Pure Na-4-mica: Synthesis and Characterization

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An innovative synthesis method for phase-pure Na-4-mica has been developed in this study. Phase pure Na-4-mica has been synthesized by using NaCl melt. In the newly developed method, not only could the postpreparation process be avoided but also the crystal size could be manipulated in the range of about 2–5 μm by the initial molar ratio of Al_2O_3/NaCl. Both the hydrated and anhydrous Na-4-mica phases possess monoclinic crystal systems with the same layer plane. The X-ray diffraction (XRD) patterns exhibited relatively strong $h0l$ peaks along with very strong $00l$ peaks. Changes in the cell parameters of β and c on hydration–dehydration indicate that the layer swelling is accompanied with a significant parallel displacement of layers. Furthermore, pure Na-4-mica has exhibited completely reversible dehydration–rehydration behavior up to 800 °C and extremely high Sr^{2+} uptake capacity without any layer collapse.

Introduction

Highly charged sodium fluorophlogopite, unofficially Na-4-mica,[1] is clearly different from both nonswelling phlogopites and expandable montmorillonites. Despite the high negative layer charge, Na-4-mica readily hydrates and swells. It exhibits high cation-exchange capacity comparable to those of Al-rich zeolites. This swelling mica has generated a lot of interest because of exceptionally high uptake ability and selectivity for harmful divalent radioactive and heavy metal cations.[2–9] Decontamination of these cations has been a principal long-term problem.[10–13] However, Na-4-mica could not be easily synthesized as a pure phase, which is essential to elucidate its inherent characteristics. Furthermore, the existing synthesis methods employ excess amount of NaF, which requires washing with H_3BO_3-saturated solution to remove any insoluble fluorides. This washing necessities subsequent saturation of exchangeable sites

by Na^+ ions because of H^+ from boric acid. Thus, there is a necessity to develop an efficient and simplified method for the synthesis of phase-pure Na-4-mica.

Na-4-mica with the theoretical chemical composition of $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot xH_2O$ was first reported by Gregorkiewitz in 1972.[1] Single crystals of Na-4-mica were separated from a heterogeneous mixture of crystalline phases synthesized from augite powder in the melt mixture of NaF and MgF_2. Characterization of these single crystals[14] revealed that the interlayer region of trioctahedral mica-type 2:1 layers accommodated an unusually large number of hydrated Na^+, which can be readily exchanged. However, not much attention had been given to Na-4-mica before Paulus et al.[2] reported its bulk synthesis and selective Sr^{2+} exchange. It was remarkable that the synthesized Na-4-mica exhibited excellent selectivity and fixation capacity for Sr^{2+} ions through the irreversible cation-exchange reaction. Collapse of interlayer structure was known to play a crucial role in the fixation of the radioactive cations such as Sr^{2+}, Ba^{2+}, and Ra^{2+}.[2,4]

The synthesized Na-4-micas always contained some anhydrous mica phase and unknown crystalline phases, which were clearly indicated by several X-ray diffraction (XRD) peaks (typically at the d spacings of 4.21 and 2.61 Å).[3–9] In fact, the powder XRD pattern of pure Na-4-mica phase was not established to the best of our knowledge. Identification of Na-4-mica phases was based on the results of single-crystal X-ray diffraction by Gregorkiewitz et al.,[14] who did not give exact d values. Furthermore, it is necessary to elucidate crucial basic features such as relationship between the hydrated and the anhydrous mica phases, dehydration–rehydration property, thermal stability, and even the effect of Sr^{2+} exchange on the layer structure. This study

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deals with a new bulk synthesis method for phase-pure Na-4-mica and its inherent characteristics.

Experimental Section

Synthesis Method. Some impurities were found in all the reported Na-4-micas. It was speculated that the presence of excess F^- was a main reason for the formation of the impurities. In this study, NaCl and MgF_2 were employed to avoid the excess use of NaF. Synthesis of pure Na-4-mica phase was attempted with the near-stoichiometric powder mixtures with the molar compositions of 2 SiO_2, Al_2O_3, 3 MgF_2, and 2−6 NaCl. Typically, SiO_2 (fumed silica from Aldrich Chemical Co.) and AlOOH (böehmite from Condea Chemie) were employed as Si and Al sources. Reactant mixture was well mixed by grinding and thermally treated in a Pt crucible at 900 °C for 15 h (hereafter named as NaCl melt method). After cooling to room temperature, the solid was washed with deionized water and dried (the resultant solid was named as NaCl melt product). For comparison, Na-4-mica was also prepared by the all-in-one method.[3] After mixed precursors were thermally treated at 900 °C for 18 h, the solid was sequentially washed with H_3BO_3-saturated solution, deionized water, NaCl solution, and deionized water (the resultant solid was named as all-in-one product).

