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Morphology control and interlayer pillaring of swellable Na-taeniolite mica crystals

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ABSTRACT

Na-taeniolite ($NaMg_2LiSi_4O_{10}F_2$) mica crystals were synthesized from nonstoichiometric raw batches containing NaCl as a flux, in order to control the morphology of mica crystals. Swellable Na-taeniolite was obtainable from both stoichiometric and nonstoichiometric batches although small amounts of different products were coprecipitated, depending on the composition of the raw batches. Samples obtained from raw batches containing ≤1 mol NaCl consisted of a single-phase swellable mica. The addition of a small amount of NaCl was effective in controlling the morphology of the mica crystals. Raw batches containing 1 mol NaCl yielded mica crystals having a hexagonal, plate-like morphology with a larger aspect ratio. Alumina-pillared micas prepared from host micas thus obtained from raw batches containing NaCl had larger specific surface areas than those obtained from stoichiometric batches. This suggests that the swellability of mica crystals is also affected by the addition of NaCl.

1. Introduction

Micas constitute a major group in clay minerals. Naturally occurring micas do not exhibit swellability in water. However, some synthetic fluorine micas can swell with water. Na-taeniolite, which has the anhydrous structural formula $NaMg_2LiSi_4O_{10}F_2$, is a typical species of synthetic swellable fluorine mica [1–3]. Synthetic swellable micas are characterized by a large cation exchange capacity, high crystallinity and high thermal durability. Na-type swellable brittle micas (Na-*n*-mica, $n = 2$, 3 and 4) [4–8] are other interesting species of synthetic fluorine mica. Park et al. reported the phase pure Na-4-mica synthesized by NaCl melt method to avoid the excess use of NaF and pointed out that the crystal size of mica could be manipulated by the molar ratio of NaCl [4]. Ravella and Komarneni synthesized swelling micas using stoichiometric amount of fluoride by NaCl melt method [5]. Swelling micas were obtained by simple washing of the as-prepared products with deionized water [4,5].

Clay-based intercalation compounds and hybrid materials attract much attention because of their interesting properties, for example, adsorption and catalysis, as well as environmental preservation and remediation [9,10]. The host clays most extensively studied are smectite group minerals, such as a naturally occurring montmorillonite. Synthetic swellable fluorine micas can also be used as host crystals for intercalation [11–13]. Through synthesis, the morphology of clay mineral crystals becomes controllable [14]. The morphology control of Na-taeniolite crystals is significant for their use as host crystals to yield high performance intercalation compounds and for finding new application.

Intercalation of bulky inorganic polycations into the interlayer region of swellable micas by cation exchange and subsequent heating treatment produces thermally stable microporous solids, i.e., pillared micas [15–20]. These pillared micas retain features of the host micas, such as a large crystal size. In the present study, Na-taeniolite mica crystals were synthesized from stoichiometric and nonstoichiometric raw batches containing NaCl as a flux, in order to control the morphology of mica crystals for the purpose of yielding more promising host crystals. The micas obtained were also used to synthesize pillared micas with microporosity in their interlayer region.

2. Experimental

Reagent-grade SiO_2 (99.9%, Wako Pure Chemical Industries, Osaka, Japan), MgO (99.9%, Wako Pure Chemical Industries), LiF (99.9%, Wako Pure Chemical Industries)and NaF(99%, Wako Pure Chemical Industries) were used as raw materials and mixed in the proportions corresponding to Na-taeniolite to obtain a stoichiometric raw mixture. Reagent-grade NaCl (99.5%, Wako Pure Chemical Industries) was added to the stoichiometric mixture to obtain nonstoichiometric raw batches. The amount of NaCl was varied from 0.1 to 9 mol against 1 mol of Na-taeniolite. The use of NaF as a flux, instead of NaCl, was also examined.

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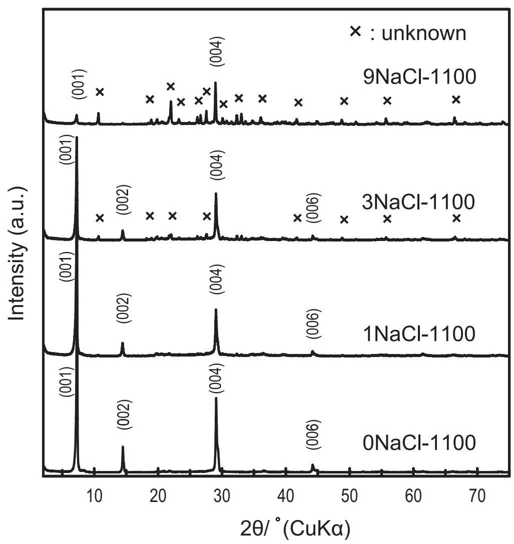

Fig. 1. XRD patterns of products obtained from stoichiometric and nonstoichiometric batches at 1100 °C.

Each batch was sealed in a platinum tube and heated at 950 °C or 1100 °C for 2 h using an electric furnace (FUH712, Advantec, Tokyo, Japan). The temperature was then lowered at a rate of −10 °C/min to 950 °C and the tube was removed from the furnace to cool in air. The as-prepared mica samples thus obtained were crushed and then washed with distilled water to rinse out the residual NaCl. The mica samples, hereafter abbreviated as *x*NaCl-*y* where *x* and *y* indicate the amount of NaCl (mol per 1 mol of Na-taeniolite) and the heat-treatment temperature, respectively, were characterized by XRD (XRD-6000, Shimadzu, Kyoto, Japan, using monochromatic Cu Kα radiation), FT-IR (FT/IR-4200, JASCO, Tokyo, Japan, using KBr tablet method) and SEM (S-4100, Hitachi, Tokyo, Japan).

