Preparation and crystal structural properties of Er$^{3+}$-exchanged GTS-type sodium titanosilicate

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Powder sample of GTS-type sodium titanosilicate (Na–GTS) was prepared using a hydrothermal method. The Er$^{3+}$-exchanged forms [Na$_{4(1-x)}$Er$_x$Ti$_4$O$_4$(SiO$_4$)$_3$·nH$_2$O] of Na–GTS with the compositions up to $x = 0.96$ were obtained by shaking the single-phase sample of Na–GTS in the ErCl$_3$ aqueous solutions (25 mL, 0.01–0.5 M) at 25 and 60 °C for 6 h. The Er$^{3+}$-exchange experiments revealed that the Er$^{3+}$-exchange amounts ($x$) increase with increasing the concentration of ErCl$_3$ aqueous solutions and the higher treatment temperature more effectively promotes ion-exchange. Thermogravimetry–differential thermal analysis (TG–DTA) measurements showed that the exchange of Na$^+$ for Er$^{3+}$ decreases the dehydration temperature and the H$_2$O content. The simulation of powder X-ray diffraction (XRD) patterns suggests that Er$^{3+}$ ions occupy both 4e and 6g sites in the assumed pseudocubic structure.

Keywords: Hydrothermal synthesis, Er$^{3+}$-exchanged Na–GTS, Microporous crystal, Cation distribution

INTRODUCTION

Microporous crystals such as zeolites are widely used in various applications because of their excellent abilities as molecular sieve, catalysts, absorbents, ion-exchangers, and heat-exchangers. Recently, grace titanosilicates (GTS) have attracted much attention as promising ion-exchangers. The GTS is a microporous titanosilicate as a structural analogue of the cubic mineral pharmacosiderite KFe$_4$(AsO$_4$)$_3$(OH)$_4$·6–7H$_2$O and has a three-dimensional tunnel-type structure. The Na–GTS, Na$_4$Ti$_4$O$_4$(SiO$_4$)$_3$·6H$_2$O, crystallizes in a rhombohedral phase with space group R$ar{3}$m; its unit cell [$a = 7.8123(6)$ Å, $\alpha = 88.794(9)^\circ$; Dadachov and Harrison, 1997] is very close to cubic cell and often described as a pseudocubic cell. Other forms such as K–GTS, HK$_3$Ti$_4$O$_4$(SiO$_4$)$_3$·4H$_2$O, have the cubic $P\bar{4}m$ symmetry [$a = 7.7644(3)$ Å; Behrens et al., 1996]. In GTS-type structures (Fig. 1), four TiO$_6$ octahedra linked by edge-sharing form a Ti$_4$O$_{16}$ cluster; the clusters are linked through SiO$_4$ tetrahedra to form a three-dimensional framework with an interconnected pore system involving cavities of 8–ring channels. The cavities are filled with water molecules and exchangeable extra-framework cations such as Na$^+$ and K$^+$, as in zeolites.

The ion-exchange properties of GTS for Cs$^+$ or divalent cations such as Co$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ have been investigated for the application to the radioactive waste treatments (Behrens et al., 1996; Behrens and Clearfield, 1997; Fujiwara et al., 2013). These studies provide im-
important insights into the development of the treatment materials of the radioactive waste water that continues to accumulate at the crippled Fukushima Daiichi Nuclear Power Plant. Meanwhile, the rare-earth ion exchanged GTS is of interest as promising optical and catalytic materials, as well as the rare-earth ion exchanged zeolites (Misono and Kondo, 1991; Chen et al., 2000). Because of such importance, our recent study (Fujiwara et al., 2017) investigated the Er$^{3+}$-exchange properties of Na-GTS in ErCl$_3$ aqueous solutions up to 0.1 M at 25 °C; consequently, Er$^{3+}$-exchanged Na-GTS, Na$_{4(1-x)}$Er$_{4x/3}$Ti$_4$O$_4$(SiO$_4$)$_3$·nH$_2$O ($0 \leq x \leq 1$), was only prepared in the compositions of $x < 0.7$. In the present study, we investigate Er$^{3+}$-exchange properties of Na-GTS under higher temperature and higher Er$^{3+}$-concentration conditions to examine whether these conditions increase the extent of cation exchange ($x \geq 0.7$). In addition, the cation distribution model of Er$^{3+}$-exchanged GTS is also discussed based on the simulation of powder XRD patterns.

