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Simplified Synthesis of Na-4-Mica from Kaolinite and Its Cation-Exchange Properties

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ABSTRACT

The synthetic process of a high-charge-density sodium fluorophlogopite mica, Na-4-mica (with an ideal chemical composition of $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot nH_2O$), using kaolinite as a raw material, has been investigated with respect to developing a simplified procedure and controlling crystal size. A fine and highly crystalline phase of the hydrated Na-4-mica, which is essential for practical applications, could be easily prepared from a mixture of kaolinite (or metakaolin) and magnesium nitrate using NaF flux at temperatures below 800°C. An increased mass of NaF flux in the simplified process at 800°C yielded somewhat larger and well-dispersed Na-4-mica crystals with hexagonal and plate-like shapes of 2–3 μm in size. Cation-exchange equilibria was studied for alkaline earth metal ions of Sr, Ba, and Ca, as well as transition metal ions of Cu and Pb, at room temperature using the hydrated Na-4-mica synthesized by the simplified process. The order of selectivity for the alkaline earth metal ions was $Ba^{2+} >> Sr^{2+} > Ca^{2+}$, and the cation-exchange capacities were 197, 83, and 77 mequiv $(100\ g)^{-1}$, respectively.

INTRODUCTION

A highly charged sodium fluorophlogopite mica, $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot xH_2O$, analogous to brittle micas, was first prepared by Gregorkiewitz et al. in 1974 and was informally named Na-4-mica (1). The ion-exchange capacities

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of clay minerals, such as the smectite and kaolinite types, are frequently less than 100 milliequivalents (meq) per 100 g of dry clay (2). However, the Na-4-mica has a theoretical cation-exchange capacity of 468 mequiv $(100\ g)^{-1}$ on an anhydrous basis. Thus, this phase extends the range of interesting clay minerals as inorganic cation exchangers (3–9). Gregorkiewiz and Rausell-Colom reported that this new synthetic silicate has a trioctahedral 2:1 layer, similar to those in fluorphlogopite, but with an unusually high Al to Si substitution in the tetrahedral sheet (3). This mica contains an unusually large number of four interlayer monovalent ions of sodium per unit cell for the compensation of the high layer charge. No mica with more than two interlayer cations per unit cell has ever been observed before. The Na-4-mica is unique among micas because it becomes hydrated on contact with water or even in air at ambient conditions. The presence of an unusually large number of interlayer cations and a resulting offset layer stacking by 1/3 *b* allows the structure to expand from a dehydrated 9.81 Å to a hydrated 12.18 Å *c*-axis spacing to achieve a more thermodynamically stable interlayer structure. Hydration of the interlayer space facilitates cation diffusion and exchange in the interlayers of this special swelling mica.

A very fine and pure phase of Na-4-mica was previously prepared by solution-sol-gel processing using tetraethoxysilane, aluminum nitrate, and magnesium nitrate, and was shown to have high cation-exchange selectivities for many divalent transition-metal ions and for strontium and barium, but not for the alkali-metal ions and the alkaline earth cations of magnesium and calcium (4, 5). This method, however, is not cost-effective because of the use of expensive chemicals, such as tetraethoxysilane, and the long and complicated procedure. For this reason a somewhat simplified procedure was later developed for the synthesis of this mica by using fumed silica as the silica source (6). For waste disposal or metals recovery applications, it is necessary to develop an even more cost-effective synthetic process for Na-4-mica.

We recently reported the synthesis of Na-4-mica using calcined kaolinite (metakaolin) as an economical aluminosilicate source (7). Na-4-mica was obtained from a mixture of NaF, ultrafine MgO, and metakaolin at 850–890°C. The selective cation-exchange properties for bivalent transition and heavy metals of Cd, Ni, Co, Mn, Zn, Pb, and Cu were previously reported using this synthesized Na-4-mica (8, 9). Naturally occurring kaolinite has the desired 1:1 Si to Al molar ratio in its theoretical chemical composition $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ and serves as a good aluminosilicate source for the synthesis of Na-4-mica. This original process yielded the plate-like and hexagonal Na-4-mica particles (Fig. 1). The crystallite size ranged between 2 to 10 μm. The clearly distinguishable edges with the hexagonal shape indicate the high crystallinity of the Na-4-mica, but many crystallites agglomerate to form massive grains. Furthermore, a small proportion of the Na-4-mica phase was frequently

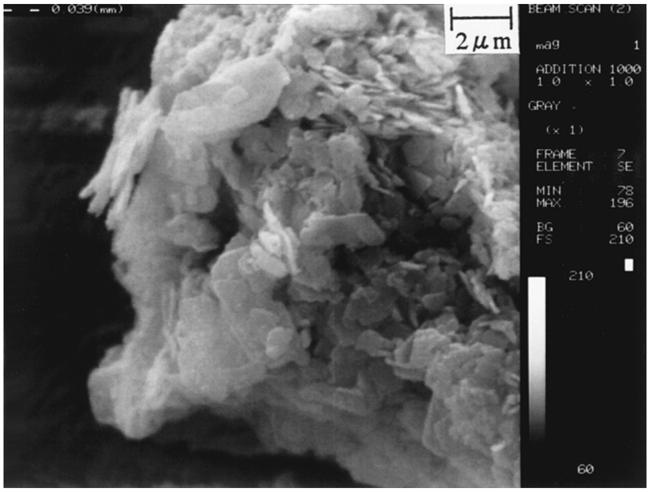

FIG. 1 SEM micrograph of the Na-4-mica prepared by the original procedure (i) at 890°C. Metakaolin (2.00 g) and ultrafine MgO (1.16 g) were mixed with an equal mass of NaF (3.16 g) for the preparation of the precursor mixture.

formed as an unhydrated phase which could not swell even by contact with water at room temperature. This could be due to the presence of a small amount of glassy phase on the edges of the particles which prevented hydration of the interlayers. The lower-temperature synthetic process from kaolinite may produce a well-dispersed and pure hydrated Na-4-mica phase with smaller crystal sizes.

We now report the development of a simplified and lower-temperature process for the preparation of pure, fine, and highly crystallized Na-4-mica from kaolinite. The cation exchange for alkaline earth metal ions of Sr, Ba, and Ca, as well as heavy metal ions of Cu and Pb, was also demonstrated at room temperature with the high-charge-density ion exchanger of the Na-4-mica synthesized by this simplified and lower-temperature procedure.

EXPERIMENTAL

Synthetic Procedures

In order to develop a simplified and lower-temperature procedure for the preparation of the Na-4-mica from kaolinite, Na-4-mica samples were prepared by a number of methods developed sequentially from this original procedure, (i). We first attempted to prepare Na-4-mica at low temperatures of 700–800°C by using this original procedure, which is briefly outlined as follows. A poorly crystallized kaolinite of composition 47.9% SiO_2, 38.3% Al_2O_3, 2.08% TiO_2, 0.98% Fe_2O_3, 0.15% FeO, and 0.03% MgO (supplied by

Georgia Kaolin Company through W. D. Johns, Department of Geology, University of Missouri, Columbia, MO 65201, USA), ultrafine MgO (supplied by Ube Industries, Ube, Japan), and NaF were the starting materials for the synthesis of the Na-4-mica. The poorly crystallized kaolinite was first calcined at 700°C for 18 hours to transform it to amorphous product (on heating to around 600°C, kaolinite is completely dehydrated and loses its crystalline character) which is the so-called metakaolin ($Al_2Si_2O_7$). The metakaolin was cooled and stored in a desiccator over silica gel at room temperature. The water content of ultrafine MgO was determined to be 6.0 wt% by thermal analysis using TG DTA 2010, Mac Science. Appropriate proportions of the ultrafine MgO (1.16 g) and the metakaolin (2.00 g) were mixed to obtain a stoichiometric composition. Then it was mixed with an equal mass of NaF (3.16 g), well homogenized using a pestle and mortar, and transferred to a platinum vessel. The precursor mixture was heated for 24 hours at 700–800°C in air using a programmed furnace. The resulting solids were ground and washed in deionized water several times to remove excess NaF. Any remaining impurity phases, such as insoluble fluoride salts, were then removed with repeated washings using saturated boric acid solution. Then the solid was washed with 1 M NaCl solution three times to completely saturate all the exchange sites with Na^+. The product was finally washed with deionized water and dried at 60°C in an oven for 2–3 days. The products thus prepared were stored in a desiccator over silica gel at room temperature.