Characterization. The NaCl melt product synthesized from the molar $NaCl/Al_2O_3$ ratio of 4.0 was used for characterization throughout this study, unless specified. Powder X-ray diffraction (XRD) patterns were recorded by Ni-filtered Cu Kα radiation at 40 kV and 100 mA at a scanning speed of 0.1° 2θ/min with a scan step of 0.01° 2θ (Phillips, X'Pert). The d spacings were determined from $K\alpha_1$ radiation ($\lambda = 1.5405$ Å) after $K\alpha_2$ stripping. No smoothing was conducted. The XRD patterns were also obtained at 800 and 900 °C, respectively. These patterns were recorded after holding for 1 h at each temperature with a heating rate of 10 °C/min. Hydration reversibility was examined by the change in the XRD pattern of the NaCl melt product after it was dehydrated at the preset temperatures (200−900 °C) for 15 h and rehydrated under water-saturated air at room temperature for 3 days. The NaCl melt product was further characterized by solid-state ^{29}Si and ^{27}Al NMR spectroscopy (Varian, Unity Plus300), scanning electron microscopy with gold coating (Hitachi, S-4200), and Sr^{2+} uptake isotherm. The ^{27}Al cross-polarization magic angle spinning (CP/MAS) spectra were recorded at a spinning speed of 5 kHz with a 1 μs excitation pulse in conjunction with recycle delays of 1 s. The 1 M $Al(H_2O)_6^{3+}$ solution was taken as a reference (chemical shift 0.0 ppm). Rotation speed of 4.5 kHz and tetramethylsilane solution were applied for the ^{29}Si NMR spectrum. The Sr^{2+} uptake isotherm was examined by equilibrating 50 mg of the NaCl melt product in 20 mL of the 2 mN Sr^{2+} solution in the presence of 0.5 M NaCl. The solution was acidified to pH 4.0 to minimize surface adsorption before the addition of the NaCl melt product. Sr^{2+} concentration in the solution was analyzed by atomic absorption spectroscopy (Shimadzu AA6601F) after the solid was removed by filtration. Uptake amounts were determined by the difference of Sr^{2+} concentrations between initial and equilibrated solutions.
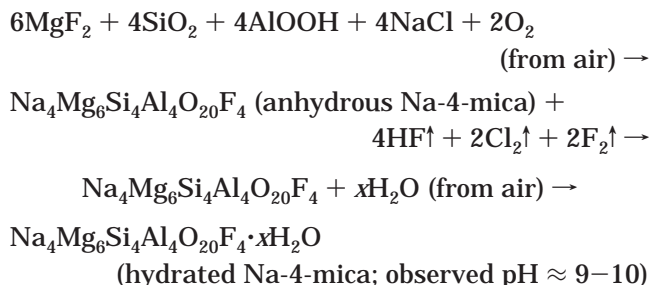
Results and Discussion

Synthesis of Pure Na-4-mica.

The XRD patterns of the NaCl melt products were compared with those of the all-in-one products (Figure 1).

The as-synthesized products exhibited the main basal peak of hydrated Na-4-mica phase, regardless of the synthesis methods. However, the peaks attributed to the impurities were observed only in the XRD patterns of the all-in-one products. The as-synthesized all-in-one product contained multiple crystalline phases such as the hydrated Na-4-mica, impurity phases, and NaF as

the major crystalline phases. The strongest peak at the d spacing of 9.9 Å was attributed to the anhydrous mica phase. The postpreparation procedures such as washings and Na^+ saturation resulted in a dramatic increase in the intensity of the basal peak of the hydrated Na-4-mica phase along with a remarkable decrease in that of the anhydrous mica phase. However, any significant changes in the intensities of the peaks at the d spacings of 4.21 and 2.61 Å were not observed throughout the postpreparation procedures.

On the other hand, the as-synthesized NaCl melt product did not show any of the peaks attributed to the impurities including anhydrous mica. Most of the strong peaks in its XRD pattern could be assigned to a series of 00l peaks of the hydrated Na-4-mica phase and the peaks assigned to NaCl (that were absent from the product synthesized with the $NaCl/Al_2O_3$ ratio of 2.0). Simple water washing resulted in a remarkable increase in the intensity of all 00l peaks together with complete disappearance of the NaCl peaks. These results clearly indicate that the NaCl melt method neither leads to the formation of the impurities nor requires any postpreparation procedures such as washing with H_3BO_3-saturated solution and Na^+ saturation. The following chemical reactions are expected in the NaCl melt method when the $NaCl/Al_2O_3$ ratio of 2.0 was employed:

$$6MgF_2 + 4SiO_2 + 4AlOOH + 4NaCl + 2O_2$$
$$\text{(from air)} \rightarrow$$

$$Na_4Mg_6Si_4Al_4O_{20}F_4 \text{ (anhydrous Na-4-mica)} +$$
$$4HF\uparrow + 2Cl_2\uparrow + 2F_2\uparrow \rightarrow$$

$$Na_4Mg_6Si_4Al_4O_{20}F_4 + xH_2O \text{ (from air)} \rightarrow$$

$$Na_4Mg_6Si_4Al_4O_{20}F_4 \cdot xH_2O$$
$$\text{(hydrated Na-4-mica; observed pH} \approx 9-10)$$

The phase transition from anhydrous to hydrated mica was observed during the postpreparation process in the existing methods including the all-in-one method. As indicated in Figure 1, the all-in-one product also clearly exhibited the phase transition of the anhydrous mica phase into the hydrated Na-4-mica phase. However, complete phase transition did not occur, as reported.[2−4,9] The formation of anhydrous mica phase was also observed in the NaCl melt method when optimum conditions were not used. For example, the anhydrous mica phase resulted from the treatment conditions such as nonstoichiometric amounts of Mg, Si, and/or Al sources and/or when the temperatures were higher or lower than 900 °C. However, the formed anhydrous phase was not affected by any postpreparation procedures. It appears that there are two different types of anhydrous micas, swelling type and nonswelling type. Both anhydrous micas probably possess the same structure but with different Si/Al ratios in tetrahedral sheets. Thus, there is a clear difference in the crystalline phases of the products between the NaCl melt method and the other existing methods to indicate a different reaction mechanism with each method.