EXPERIMENTAL

Sample preparation

The Na-GTS, Na$_4$Ti$_4$O$_4$(SiO$_4$)$_3$·6H$_2$O, was prepared by a hydrothermal method according to the procedure reported by the previous studies (Kostov-Kytin et al., 2007; Fujiwara et al., 2010). The starting materials were special grade reagents of NaOH (FUJIFILM Wako Pure Chemical Co.), amorphous SiO$_2$ fine powder (Merck KGaA), TiCl$_4$ aqueous solution (Toho Titanium Co., Ltd), and HCl (FUJIFILM Wako Pure Chemical Co.). The mixture with the compositional ratios of TiO$_2$/SiO$_2$ = 0.320 and Na$_2$O/TiO$_2$ = 5.625 was heat-treated at 100 °C for 24 h in a closed pressure-resistant vessel. The obtained sample was filtered with ultrapure water and dried at 80 °C for 24 h to gain Na-GTS. The Er$^{3+}$-exchanged forms were obtained by shaking the prepared Na-GTS (0.5 g) in the ErCl$_3$ aqueous solutions (25 mL) at 25 and 60 °C for 6 h; the aqueous solutions were produced by dissolving 3N-grade ErCl$_3$ powder (Rare Metallic Co., Ltd) in ultrapure water. The concentrations of Er$^{3+}$ ($C_{Er}$) in the aqueous solutions were varied between 0.01 and 0.5 M, where the 25 mL of 0.0364 M ErCl$_3$ aqueous solution is theoretically necessary for complete exchange of Na$^+$ in Na-GTS for Er$^{3+}$. The obtained samples were filtrated, washed and dried at 80 °C for 24 h.

Characterization

Atomic absorption spectrometry (AAS) using a Hitachi Z-5310 spectrophotometer was employed for analyses of the cationic contents in the obtained samples. The experimental procedure and techniques for AAS are the same as those described by Fujiwara and Mizota (2001), who studied the ion-exchange of A-type zeolite. The ion-exchange amounts of the Er$^{3+}$-exchanged forms, i.e., the $x$ values in Na$_{4(1-x)}$Er$_{4x/3}$Ti$_4$O$_4$(SiO$_4$)$_3$·nH$_2$O ($0 \leq x \leq 1$) were evaluated from AAS for Na$^+$ eluted into the supernatant solutions from Na-GTS after the ion-exchange experiments. Here, $x$ was defined as $n$(Na)/4$n$(Na-GTS) based on the ion-exchange reaction 4$x$/3Er$^{3+}$ + Na$_4$Ti$_4$O$_4$(SiO$_4$)$_3$ → Na$_{4(1-x)}$Er$_{4x/3}$Ti$_4$O$_4$(SiO$_4$)$_3$ + 4$x$Na$^+$; $n$(Na-GTS) is the amounts of as-prepared Na-GTS used in the ion-exchange experiments, and $n$(Na) is the amounts of Na$^+$ in the supernatant solutions after the ion-exchange experiments. The TG-DTA measurements using a MAC Science TG-DTA2000S analyzer were performed in the air for the determination of H$_2$O contents and the examination of dehydration process in the samples. The heating rate of 10 °C/min and the cooling rate of 20 °C/min were applied in the TG-DTA measurements. The phase identification and structural characterization of the obtained samples were performed by powder XRD measurements using a Rigaku RINT2200 diffractometer. The program Powder Cell (Kraus and Nolze, 1996) was used for the simulation of powder XRD patterns.

RESULTS AND DISCUSSION

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

Figure 2 shows the Er$^{3+}$ compositions ($x$) of the Er$^{3+}$-exchanged Na-GTS, Na$_{4(1-x)}$Er$_{4x/3}$Ti$_4$O$_4$(SiO$_4$)$_3$·nH$_2$O ($0 \leq x \leq 1$) prepared at each temperature of 25 and 60 °C.
$x \leq 1$), prepared at each temperature as a function of the concentration of ErCl$_3$ aqueous solution ($C_{Er}$). As shown in the figure, the increase in $C_{Er}$ increases the Er$^{3+}$-exchange amounts ($x$). In our previous study (Fujiwara et al., 2017), the $x$ value only reached 0.68 at 25 °C even under a condition of $C_{Er} = 0.1$ M, much higher than the minimum $C_{Er} (= 0.0364$ M) being necessary for complete ion-exchange of $x = 1$. However, the present study shows that the further increase in $C_{Er}$ to 0.5 M successfully increases the $x$ value to 0.80 at 25 °C. Moreover, the Er$^{3+}$-exchange treatments up to $C_{Er} = 0.5$ M at a higher temperature of 60 °C enhance the $x$ values up to 0.96, very close to unity corresponding to the complete Er$^{3+}$-exchange. Thus, the increase in treatment temperature is considerably effective for promotion of ion-exchange, as well as in $C_{Er}$. The present AAS result of $x \approx 1$ indicates that the amount of Na$^+$ eluted into the supernatant solutions from Na-GTS after the ion-exchange experiment is approximately 4 ions per formula unit. This suggests that there are no significant amounts of hydronium (H$_3$O$^+$) and hydrogen (H$^+$) ions in the present Na-GTS, in contrast to the K-GTS reported by Behrens et al. (1996).

**Dehydration behaviour and water content**

Figure 3 show TG and DTA curves of the Er$^{3+}$-exchanged samples prepared under each condition, together with those of as-prepared Na-GTS sample. The TG

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**Figure 3.** TG and DTA curves of as-prepared Na-GTS and its Er$^{3+}$-exchanged forms prepared at each temperature of 25 and 60 °C. The data in $0 < x \leq 0.68$ at 25 °C are quoted from our previous study (Fujiwara et al., 2017), where the revised $x$ values are provided as in Figure 2.
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 with heating up to 800 °C vary between 17 and 20% for each sample. Because the DTA curves of each sample show the endothermic peaks between 230 and 270 °C, these weight-losses can be due to dehydration from the samples. The exchange of Na⁺ for Er³⁺ decrease the endothermic peak temperatures and the H₂O contents calculated from the weight-losses (Fig. 4).