As discussed later, the above original procedure did not yield a pure phase of Na-4-mica at temperatures between 700 and 800°C. Thus, in order to synthesize a pure Na-4-mica phase from kaolinite at these low temperatures, three modified procedures were attempted at 700–800°C as follows. For the second method, designated as (ii), the same basic procedure as for (i) was employed but magnesium nitrate was used as the magnesium source instead of ultrafine MgO. $Mg(NO_3)_2 \cdot 6H_2O$ (6.92 g) and metakaolin (2.00 g) (at a stoichiometric ratio) were mixed with 3.16 g of NaF [the same mass of NaF flux as used in the procedure (i)], and well homogenized using a pestle and mortar. For the third method, designated as (iii), the same procedure as for (ii) using magnesium nitrate was employed but an increased mass of NaF flux was used. $Mg(NO_3)_2 \cdot 6H_2O$ (6.92 g) and metakaolin (2.00 g) were mixed with an equal mass of NaF (8.92 g) and well homogenized. For the fourth method, designated as (iv), the first step of the calcination of poorly crystallized kaolinite at 700°C for the preparation of metakaolin was eliminated from procedure (iii). Poorly crystallized kaolinite was used directly for the preparation of the precursor mixture. The poorly crystallized kaolinite (2.00 g) and $Mg(NO_3)_2 \cdot 6H_2O$ (5.93 g) (at a stoichiometric ratio) were mixed with an equal mass of NaF (7.93 g) and well homogenized. The water content of poorly crystallized kaolinite was previously determined to be 14.16 wt% by thermal analysis. The precursor mixture was calcined directly between 700 and 800°C.

Characterization of Products

Powder x-ray diffraction (XRD) was carried out to check for phase purity and to determine the basal spacings of Na-4-mica using a Rigaku RAD-γA diffractometer with CuKα radiation. Scanning electron microscopy (SEM) was used to determine the particle size and shape (EPMA-8705, Simadzu). The water content of hydrated Na-4-mica was determined by thermal analysis.

Cation-Exchange Studies

The $2Na^+ \rightarrow M^{2+}$ (M = Sr, Ba, Ca, Cu, and Pb) exchange reaction was studied using Na-4-mica which was prepared by the most simplified procedure (iv) at 800°C. The ion-exchange isotherms were determined as follows. A 25-mg portion of Na-4-mica (anhydrous basis) was equilibrated with 25 cm^3 of the mixed solution having different mole ratios of Na^+/M^{2+} with shaking at 25°C for 4 weeks. The total normality of the solutions was kept constant at 0.00468 N ($Na^+/M^{2+} = 0.0$–0.9). The prepared Na-4-micas were basic; when the mica was added into the solution without adjusting the pH (25 mg of anhydrous mica + 25 cm^3 of the solution), the pH of the solution quickly increased to 8–9 where copper and lead precipitated by hydrolysis. Thus, for the Cu and Pb exchange reactions, to avoid the hydrolysis of cations in the solution and the precipitation of metal hydroxides and oxides, the pH's of the solutions were previously set to 3.0 by adding HCl solution before the cation exchange reaction. The pH of the solution for the Cu and Pb exchange reaction increased in a few minutes to about 4–5 upon equilibration with mica. This increase of the pH of the solution was because the OH^- species absorbed on the surface of the mica were neutralized. After 4 weeks equilibration the supernatant solution was analyzed for the divalent metal ions by atomic emission spectrometry (ICP, Seiko Instruments SPS-1500V). The amounts of metal ions exchanged or released by Na-4-mica were determined from the difference in the concentration between the sample solution and the reference. The theoretical cation-exchange capacity [468 mequiv $(100\ g)^{-1}$ of the anhydrous form] was used to represent the ion exchange isotherm.

The distribution coefficient, K_d, was determined as follows. A 20-mg sample of the mica (anhydrous basis) was equilibrated with 25 cm^3 of a 0.5 N NaCl containing 0.0001 N MCl_2 ($M = Sr^{2+}$, Ba^{2+}, and Ca^{2+}) at 25°C. After 24 hours the solid and solution phases were separated by centrifugation. The solutions were analyzed for M^{2+} by ICP to determine the amount remaining in solution. The uptake of M^{2+} was determined from the difference in the concentration between the sample and the reference. The K_d was calculated by the following equation:

$$K_d = \frac{[\text{amount of metal ions in exchanger (mequiv/g)}]}{[\text{amount of metal ions in solution (mequiv/cm}^3)]} \qquad (1)$$

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All the above cation-exchange experiments (isotherm and K_d determinations) were conducted in triplicate to check for reproducibility. The errors in the triplicates were about ±5%.

THEORETICAL

Ion-exchange theory used in the present work is described in previous papers (8, 9) and is briefly outlined as follows. The mono-divalent ion exchange process in the Na-4-mica is represented by

$$2\overline{\mathrm{Na}}^{+} + \mathrm{M}^{2+} \rightleftarrows 2\mathrm{Na}^{+} + \overline{\mathrm{M}}^{2+} \tag{2}$$

where the bar above symbols represents the ion-exchanger phase. $\overline{X}_i$ is an equivalent fractions of ion i in the ion-exchanger phase, defined by

$$\overline{X}_{\mathrm{Na}} = \frac{[\overline{\mathrm{Na}}^{+}]}{2[\overline{\mathrm{M}}^{2+}] + [\overline{\mathrm{Na}}^{+}]}, \qquad \overline{X}_{\mathrm{M}} = \frac{2[\overline{\mathrm{M}}^{2+}]}{2[\overline{\mathrm{M}}^{2+}] + [\overline{\mathrm{Na}}^{+}]} \tag{3}$$

The molarities $[\mathrm{Na}^{+}]$ and $[\mathrm{M}^{2+}]$ can be replaced by the equivalent fractions of the ions in the solution (X_i):

$$X_{\mathrm{Na}} = \frac{[\mathrm{Na}^{+}]}{2[\mathrm{M}^{2+}] + [\mathrm{Na}^{+}]}, \qquad X_{\mathrm{M}} = \frac{2[\mathrm{M}^{2+}]}{2[\mathrm{M}^{2+}] + [\mathrm{Na}^{+}]} \tag{4}$$

$$[\mathrm{Na}^{+}] + 2[\mathrm{M}^{2+}] = TN \tag{5}$$

where TN represents the total normality of the solution. Using a corrected selectivity coefficient, $\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}}$, the thermodynamic equilibrium constant is rewritten as (10)

$$\mathbf{K} = \frac{[\mathrm{Na}^{+}]^2\, \overline{X}_{\mathrm{M}} \gamma_{\mathrm{Na}}^2 f_{\mathrm{M}}}{[\mathrm{M}^{2+}]\, \overline{X}_{\mathrm{Na}}^2 \gamma_{\mathrm{M}} f_{\mathrm{Na}}^2} = \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} \frac{f_{\mathrm{M}}}{f_{\mathrm{Na}}^2} \tag{6}$$

where

$$\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = \frac{X_{\mathrm{Na}}^2\, \overline{X}_{\mathrm{M}} \gamma_{\mathrm{Na}}^2}{X_{\mathrm{M}} \overline{X}_{\mathrm{Na}}^2 \gamma_{\mathrm{M}}} [2(TN)] = \frac{(1 - X_{\mathrm{M}})^2\, \overline{X}_{\mathrm{M}} \gamma_{\mathrm{Na}}^2}{X_{\mathrm{M}} (1 - \overline{X}_{\mathrm{M}})^2 \gamma_{\mathrm{M}}} [2(TN)] \tag{7}$$

where $[\mathrm{Na}^{+}]$ and $[\mathrm{M}^{2+}]$ are molarities of the ions in solution. γ_i and f_i are activity coefficients in the solution phase and in the ion-exchanger phase, respectively. When the total normality, $TN = [\mathrm{Na}^{+}] + 2[\mathrm{M}^{2+}]$, is lower than 0.01 N, $\gamma_{\mathrm{Na}}^2/\gamma_{\mathrm{M}}$ will be close to unity.