The presumably pure Na-4-mica by the NaCl melt method, based on the XRD patterns, could be also synthesized from various raw materials and modified initial mixtures. For example, silica gel instead of silica
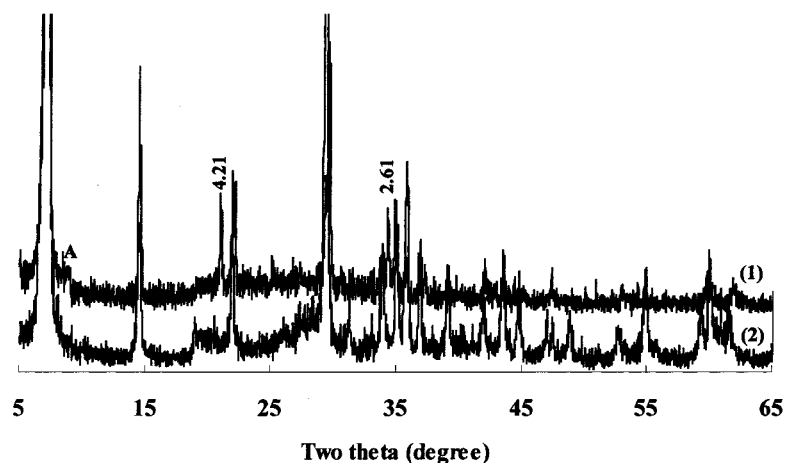
As-synthesized products
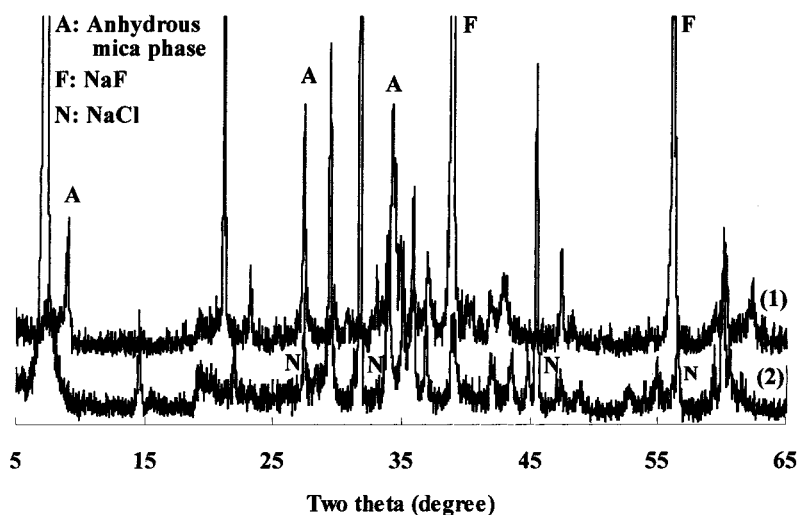
Washed products

Figure 1. XRD patterns of as-synthesized and washed products of all-in-one and NaCl melt methods. (1) With all-in-one method; (2) with NaCl melt method.

and NaOH as mineralizer also resulted in the pure hydrated Na-4-mica phase. However, the synthesized hydrated Na-4-mica phase quickly degenerated under open-air environment within a few days. Their ^{29}Si NMR spectra revealed the presence of hydroxyl groups (Si atoms at the chemical shift value -61.0 ppm)[4,15−17] that led to rapid deterioration of layer structure.[18−20] Typically, stable and pure Na-4-mica was easily obtained with the employment of MgF_2 and silica. In this study, the synthesis of stable and pure Na-4-mica was achieved by the thermal treatment of powder mixtures with the mole ratio of 3 MgF_2:2SiO_2:2AlOOH:2−6NaCl at 900 °C for 15 h. Water washing was not compulsory, although it enhanced the crystalline property significantly. The chemical composition of the synthesized

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pure hydrated Na-4-mica was determined to be $Na_{4(\pm 0.3)}Mg_{6(\pm 0.2)}Al_{4(\pm 0.3)}Si_{4(\pm 0.2)}O_{20}F_{4(\pm 0.4)}\cdot nH_2O$ from the elemental analysis.

Physicochemical Properties of the Synthesized Hydrated Na-4-mica. Chemical environments of framework Si and Al atoms in the NaCl melt product were examined by ^{27}Al and ^{29}Si NMR spectra (Figure 2).

