 0.142   | 0.360    | 0       |
| E      | 0.107    | 0.071   | 0        | 0.240   |
| F      | 0.107    | 0.071   | 0.360    | 0       |
4. Conclusion

The Er\textsuperscript{3+}-exchanged Na-GTS samples [Na\textsubscript{4(1-x)}Er\textsubscript{(4/3)x}Ti\textsubscript{4}Si\textsubscript{3}O\textsubscript{16}·nH\textsubscript{2}O] with the compositions in the range of 0.28 ≤ x ≤ 0.64 have successfully been prepared and characterized by TG-DTA and XRD techniques. The exchange of Na\textsuperscript{+} for Er\textsuperscript{3+} up to x = 0.64 brings about a slight decrease in the water contents and the dehydration temperatures. The increase in the Er\textsuperscript{3+} composition (x) decreases the lattice parameter a and increases the lattice parameter a to decrease the unit-cell volume V. Moreover, with increasing x, the intensity ratios I(hkl)/I(100) of pseudo-cubic 110, 111, 221+300 (overlapped peak of 221 and 300), 310 and 400 peaks increase, but those of pseudo-cubic 200, 211, 220 and 311 peaks decrease. The comparison of observed and calculated XRD patterns leads to a conclusion that the preferential occupied sites of Er\textsuperscript{3+} and Na\textsuperscript{+} ions are the 4\textit{e} and 6\textit{g} sites, respectively.
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