A corrected selectivity coefficient larger than unity ($\ln \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} > 0$) indicates selectivity for the ion M^{2+} (11). Na^{+} ions are more preferred if $\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}}$ is smaller than unity ($\ln \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} < 0$). When $\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}}$ is equal to unity ($\ln \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = 0$), no preference between these ions is indicated.

A plot of log $\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}}$ vs $\overline{X}_{\mathrm{M}}$ or the Kielland plot is experimentally expressed by the polynomial function (12, 14):

$$\log \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = \sum_{m=1} (m+1) C_m \overline{X}_{\mathrm{M}}^{m} + \log(\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}})_{X_{\mathrm{M}} \to 0} \tag{8}$$

where the coefficient C_m is called the generalized Kielland coefficient. If the Gibbs–Duhem equation is applied to the ion-exchange reaction, the thermodynamic equilibrium constant, K, is given by the integration of the Kielland plot from $\overline{X}_{\mathrm{M}} = 0$ to $\overline{X}_{\mathrm{M}} = 1$ (15, 16):

$$\ln \mathbf{K} = (Z_{\mathrm{Na}} - Z_{\mathrm{M}}) + \int_0^1 \ln \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} d\, \overline{X}_{\mathrm{M}} + \Delta \tag{9}$$

Here, Z_{Na} and Z_{M} are the number of charges on Na^{+} and M^{2+}. The third term on the right, Δ, is negligible when compared with experimental accuracy in measuring the equilibrium (10).

The distribution coefficient, K_{d}, at infinitesimal exchange (very small $\overline{X}_{\mathrm{M}}$) is very important for interpreting the chromatographic behavior of metal ions. It is defined by

$$K_{\mathrm{d}} = [\overline{\mathrm{M}}^{n+}]/[\mathrm{M}^{n+}] \tag{10}$$

It can be calculated by Eq. (1).

RESULTS AND DISCUSSION

Materials Synthesis

Figure 2 shows XRD patterns of the resultant solids prepared at 700–800°C by using the original procedure, (i). That Na-4-mica was synthesized is evident from the presence of the first-order (001) reflection in the XRD pattern. In the XRD pattern of the product at 800°C (Fig. 2a), a strong peak for the (001) reflection was observed around $d = 11.96$ Å, which corresponded to a basal spacing of the hydrated form of Na-4-mica with a single sheet of interlayer water (3). However, many other peaks for impurity phases are also observed. The peaks of $d = 4.10$, 3.80, 3.23, and 2.98 Å are assigned to those of topaz ($\mathrm{Al_2SiO_4F_2}$). Two unknown peaks are observed at $d = 8.01$ and 2.85 Å. The peak intensities of topaz became stronger in the XRD patterns of the products prepared at 750 and 700°C (Figs. 2b and 2c). A peak for another impurity phase appears around $d = 4.14$–4.17 Å at 700–750°C; it may be due to cristobalite ($\mathrm{SiO_2}$). This peak became very strong at 700°C, and the (001) reflection peak of Na-4-mica became less intense and broadened at 700°C. A pure Na-4-mica phase could not be prepared by the original procedure by using a mixture of metakaolin, ultrafine MgO, and NaF at 700–800°C.

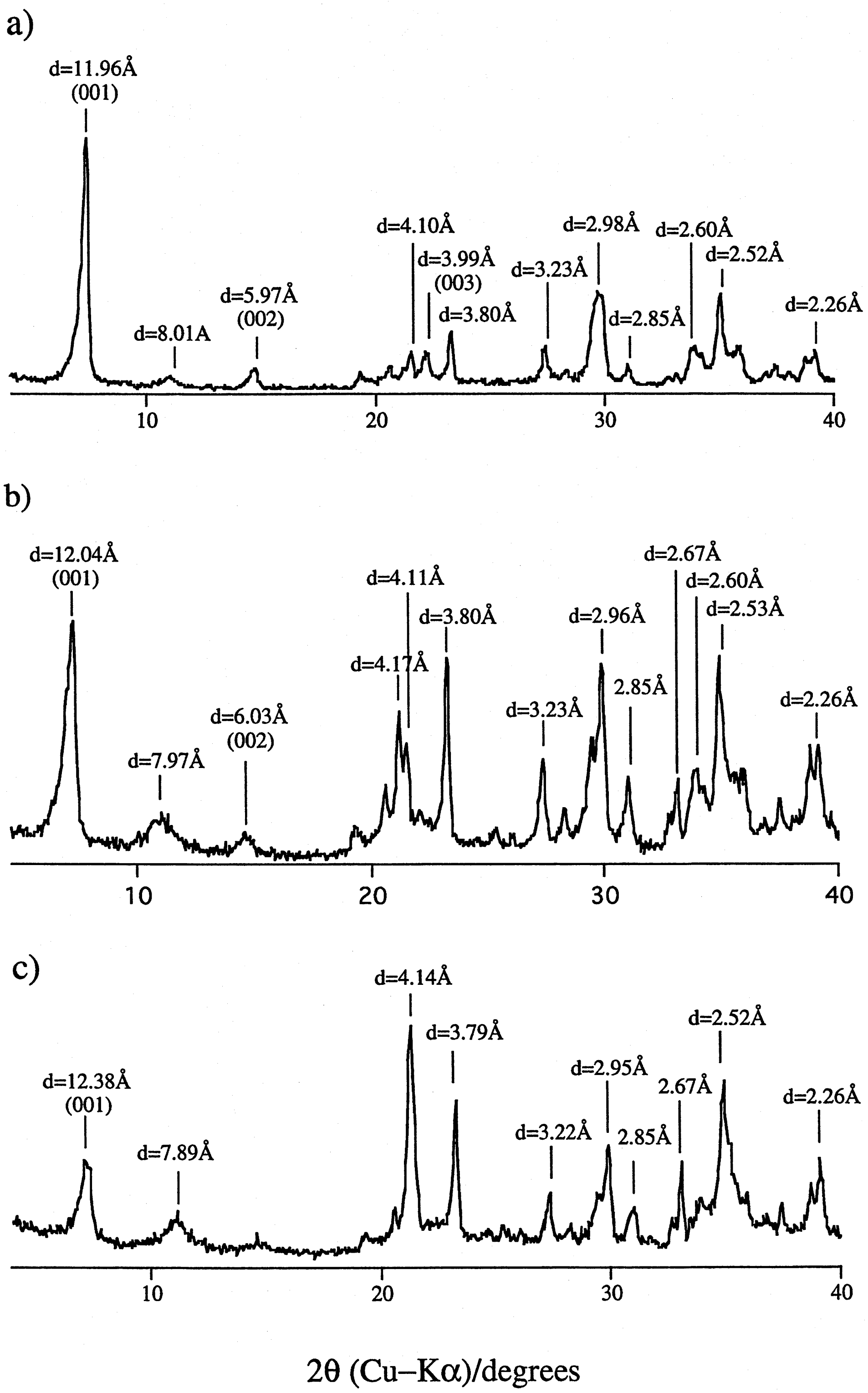

FIG. 2 XRD patterns of the Na-4-micas prepared by the original procedure (i) at a) 800, b) 750, and c) 700°C. Metakaolin (2.00 g) and ultrafine MgO (1.16 g) were mixed with an equal mass of NaF (3.16 g) for the preparation of the precursor mixture.