The ^{27}Al spectrum exhibited one strong peak at the chemical shift value of 60.5 ppm that was attributed to tetrahedral Al atoms.[4,15,17] The very weak and broad peaks around this peak are apparently spinning sidebands. No noticeable peaks near 0 ppm were detected, which indicated the absence of octahedral Al atoms. This result suggested that all Al atoms were incorporated into tetrahedral sheets. The ^{29}Si NMR spectrum showed two chemical shift values at -78.2 and -81.7 ppm, confirming the Q^3 environment of all Si atoms.[4,15,16] Ideally, all Si atoms in Na-4-mica are surrounded by three Al atoms through oxygen bridge, Si(3Al) environment. It was reported that the Si(3Al) environment resulted in a chemical shift value of about -77 ppm, while the Si(2Al) environment gave a chemical shift of about -82 ppm.[4] However, the chemical shift values
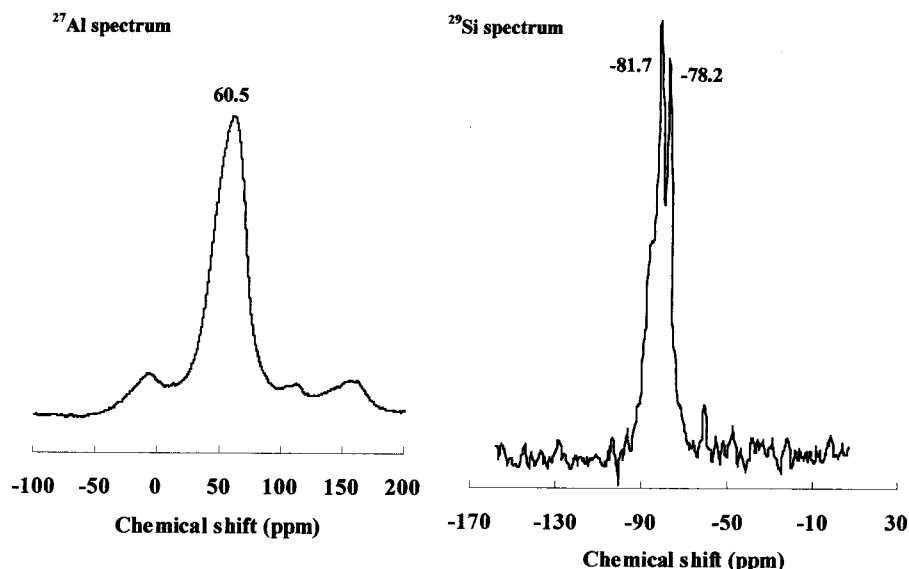
Figure 2. ^{29}Si and ^{27}Al NMR spectra of the NaCl melt product.
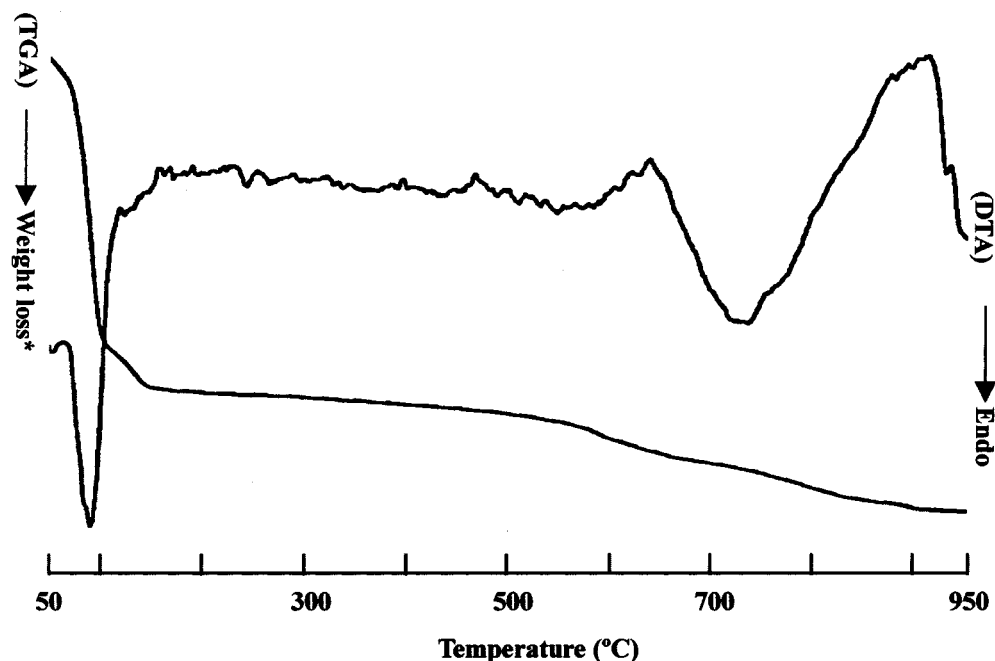

Figure 3. DT/TGA curves of the NaCl melt product. *Total weight loss between 28 and 950 °C was 9.7 wt %.

were significantly affected by synthesis methods.[4,15,16] For example, the peaks with chemical shift values of −75.4 and −77.3 were also assigned to a Si(3Al) environment.[4] Therefore, the peaks observed in this study could be assigned to a Si(3Al) environment, although it was not clear whether two peaks resulted from the variation of Si/Al ratio in tetrahedral sheets or from other factors such as water molecules, Na$^+$, and F$^-$.

Thermal analyses of the NaCl melt product (Figure 3) indicated that major weight loss occurred as an endothermic response below 120 °C. Between 160 and 550 °C, no appreciable weight losses were observed. Small weight losses were detected around 600 and 760 °C. A major weight loss (estimated to be 7.0% of total weight) apparently resulted from dehydration of interlayered water molecules. The number of water molecules per unit cell was estimated to be 3.6 (±0.3). The other weight losses accompanying one broad endother-

mic response around 740 °C seemed to arise from dehydroxylation of surface hydroxides.[21,22] The endothermic responses above 900 °C suggested that structural change, mostly structural decomposition, took place above this temperature.

Hydration−dehydration behavior of the NaCl melt product was examined by the change in the XRD pattern at high temperatures. Figure 4 shows the XRD patterns of the NaCl melt product at 800 (spectrum 2 in Figure 4) and 900 °C (spectrum 3 in Figure 4) along with that of the air-cooled NaCl melt product (spectrum 1 in Figure 4) that had been treated at 800 °C for 15 h. The temperatures of 800 and 900 °C were chosen because thermal analyses suggested a structural decomposition of the NaCl melt product above 900 °C.