Some of the samples (0NaCl and 1NaCl-series micas) were then transformed into Li^+-exchanged forms by repeated treatment with a 2 mol/L LiCl aqueous solution [16]. The Li^+-exchanged micas were reacted with a polyhydroxoaluminum (PHA) solution [17,21], which had an OH/Al ratio of 2.50 and an Al concentration of 0.05 mol/L, at 60 °C for 2 h under vigorous stirring. The products were washed 10 times, dried at 60 °C and then calcined at 400–700 °C for 2 h to obtain microporous alumina-pillared micas. The pillared micas were characterized by XRD and N_2 adsorption–desorption at liquid nitrogen temperature (ASAP-2010, Micromeritics, USA). The BET specific surface area and pore size distribution (BJH) of the pillared micas were evaluated from N_2 adsorption isotherms.

3. Results and discussion

Fig. 1 shows XRD patterns of the products obtained from different raw batches at 1100 °C. Swellable Na-taeniolite could be obtained from both stoichiometric (0NaCl) and nonstoichiometric (1–9NaCl) batches; the sharp (0 0 1) diffraction peak at 7.2° (Cu Kα) and high order (0 0 *l*) peaks were assignable to a single-layer hydrate state of the swellable mica [1]. The residual NaCl in the as-prepared products could be rinsed out thoroughly by simple washing with distilled water. Thus, this washing process resulted in a marked increase in the 0 0 1 peak intensity owing to the dissolution of the NaCl phase.

Unknown phases coprecipitated in the samples obtained from Na-rich raw batches (≥3 mol NaCl). These impurity phases could not be removed from swellable mica even after multiple rinses with distilled water. By contrast, XRD patterns of the products obtained from raw batches containing 0 or 1 mol NaCl indicated that only mica was formed, suggesting that Na-taeniolite and NaCl are immiscible for a NaCl content of ≤1 mol.

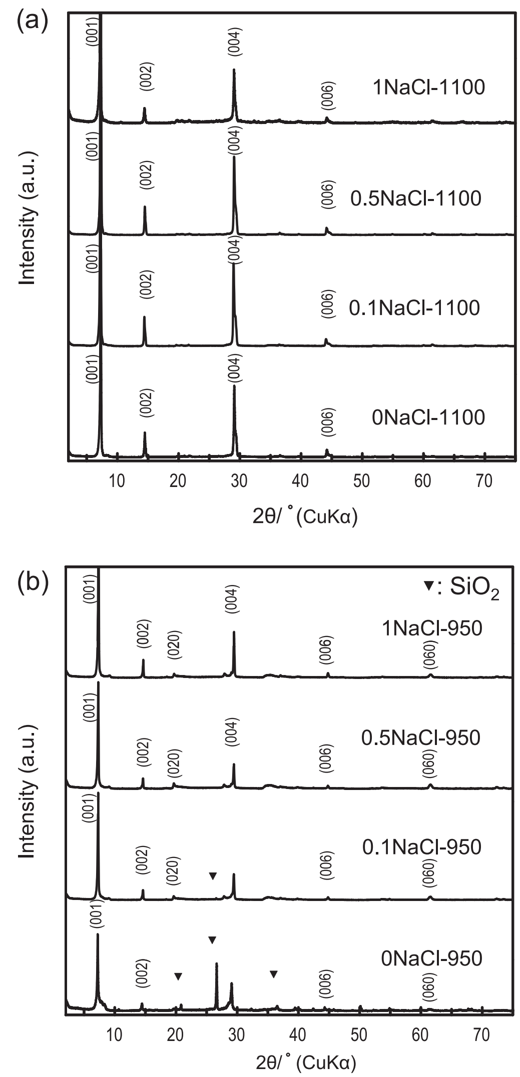

Fig. 2. XRD patterns of products obtained from different raw batches containing 0–1 mol NaCl at (a) 1100 °C and (b) 950 °C.

Fig. 2 shows XRD patterns of the products obtained from raw batches containing ≤1 mol NaCl at 1100 °C and 950 °C. Swellable Na-taeniolite was formed as a single phase at 1100 °C although a small amount of SiO_2 coprecipitated in the 0NaCl-950 and 0.1NaCl-950 samples.

Heat-treatment temperatures between 950 and 1100 °C did not yield homogeneous melting, but they gave sintered products. Swellable Na-taeniolite series fluorine micas were synthesized as a single phase from the stoichiometric raw batch by melting in a sealed platinum tube at 1400–1420 °C [1,2]. A preliminary study also showed that synthesis by the melting method at 1250 °C or 1400 °C yields swellable micas. However, it is found that the morphology of the mica crystals obtained at these higher temperatures is hardly controllable.

Fig. 3 shows SEM micrographs of Na-taeniolite obtained at 1100 °C and 950 °C from different raw batches. All the samples show typical flake-like crystals of synthetic micas. Clearly, the addition of a small amount (0.1–1 mol) of NaCl is very effective in controlling the morphology of Na-taeniolite crystals. Raw batches with even a very low NaCl content (0.1 mol) yielded mica crystals having a more defined shape compared to those obtained from