When magnesium nitrate was used as a source of magnesium instead of ultrafine MgO and using exactly the same masses of metakaolin and NaF flux as used in the original procedure (i), this procedure, (ii), gave pure phases of hydrated Na-4-mica at 700–800°C (Fig. 3). A strong peak for the (001) reflection of hydrated Na-4-mica with a single sheet of interlayer water is observed in the XRD patterns. Peaks observed around $d = 6.05$, 4.01, and 3.02Å are assigned to (002), (003), and (004) reflections of *c*-axis spacing of hydrated Na-4-mica. Specific characteristic peaks observed at 2.64, 2.56, and 2.51Å were almost consistent with the limited powder XRD data reported previously for hydrated Na-4-mica (5–7). The SEM micrograph of Na-4-mica prepared by procedure (ii) at 800°C shows crystallites of about 0.2–0.5 μm (Fig. 4a). The crystallites were somewhat plate-like but the hexagonal shapes are not clearly observed. Many crystallites agglomerated to form larger particles. Similar sized crystallites formed at 700 and 750°C, but almost all of the crystallites agglomerated to form massive grains (Figs. 4b and 4c). It is clear that magnesium nitrate has a much higher reactivity than ultrafine MgO and favors the low-temperature formation of the Na-4-mica, probably because $Mg(NO_3)_2$ melts at low temperatures which leads to better homogenization.

In procedure (iii) an increased mass of NaF flux was used compared to procedure (ii). The mixture of magnesium nitrate and metakaolin was mixed with an equal mass of NaF. The amount of NaF flux used was 2.8 times larger than in procedure (ii). A pure phase of the hydrated Na-4-mica was again produced at 800°C (Fig. 5a). The shoulder peak for the (001) reflection is due to the hydrated form with a structure containing double sheets of interlayer water (3). This suggests that this phase is more readily hydrated in comparison with that prepared by procedure (ii). In the SEM micrograph of the Na-4-mica prepared at 800°C (Fig. 6a), the hexagonal-shaped crystals are clearly observed, indicating the high crystallinity of the Na-4-mica. The crystallites grew larger in size and became well-dispersed in comparison to the Na-4-mica prepared using a smaller mass of NaF flux (procedure ii) at the same temperature. The Na-4-mica had a size distribution between 0.5 and 5 μm, and most of the crystallites were about 2–3 μm. The Na-4-mica crystals can grow in a larger mass of NaF flux and become dispersed. An almost pure phase of hydrated Na-4-mica was formed at 750°C although very small peaks at $d = 6.33$, 3.83 (topaz), and 3.67 Å, which are due to impurity phases, appeared in the XRD pattern (Fig. 5b). In the XRD pattern of the product prepared at 700°C, the unknown peak for $d = 3.67$ Å became more intense (Fig. 5c). The unknown peak for the impurity phase also appeared at $d = 7.94$ Å, which was observed for XRD patterns of the products prepared by the original procedure (i) at 700–800°C (Fig. 2). The SEM micrograph of Na-4-mica prepared at 750°C (Fig. 6b) shows that the crystallite sizes are almost the same as those prepared at 800°C, but the sample prepared at 800°C has the most clearly distinguishable edges with the

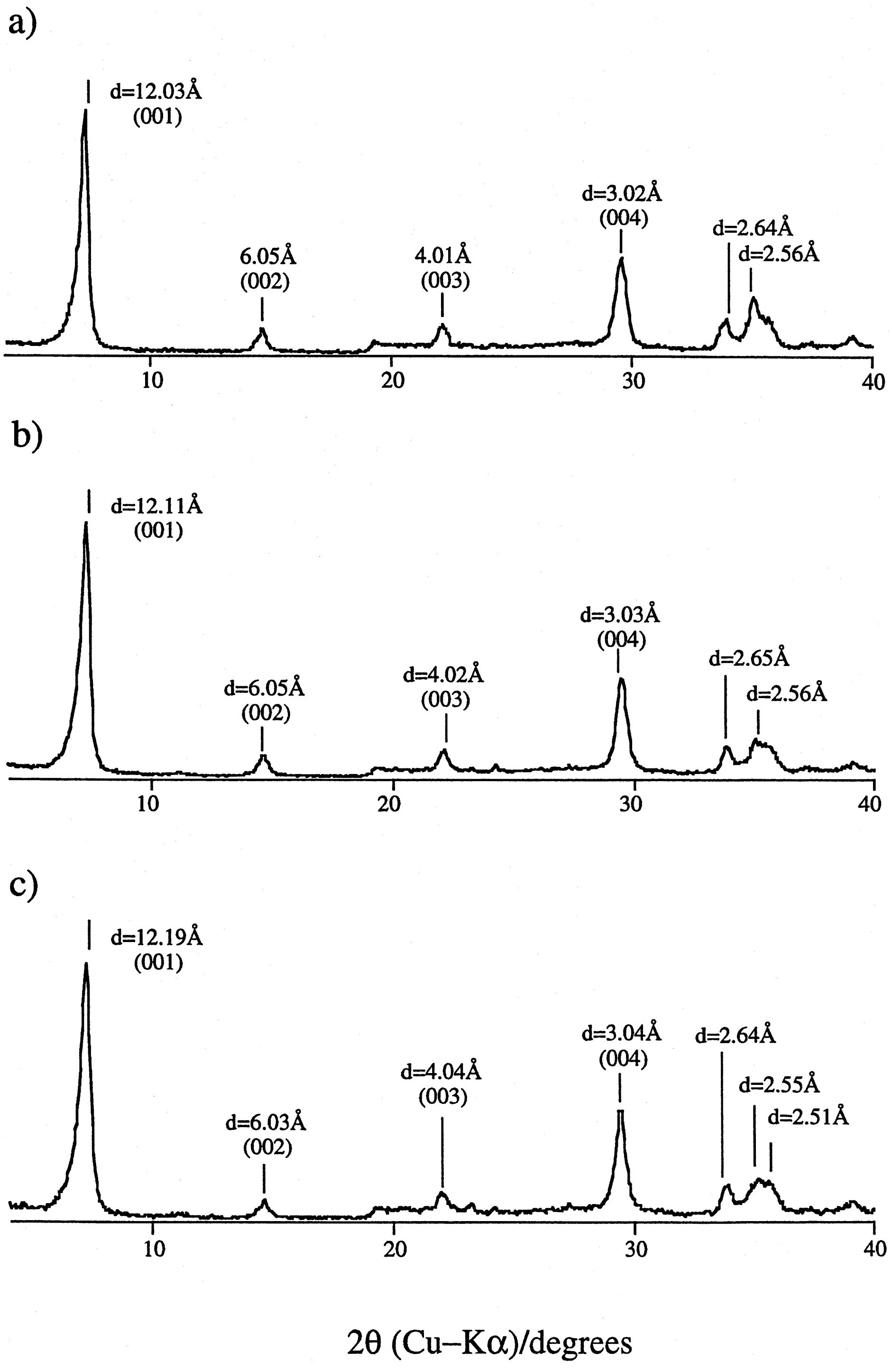

FIG. 3 XRD patterns of the Na-4-micas prepared by procedure (ii) at a) 800, b) 750, and c) 700°C. Metakaolin (2.00 g) and $Mg(NO_3)_2 \cdot 6H_2O$ (6.92 g) were mixed with the same mass of NaF (3.16 g) as used in procedure (i) for the preparation of the precursor mixture.