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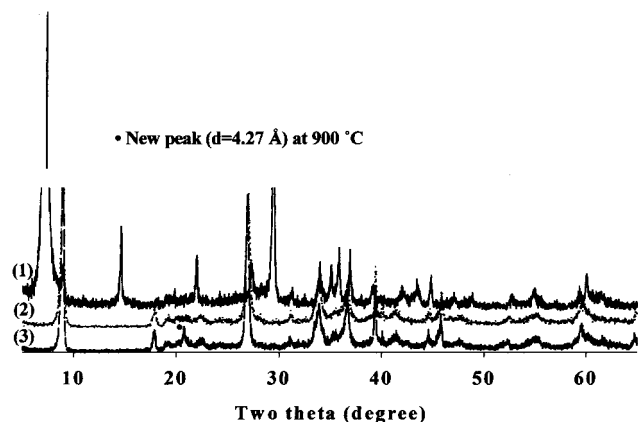(22) Zhuravlev, L. T. *Pure Appl. Chem.* **1989**, *61*, 1969−1976.

Figure 4. XRD patterns of the NaCl melt products at various temperatures and of the rehydrated NaCl melt product. (1) Rehydrated; (2) at 800 °C; (3) at 900 °C.

The change in the XRD pattern at high temperatures suggests that the thermal treatment at 800 °C results in complete dehydration of the hydrated Na-4-mica phase into a corresponding anhydrous Na-4-mica phase (spectrum 2 in Figure 4). Exposure of the anhydrous Na-4-mica phase to open air resulted in rapid restoration back into the hydrated Na-4-mica phase, as indicated by the XRD pattern of the air-cooled NaCl melt product (spectrum 1 in Figure 4). When the anhydrous Na-4-mica that resulted from the thermal treatment typically between 200 and 800 °C for 15 h was exposed to water-saturated air, their XRD patterns completely reverted to that of the hydrated Na-4-mica. All peaks including weak and broad ones were restored. It was very interesting that phase transition between the anhydrous and the hydrated Na-4-micas was perfectly reversible up to 800 °C. However, the thermal treatment at 900 °C led to formation of other crystalline phases, indicated by the appearance of new peaks in the XRD pattern (spectrum 3 in Figure 4). Structural decomposition at 900 °C was confirmed by the result that the new peaks did not disappear by the rehydration procedure. In fact, thermal treatment at 900 °C for 15 h resulted in total decomposition of the Na-4-mica phase into other crystalline phases. This result confirmed that an endothermic response above 900 °C resulted from structural decomposition.

Na-4-mica had been known to be stable below 600 °C, although no established information was available. Gregorkiewitz and Rausell-Colom[14] reported that the thermal treatment at 750−900 °C for 1 day led to transformation of hydrated Na-4-mica into an amorphous phase. They also found that restoration of the anhydrous Na-4-mica phase to the hydrated Na-4-mica phase occurred only below 300 °C. We also noticed in the XRD patterns of the all-in-one products that the relative intensity of the basal peak of the anhydrous mica phase was increased by prolonged exposure to temperatures above 105 °C. Restoration of the hydrated Na-4-mica phase was incomplete by the subsequent rehydration procedure. In general, drying below 60 °C had been recommended for the preparation of Na-4-mica.[2−9] However, the thermal stability and dehydration−rehydration behavior observed in this study clearly shows that drying and storage of the NaCl melt product could be conducted at any temperature less than
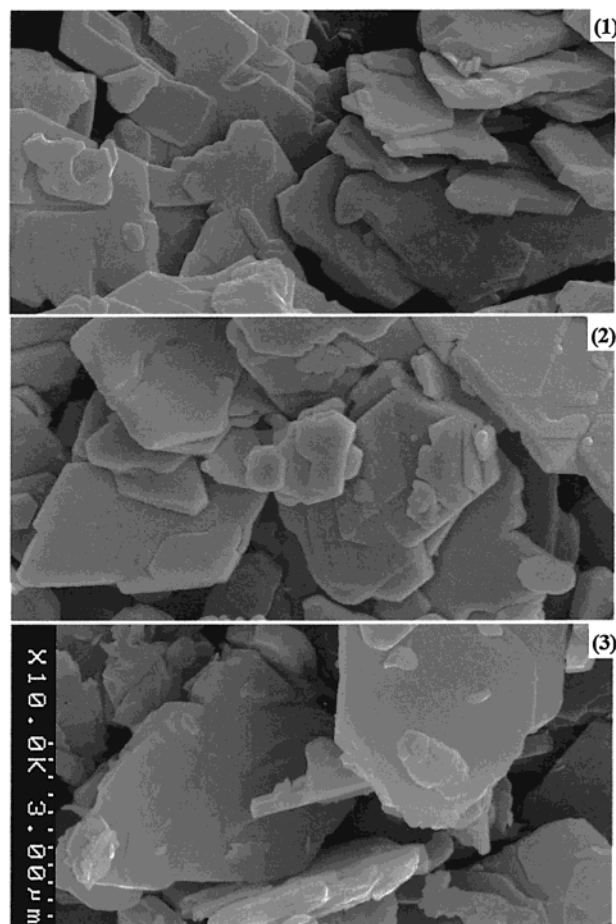

Figure 5. Scanning electron micrographs of the washed NaCl melt products synthesized from different molar $NaCl/Al_2O_3$ ratios. (1) From the ratio of 6.0; (2) from the ratio of 4.0; (3) from the ratio of 2.0.

800 °C. Furthermore, reversible shift of all the peaks on dehydration−rehydration process strongly suggests the presence of a single crystalline phase, the pure Na-4-mica, in the NaCl melt product.