The previous Rietveld analysis of Na-GTS (Dadachov and Harrison, 1997) using powder X-ray diffraction data showed that the number of H₂O molecules coordinating to the extra-framework cation Na⁺ is 6 molecules per formula unit (mpfu). In the present study, the H₂O content of as-prepared Na-GTS powder sample calculated from the weight-loss is 8.2 mpfu, larger than the ideal H₂O content of 6 mpfu. Fujiwara et al. (2010) indicated the presence of two types of excess water in a powder sample of GTS-type (K,Na,H)₄Ti₂O₇(SiO₄)₃·nH₂O from the hydration-heat measurement: (1) adsorbed water on grain surface or capillary-condensed water between grains; (2) adsorbed water in the framework without any coordination to extra-framework cations. The deviation of the present H₂O content in as-prepared Na-GTS (8.2 mpfu) from the ideal one (6 mpfu) can be due to such excess water. Although the excess water can also be present in the present Er³⁺-exchanged powder sample, it is noteworthy that the H₂O content decreases almost linearly with increasing the Er³⁺ composition (x) (Fig. 4). This correlation can closely be related to the reduction in the number of extra-framework cations due to the substitution of 3Na⁺ → Er³⁺, because it would reduce the number of H₂O molecules coordinating to extra-framework cations.

**Powder X-ray diffraction and possible Er³⁺ distribution**

Figure 5 shows the observed powder XRD patterns of the Er³⁺-exchanged samples prepared under each condition, together with that of as-prepared Na-GTS. We evaluated the unit-cell parameters by a profile fitting method assuming a rhombohedral unit-cell. The compositional dependence of the obtained unit-cell parameters (a, α) and unit-cell volume (V) is shown in Figure 6. The increase in x, on the whole, decreases the c-axis length and increases the α angle to decrease the unit-cell volume V. This observation can be attributed to the reductions in the number and mean size of extra-framework cations [ionic radii: e.g., r(Na⁺) = 1.02 Å and r(Er³⁺) = 0.890 Å in CN = 6; Shannon, 1976] and in the number of H₂O molecules coordinating to them.
accompanying the substitution of $3\text{Na}^+ \rightarrow \text{Er}^{3+}$. On the other hand, such reductions can expand void space in the cavity and consequently may increase the amounts of H$_2$O molecules adsorbed only by hydrogen–bonding to framework O atoms. This effect increases the unit–cell volume, which may yield the somewhat large scattering of the data in Figure 6. The $\alpha$ angles range between 89.08° and 89.47° and are very close to 90°, corresponding to cubic cell, over the investigated $x$ range. The diffraction peaks in Figure 5 are therefore indexed as pseudocubic cell for convenience.

The previous single–crystal XRD analysis of a natural sample of Sr–GTS with cubic space group $P43m$ (Spiridonova et al., 2011) reported 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. To examine the Er$^{3+}$–distribution in the Er–GTS ($x = 1$) with the pseudocubic structure, its powder XRD patterns were simulated on the three cation–distribution models shown in Table 1. The simulations were based on the assumptions that the Er–GTS is isostructural with the Sr–GTS and the possible occupied sites of its Er$^{3+}$ are the same as those of Sr$^{2+}$ in the Sr–GTS.

Figure 7 shows the comparison of the simulated powder XRD pattern of the present Er$^{3+}$–exchanged Na–GTS ($x = 0.96$) with the simulated ones of Er–GTS ($x = 1$) from the cation–distribution models (A), (B) and (C) in Table 1. The simulation of powder XRD patterns was performed using the program Powder Cell (Kraus and Nolze, 1996). The diffraction indices are labeled assuming the pseudocubic structure.

| Models | Site occupancy factors of Er$^{3+}$ |
|--------|-----------------------------------|
|        | 4e site* | 6g site* |
| A      | 0.333    | 0        |
| B      | 0        | 0.222    |
| C      | 0.133    | 0.133    |

* The Sr$^{2+}$ sites (4e, 6g) in Sr–GTS with the cubic $P43m$ structure determined from the single–crystal XRD analysis (Spiridonova et al., 2011) were assumed as possible occupied sites of Er$^{3+}$ in Er–GTS ($x = 1.0$) with the pseudocubic structure.
other hand, Fujiwara et al. (2017) suggested that in the sample with $x = 0.64$, Er$^{3+}$ and Na$^+$ ions preferentially occupied the 4e and 6g sites, respectively. Further study is necessary to examine the influence of the coexistence of Na$^+$ on the site preference of Er$^{3+}$.

ACKNOWLEDGMENTS

This work was partly supported by JSPS KAKENHI Grant Numbers JP16K06927 and JP24561005.

SUPPLEMENTARY MATERIAL

Color version of Figure 1 is available online from https://doi.org/10.2465/jmps.191002.

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Manuscript received October 2, 2019
Manuscript accepted January 20, 2020
Manuscript handled by Atsushi Kyono