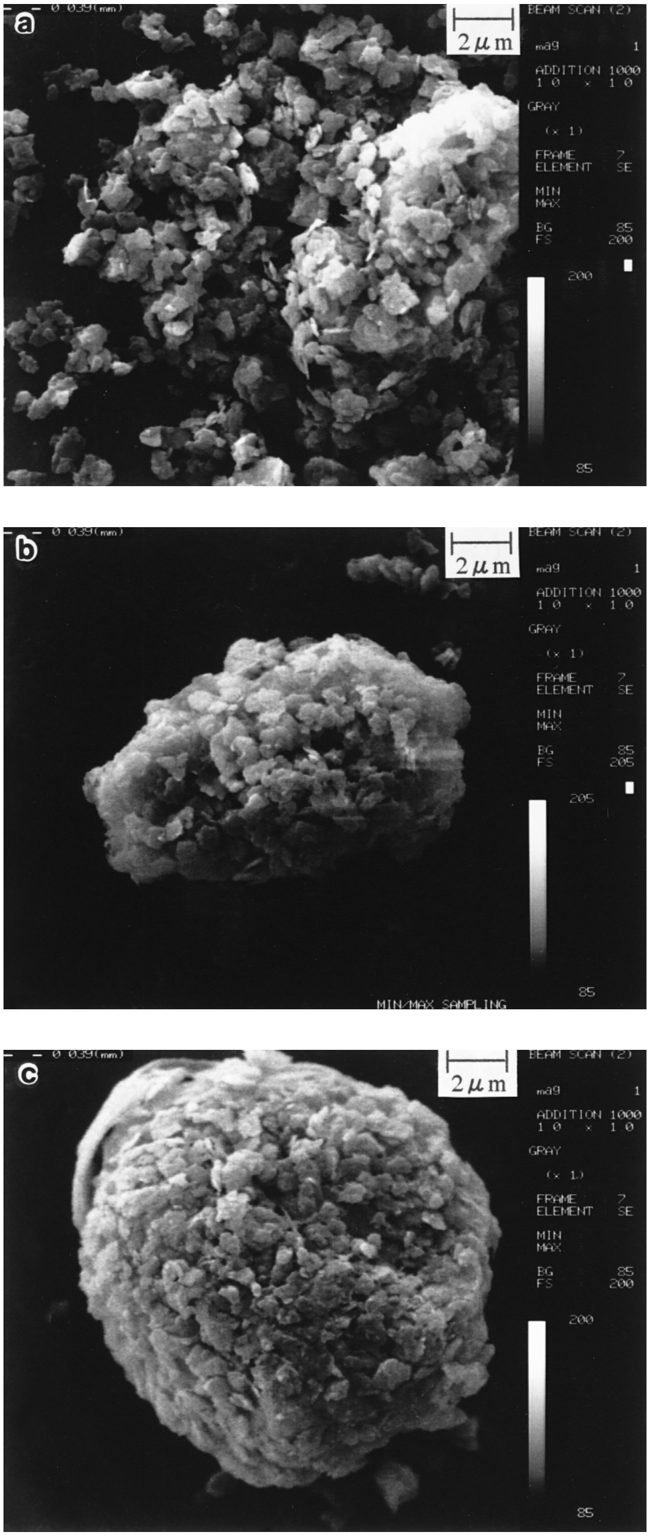

FIG. 4 SEM micrographs of the Na-4-micas prepared by procedure (ii) at a) 800°C, b) 750°C, and c) 700°C. The mixture of metakaolin (2.00 g), $Mg(NO_3)_2 \cdot 6H_2O$ (6.92 g) and NaF (3.16 g) was used as the precursor.

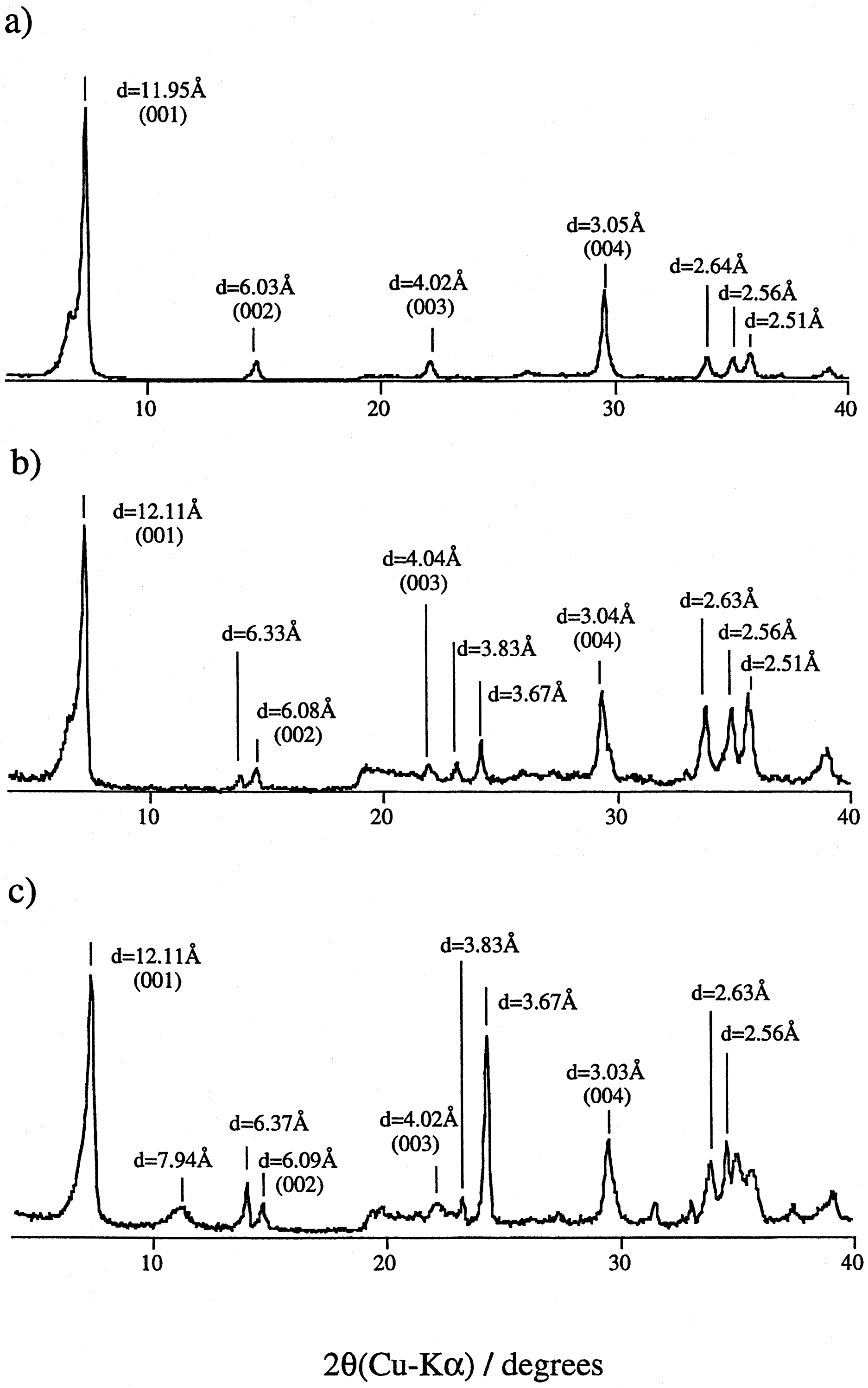

FIG. 5 XRD patterns of the Na-4-micas prepared by procedure (iii) at a) 800, b) 750, and c) 700°C. Metakaolin (2.00 g) and $Mg(NO_3)_2{\cdot}6H_2O$ (6.92 g) were mixed with an equal mass of NaF (8.92 g) for the preparation of the precursor mixture.