Scanning electron micrographs (Figure 5) reveal hexagonal crystallites typical of mica morphology. The morphologies such as granule or sphere that were frequently found previously[3,4] were not detected. Another interesting result was that crystal size was significantly affected by the ratio of NaCl in the initial reactant mixture. As shown in Figure 5, larger amounts of NaCl led to smaller crystal size as well as more homogeneous particle size distribution. The approximate crystal size of 3 μm, similar to those of the reported Na-4-mica,[3,4] was obtained when the molar ratio of $NaCl/Al_2O_3$ was adjusted to the value of 4.0, whereas the increase of the above molar ratio to a value of 6.0 led to a decreased crystal size of approximate 2 μm in length, which was comparable to that of a reported ultrafine Na-4-mica.[9] Because Na-4-mica has layered structure, the crystal size greatly influences the cation-exchange kinetics, especially those of larger cations. It was shown that faster cation-exchange reaction could be accomplished by smaller crystal size.[4,8,9] The above result clearly shows that the crystal size of the NaCl melt product could be manipulated to a limited extent simply by controlling the NaCl content in the initial reactant mixture.

Table 1. Observed and Calculated *d* Values of Hydrated and Anhydrous Na-4-micas for Indexed Reciprocal Lattices

h	k	l	observed *d* value (Å)	calculated *d* value (Å)	observed relative intensity
			Hydrated Na-4-mica		
0	0	1	12.1092	12.1999	100
0	0	2	6.0669	6.1000	5
0	0	3	4.0474	4.0666	4
0	0	4	3.0415	3.0500	22
0	2	3	3.0387	3.0380	18
1	3	0	2.6421	2.6425	5
2	0	−**1**	2.6338	2.6337	5
2	0	1[a]	2.5552	2.5554	6
2	0	−**2**	2.5007	2.5013	8
0	0	5	2.4396	2.4400	3
2	0	−3[a]	2.3008	2.3006	3
2	2	0[a]	2.2951	2.2953	3
1	2	4	2.2376	2.2370	2
2	2	1[a]	2.2302	2.2304	2
2	0	−**4**[a]	2.0782	2.0784	4
2	1	−**4**	2.0265	2.0268	2
0	0	6	2.0242	2.0333	2
1	4	2[a]	1.9677	1.9674	3
2	0	4	1.9340	1.9339	1
2	0	−5[a]	1.8653	1.8651	1
2	0	5	1.7348	1.7346	2
2	0	−**6**	1.6735	1.6739	2
3	1	3[a]	1.5578	1.5580	2
2	1	6[a]	1.5380	1.5380	4
0	1	8[a]	1.5045	1.5042	2
3	0	−**3**[a]	1.6676	1.6675	2
			Anhydrous Na-4-mica		
0	0	1	9.9055	10.0291	100
0	0	2	4.9540	5.0145	9
0	2	0	4.5998	4.5992	4
0	2	2	3.3189	3.3895	80
0	0	3	3.3065	3.3430	80
1	3	0	2.6477	2.6477	25
2	0	−1	2.6497	2.6491	25
1	1	3	2.5290	2.5286	7
2	0	1[a]	2.4424	2.4426	23
1	3	2[a]	2.2646	2.2647	34
−**2**	0	3[a]	2.2539	2.2536	8
2	0	2[a]	2.1820	2.1822	5
0	4	1[a]	2.2417	2.2414	9
2	0	−**4**	1.9820	1.9844	17
2	0	3	1.9162	1.9165	3
1	3	4[a]	1.7491	1.7492	3
−**2**	0	5[a]	1.7385	1.7386	3
2	0	4[a]	1.6799	1.6798	4
−**1**	3	5	1.6670	1.6672	4
3	1	2[a]	1.5510	1.5509	11
−**3**	1	4[a]	1.5393	1.5394	11
0	0	7	1.4330	1.4329	5

[a] Applied for calculation of cell parameters.

Table 2. Calculated Cell Parameters for Hydrated and Anhydrous Na-4-micas

cell parameter	hydrated Na-4-mica	anhydrous Na-4-mica
a (Å)	5.3221 (0.0002)[a]	5.3248 (0.0004)
b (Å)	9.1423 (0.001)	9.1986 (0.003)
c (Å)	12.2342 (0.0007)	10.1762 (0.003)
β (deg)	94.175 (0.004)	99.517 (0.004)
cell volume (Å^3)	593.7 (0.07)	491.4 (0.06)

[a] Standard deviation error.

Redfern.[24] Indexed *d* spacings and calculated cell parameters are given in Tables 1 and 2.

Monoclinic crystal system could be applied to both the anhydrous and the hydrated Na-4-mica phases. All the identifiable peaks 3 times stronger than background noise were successfully indexed within the average standard deviation of 0.01° 2θ. Cell parameters were calculated from the marked peaks (see Table 1) positioned in the 2θ range from 35° to 65° within the standard deviation of less than 0.004° 2θ. For the XRD pattern of the anhydrous form that was recorded at 800 °C, the peaks with 2θ values less than 35° were excluded for the calculation of average standard deviation because of larger deviations. However, the peak with $l = 0$ was indexed within the average standard deviation.

Calculated cell parameters of the anhydrous Na-4-mica phase were $a = 5.3248$ Å, $b = 9.1986$ Å, $c = 10.1762$ Å, and $\beta = 99.545°$, whereas those of the hydrated Na-4-mica phase were $a = 5.3221$ Å, $b = 9.1423$ Å, $c = 12.2342$ Å, and $\beta = 94.175°$. Taking account of the fact that the observed *d* values of the anhydrous Na-4-mica phase were obtained at 800 °C, it is reasonable that the unit cell parameters of *a* and *b* are same in both the anhydrous and hydrated Na-4-mica phases. Decrease in the β value by hydration indicates that displacement and swelling of layers take place to accommodate water molecules between the interlayers.

The 00*l* peaks were very strong, which indicates a typical layered structure. In addition, the *h*0*l* peaks were found also to be relatively strong. The calculated cell parameters and monoclinic crystal system were very similar to those reported by Gregorkiewitz and Rausell-Colom.[14] The anhydrous phase exhibited a larger *c* value than the reported one, probably due to extremely high temperature, whereas the β value of the hydrated phase was much less than the reported one, indicating more displacement. The other cell parameters were similar to the reported ones. This result confirms that Na-4-mica could be stabilized through the unique displaced stacking mode suggested by Gregorkiewitz and Rausell-Colom.[14] In this stacking mode, adjacent layers are displaced parallel to the layer plane so that every hole formed by the hexamer silicate rings becomes an independent cavity to accommodate four Na cations per unit cell. The one sheet of water molecules between adjacent layers satisfies the coordination number of the interlayered Na$^+$ to result in the stable hydrated form.

The XRD pattern of the all-in-one product looked very similar to that of the NaCl melt product except for several impurity peaks. Typically, the peaks at *d* values of 4.21 and 2.60 Å were found to be relatively strong.

Powder XRD Patterns of the NaCl Melt Product. The powder XRD patterns of pure Na-4-mica phases were evaluated with the XRD patterns of the NaCl melt product because the above results suggest the absence of impure crystalline phases in the NaCl melt product. The XRD pattern at room temperature (the washed products in Figure 1) was taken for the hydrated Na-4-mica phase, and that (spectrum 2 in Figure 4) at 800 °C for the corresponding anhydrous Na-4-mica phase. General procedures such as the Ito method[23] were employed to index the XRD peaks. Cell parameters were calculated by the program developed by Holland and

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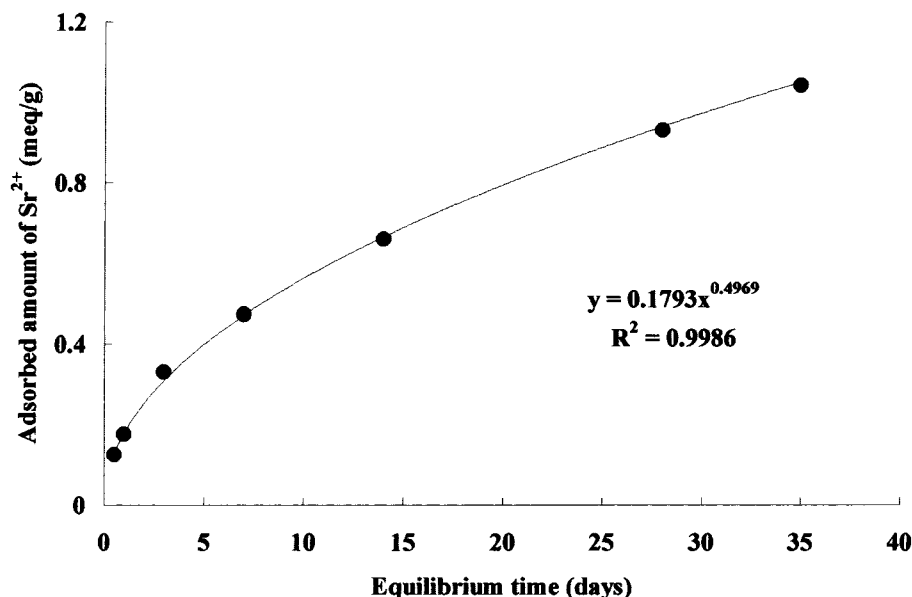
Figure 6. Sr^{2+} uptake isotherm of the NaCl melt product in the 2 mN Sr^{2+} solution in the presence of 0.5 N NaCl.

Careful comparison of the XRD patterns revealed that these peaks, including the weak peaks at the *d* values of 2.10 and 1.82 Å, were mostly due to the presence of sodium aluminosilicate phase ($Na_6Al_4Si_4O_{17}$, JCPDS no. 10-0033). In addition, the fact that the all-in-one product did not show several peaks present in the NaCl melt product is apparently due to low quality of the synthesized crystals in the former method.

Sr^{2+} Exchange Property of Pure Na-4-mica. Exchange reaction of Na-4-mica with large cations such as Sr^{2+} and Ba^{2+} had been known to deteriorate the layer structure of hydrated Na-4-mica.[2,4,6] The subsequent layer collapse was reported to result in the immobilization of the radioactive cations. In this study, cation-exchange properties of pure Na-4-mica were examined with Sr^{2+}. The Sr^{2+} uptake behavior of the NaCl melt product was studied in the 2 mM Sr^{2+} solution in the presence of 0.5 N NaCl (Figure 6), and the NaCl melt products treated in the 2–10 mM Sr^{2+} solutions for 4 weeks were also examined by XRD (Figure 7).