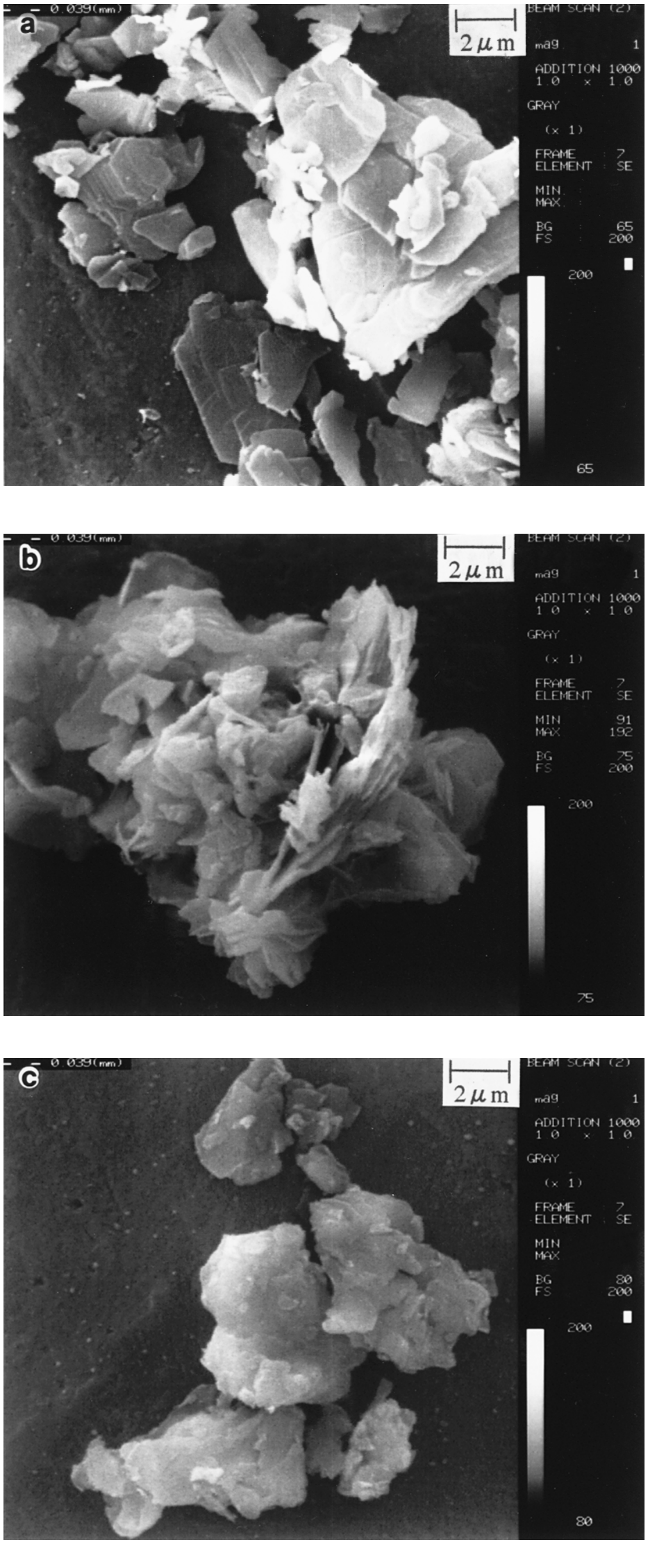

FIG. 6 SEM micrographs of the Na-4-micas prepared by procedure (iii) at a) 800, b) 750, and c) 700°C. The mixture of metakaolin (2.00 g), $Mg(NO_3)_2 \cdot 6H_2O$ (6.92 g), and NaF (8.92 g) was used as the precursor.

hexagonal shape (Fig. 6a). Undifferentiated plate-like particles were formed at 700°C (Fig. 6c). The crystallites tend to agglomerate and be glued together at a lower temperature.

In the final procedure (iv), poorly crystallized kaolinite was directly used for the preparation of the precursor mixture, eliminating the first step for the preparation of metakaolin from procedure (iii). Similar XRD and SEM results were obtained for procedure (iv) compared to procedure (iii) between 700 to 800°C, indicating that there is no difference in the reactivity between metakaolin and the original kaolinite for the preparation of Na-4-mica. In procedure (iv) we have succeeded in synthesizing well-dispersed and highly crystallized crystals of hydrated Na-4-mica of 2–3 μm size by one-step processing directly from a mixture of kaolinite, magnesium nitrate, and NaF at 800°C.

Ion Exchange for Cu and Pb

We previously reported the $2Na^+ \rightarrow Cu^{2+}$ or Pb^{2+} exchange isotherm and the Kielland plots with the Na-4-mica synthesized by procedure (i) at 890°C (9). In this report, highly selective Cu^{2+} and Pb^{2+} exchange was demonstrated at room temperature: the cation-exchange capacities were 225 and 257 mequiv $(100\ g)^{-1}$ of dry clay for Cu^{2+} and Pb^{2+}, respectively. Similar ion-exchange isotherms and Kielland plots were observed in the present work for the $2Na^+ \rightarrow Cu^{2+}$ and Pb^{2+} exchange reactions which were demonstrated with the Na-4-mica synthesized by the simplified procedure (iv) at 800°C (Fig. 7).

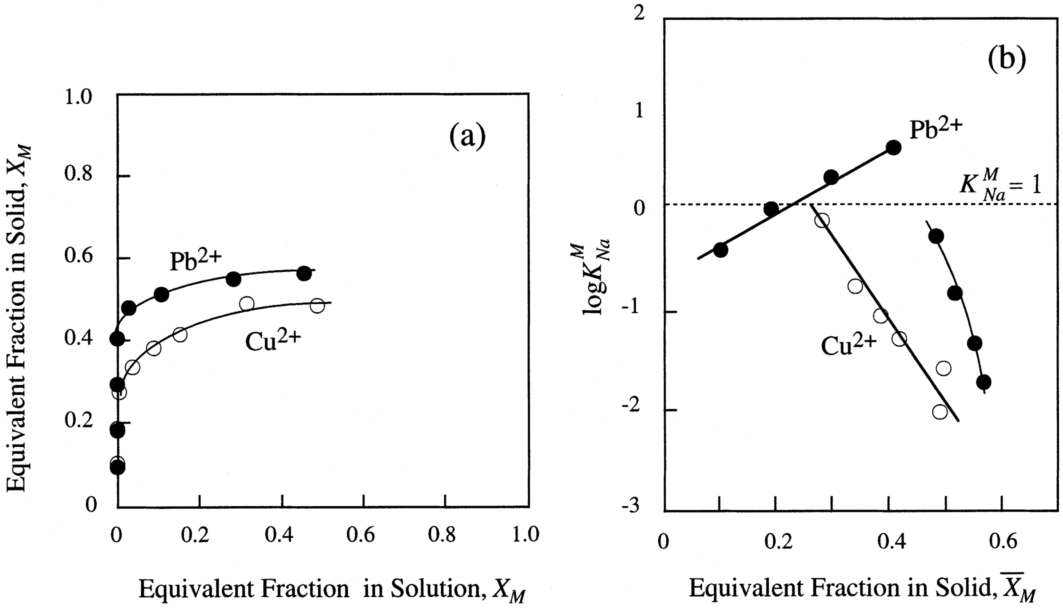

FIG. 7 Cation-exchange isotherms (a) and the Kielland plots (b) for $2Na^+ \rightarrow Cu^{2+}$ or Pb^{2+} exchange on the Na-4-micas prepared by procedure (iv) at 800°C. Total normality in the solution (*TN*) was 0.00468 N. Symbols: (○) Cu^{2+} and (●) Pb^{2+}.

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The Na-4-mica sample prepared by procedure (iv) at 800°C was used for all of the ion-exchange experiments reported in the present work. The cation-exchange capacities observed at $TN = 0.00468$ N had almost the same values as reported in the previous work, being 229 and 267 mequiv $(100\ \mathrm{g})^{-1}$ for Cu^{2+} and Pb^{2+}, respectively. The Kielland plots for the $2\mathrm{Na}^{+} \rightarrow \mathrm{Cu}^{2+}$ exchange gave a linear relation (Fig. 7b). The Kielland plots often give linear relationships with a slope of $2C_1$ in ion exchange with inorganic ion-exchange materials (17–19), in which case Eq. (8) can become

$$\log \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = 2\mathbf{C}_1\overline{X}_{\mathrm{M}} + \log(\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}})_{\overline{X}_{\mathrm{M}}\rightarrow 0} \qquad (11)$$

The generalized Kielland coefficient, C_1, is related to the energy term for the steric limitation or jumping barrier for the exchanging ions in the interlayer (13, 17). The linear relation indicates that the single-site ion exchange has the same energy term as the steric limitation in the interlayer. Generally, the C_1 value is negative, which means that ion exchange becomes difficult with progressive exchange. In this case the energy term for the steric limitation is larger as the $|\, C_1 \,|$ value is larger. By fitting the experimental $\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}}$ and corresponding $\overline{X}_{\mathrm{M}}$ values to a linear equation (Table 1), the Kielland coefficient C_1 was calculated to be -3.92. On the other hand, for $2\mathrm{Na}^{+} \rightarrow \mathrm{Pb}^{2+}$ exchange, a break point was observed at around $\overline{X}_{\mathrm{Pb}} = 0.40$ in the Kielland plots. The presence of a break point in the $2\mathrm{Na}^{+} \rightarrow \mathrm{Pb}^{2+}$ exchange isotherm is due to the collapse of the interlayer spacing of Na-4-mica, as indicated in the previous work (9), which was confirmed by powder x-ray diffraction which showed that the peak for (001) reflection at 12.1 Å rapidly became very weak or almost disappeared when $\overline{X}_{\mathrm{Pb}}$ became larger than about 0.40. This collapse of the basal spacing leads to the break point in the Kielland plots. By fitting the Kielland plots to a linear equation (Table 1), the Kielland coefficient C_1 for the initial stage of the lead-exchange reaction was estimated to be 1.65. It is interesting that the C_1 value is positive in this initial stage, which suggests that the energy term for the steric limitation or jumping barrier is rather reduced with progressive lead exchange in the initial stage. The same phenomenon was observed for Na-4-micas prepared by the original procedure (i) and solution-sol-gel processing at 890°C (9).

Almost the same cation-exchange behaviors to those in the previous work were observed on the selectivities and cation-exchange capacities for copper and lead exchange in the present work. These results suggest that Na-4-mica prepared by the simplified procedure has similar properties for cation-exchange equilibria to the one synthesized by the original procedure at 890°C. In the present work the values of $\Delta G°$ for the overall ion-exchange reaction could not be calculated because the Kielland plots were not obtained for high equivalent fractions (> 0.6) of metal in the micas.

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TABLE 1
Results of Fitting of the Experimental $\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}}$ and Corresponding $\overline{X}_{\mathrm{M}}$ Values to a Linear or Polynomial Equation

Exchanging ion	Range	Fitting	Equation	R[a]
Cu^{2+}	0.11–0.49	Linear	$\log \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = 2.03 - 7.83\overline{X}_{\mathrm{M}}$	0.097
Pb^{2+}	0.10–0.40	Linear	$\log \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = -0.64 + 3.29\overline{X}_{\mathrm{M}}$	0.048
	0.48–0.57	Polynomial	$\log \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = +0.22 + 12.6\overline{X}_{\mathrm{M}} - 28.1\overline{X}_{\mathrm{M}}^2$	0.080
Ba^{2+}	0.09–0.42	Linear	$\log \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = +2.73 - 12.2\overline{X}_{\mathrm{M}}$	0.201
Sr^{2+}	0.10–0.18	Polynomial	$\log \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = -11.7 + 208\overline{X}_{\mathrm{M}} - 919\overline{X}_{\mathrm{M}}^2$	0.115
Ca^{2+}	0.07–0.17	Polynomial	$\log \mathbf{K}_{\mathrm{Na}}^{\mathrm{M}} = -2.48 + 16.3\overline{X}_{\mathrm{M}} - 137\overline{X}_{\mathrm{M}}^2$	0.156

[a] The error of the fitting, $R = \dfrac{\sqrt{\sum_{n=1}^{N} (\log \mathbf{K}_{\mathrm{Na}_{\mathrm{obs}}}^{\mathrm{M}} - \log \mathbf{K}_{\mathrm{Na}_{\mathrm{calc}}}^{\mathrm{M}})^2}}{N - M - 1}$, where N is the number of $\mathbf{K}_{\mathrm{Na}}^{\mathrm{M}}$ and $\overline{X}_{\mathrm{M}}$ pairs, and M is the order of the polynomial.

Ion Exchange for Alkaline Earth Metals of Sr, Ba, and Ca

The distribution coefficients, K_ds, for the exchange of Sr^{2+}, Ba^{2+}, and Ca^{2+} from a background solution of 0.5 N NaCl are presented in Table 2. This mica was highly selective for Ba^{2+}, and the order of the selectivity was $Ba^{2+} >> Sr^{2+} > Ca^{2+}$. Ba^{2+} ion is less hydrated (Stokes radius: $r_s = 290$ pm) in comparison to Sr^{2+} and Ca^{2+} (r_ss $= 310$ pm), which may facilitate the migration of cation in the interlayer spacings.

Figure 8(a) shows the $2Na^+ \rightarrow Sr^{2+}$, Ba^{2+}, and Ca^{2+} exchange isotherms. The barium-exchange capacity at $TN = 0.00468$ N, 197 mequiv (100 g)$^{-1}$, was 42% of the theoretical exchange capacity of Na-4-mica. The strontium- and calcium-exchange capacities at $TN = 0.00468$ N were only 83 and 77 mequiv (100 g)$^{-1}$, respectively, which were only about 17–18% of the the-

TABLE 2
Distribution Coefficients, K_ds, of the Na-4-mica for Alkaline Earth Metals of Ba^{2+}, Sr^{2+}, and Ca^{2+}

Exchanging cation	K_d (cm^3·g^{-1})
Ba^{2+}	22,400
Sr^{2+}	903
Ca^{2+}	182

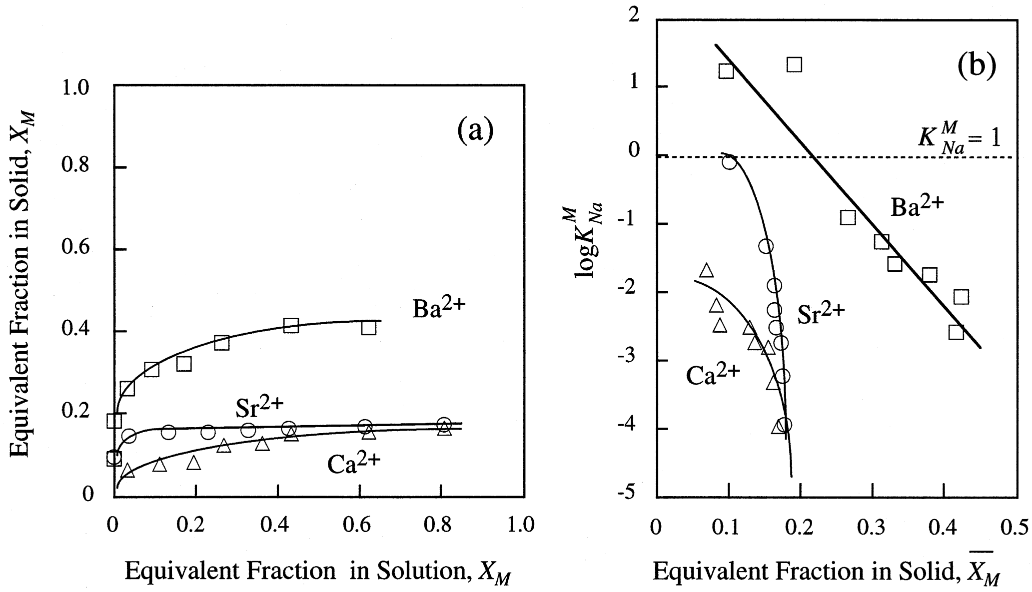

FIG. 8 Cation-exchange isotherms (a) and the Kielland plots (b) for $2Na^+ \rightarrow Sr^{2+}$, Ba^{2+}, or Ca^{2+} exchange on the Na-4-micas prepared by procedure (iv) at 800°C. Total normality in the solution (TN) was 0.00468 N. Symbols: (○) Sr^{2+}, (□) Ba^{2+}, and (△) Ca^{2+}.