The Sr^{2+} uptake by the NaCl melt product was found to proceed more slowly and steadily than reported.[3,6,9] Even 5 weeks was not enough for the reaction to be equilibrated. The Sr^{2+} uptake isotherm was well described by the power function model that is indicative of the diffusion-controlled reaction.[25,26] On the other hand, any noticeable structural deterioration by the Sr^{2+} uptake was not found in the XRD patterns (Figure 7). Only a slight increase in the *d* spacings and a change in the relative intensities were clearly observed in the XRD patterns (the peaks at the *d* spacings of 2.824 and 1.998 Å in Figure 7 are from the presence of NaCl). Furthermore, the observed Sr^{2+} uptake capacity of the NaCl melt product was estimated to be 295 mequiv/100 g in the 0.1 M Sr^{2+} solution in the presence of 0.5 M NaCl with the 8-day equilibrium time (no structural deterioration was also observed).
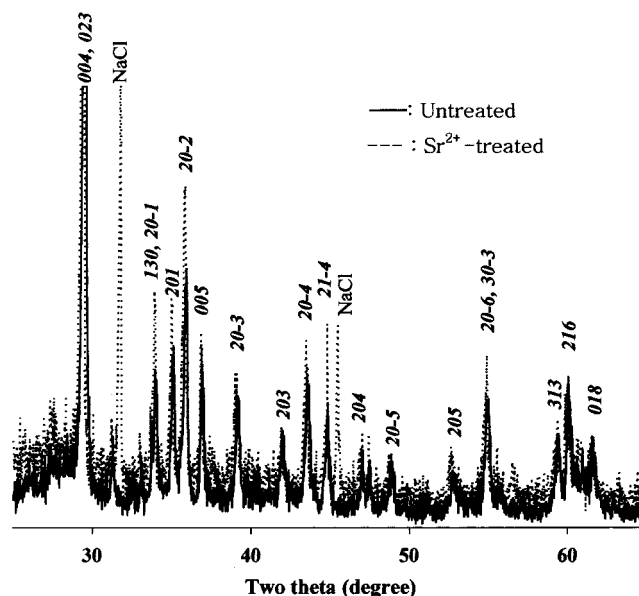
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Figure 7. Change in the XRD pattern of the NaCl melt product by the treatment of the 10 mN Sr^{2+} solution in the presence of 0.5 N NaCl for 4 weeks.

It had been postulated that layer collapse of hydrated Na-4-mica into a stable anhydrous phase could be expected when the Na^+ ions were replaced by larger cations and at the same time the number of interlayer cations was reduced to two per unit cell.[14] Replacement of Na^+ ions by Sr^{2+} ions would meet this requirement. On the basis of this postulation, it is possible that all Na ions could be exchanged by Sr^{2+}. However, it was reported that Sr^{2+} exchange reaction led not to the transformation of hydrated Na-4-mica into the anhydrous phase but to a disordered structure.[2,4,5] The structural disorder had been explained by the localized collapse among the expanded layers.[2,4,5,14] The exchange reaction of hydrated Na-4-mica would proceed gradually from the edges of crystals to the interior due to its layered structure. The initial exchange reaction at the edges would result in the localized layer expansion with subsequent layer collapse at the edges when enough

Sr^{2+} was taken up. This would prevent the exchange reaction from proceeding to the interior of the crystals. Consequently, low Sr^{2+} uptake capacity had been considered to be inevitable despite the extremely high cation-exchange capacity (the maximal uptake capacity of Na-4-mica for Sr^{2+} had been roughly estimated to be half of its cation exchange capacity, 468 mequiv/100 g on an anhydrous basis[2]).

However, it is highly feasible that the localized layer collapse can be avoided if the Sr^{2+} exchange reaction proceeds through homogeneous layer expansion of a whole crystal. Our results (Figures 6 and 7) indicate that the homogeneous layer expansion takes place to result in high stability against the Sr^{2+} exchange reaction. The layer expansion was well reflected by the increase in the d spacings without any noticeable decrease in overall intensity, while the Sr^{2+} exchange reaction resulted in a change of the relative intensities. In addition, the compliance of the Sr^{2+} uptake isotherm to the power function model also indirectly supports the homogeneous layer expansion. The diffusion of large Sr^{2+} ions could be allowed only when the interlayers are expanded. The crucial role of the Sr^{2+} diffusion in the uptake rate implies a wide range of layer expansion. The slow uptake rate could also be explained by the homogeneous layer expansion that apparently requires enough time, although the uptake rate is greatly affected by the crystal size. Recently, Kodama et al.[9] also reported that the nearly pure and ultrafine Na-4-mica

allowed more than 70% of Na ions to be replaced by Sr^{2+} without layer collapse (its Sr^{2+} uptake capacity was estimated to be about 300 mequiv/100 g in 0.1 M Sr^{2+} solution with the 8-day equilibrium time at 70 °C), although neither detailed structural information nor any reasonable explanations were available. From these results, it appears that the reported structural collapse may have resulted from the presence of the intergrown anhydrous impurities. Because the nonswelling impurities were intergrown with Na-4-mica crystals, their presence in Na-4-mica crystal inhibited the homogeneous layer expansion. Therefore, pure Na-4-mica could accommodate the theoretical amount of Sr^{2+} without the layer collapse through the homogeneous interlayer expansion.

Conclusions

We developed a NaCl melt method for the bulk synthesis of phase-pure Na-4-mica that does not require tedious postpreparation procedures. The powder XRD patterns indicated that the series of $h0l$ peaks were relatively strong along with the very strong $00l$ peaks. Pure Na-4-mica synthesized here showed extremely high thermal stability, completely reversible dehydration−rehydration behavior, and exceptionally high uptake capacity and stability with Sr^{2+}.