oretical exchange capacity of Na-4-mica. The Kielland plots for the barium exchange almost gave a linear relation (Fig. 8b). The selectivity gradually decreased as the $\overline{X}_{Ba}$ increased. The dotted line in Fig. 8(b) indicates that the corrected selectivity coefficient is equal to unity. The Kielland plots fall above the dotted line at $\overline{X}_{Ba} < 0.22$, indicating selectivity for Ba^{2+}. At $\overline{X}_{Ba} > 0.22$, however, Na^+ ions are more preferred than Ba^{2+}. The C_1 was determined to be -6.10 by fitting the Kielland plots to a linear equation (Table 1). On the other hand, for the strontium and calcium exchange, the Kielland plots did not gave linear relations and the corrected selectivity coefficient decreased very quickly when $\overline{X}_M$ became larger than 0.10. This suggests that, for the strontium- and calcium-exchange reactions, the energy term for steric limitation does not have the same value for all the exchangeable sites and quickly becomes very large when $\overline{X}_M > 0.10$. The higher hydrated radii of Sr^{2+} and Ca^{2+} ions may make it difficult for the cations to migrate in the narrow hydrated interlayer spacings of this high-charge-density clay, preventing the exchange from proceeding to the interior of the crystals. The number of Na^+ sites which are readily exchanged with Sr^{2+} and Ca^{2+} is small, and they are probably located close to the edges of the crystals. The experimental $\mathbf{K}_{Na}^{M}$ and corresponding $\overline{X}_M$ values were fitted to a polynomial equation of the form

$$\log\mathbf{K}_{Na}^{M} = a + b\overline{X}_M + c\overline{X}_M^2 \tag{12}$$

The results are given in Table 1. Because the range of $\overline{X}_M$ was very small, values of the order of the polynomial larger than 3 in the equation could not give good fittings.

In the XRD patterns of all the barium-, strontium-, and calcium-exchanged Na-4-micas obtained in the present work, strong peaks due to the hydrated

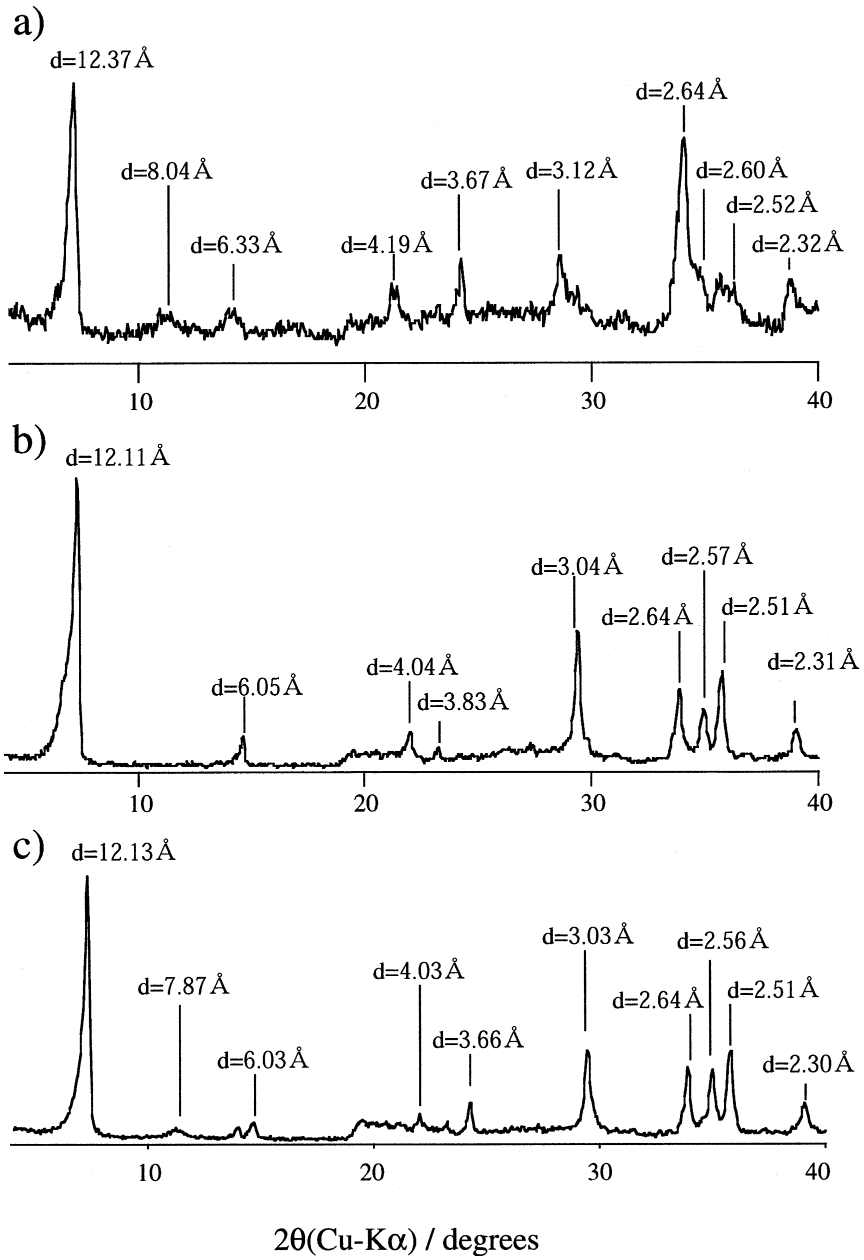

FIG. 9 XRD patterns of the a) barium-, b) strontium-, and c) calcium-exchanged Na-4-micas. The equivalent fractions of barium, strontium, and calcium in the micas were $\overline{X}_{Ba} = 0.42$, $\overline{X}_{Sr} = 0.18$, and $\overline{X}_{Ca} = 0.17$.

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mica were observed, although small or broadened unknown peaks appeared, e.g., at $d = 7.8–8.0$ and 3.6–3.8 Å (Fig. 9). The basal spacing of barium-exchanged mica with $\overline{X}_{\mathrm{Ba}} = 0.42$ increased from $d = 11.96$ to 12.37 Å. The hydrated phase was still retained when about half of the exchange sites were occupied by barium ions. The barium may also be hydrated in the interlayer, thereby preventing the collapse of the hydrated structure. For the strontium and calcium exchange, the basal spacings slightly increased to $d =$ 12.11–12.13 Å ($\overline{X}_{\mathrm{Sr}} = 0.18$ and $\overline{X}_{\mathrm{Ca}} = 0.17$). In the case of strontium and calcium, cation exchange might occur only at the crystal edges.

CONCLUSIONS

A simplified synthetic process using kaolinite, magnesium nitrate, and NaF as starting materials yielded fine and pure phase of hydrated Na-4-mica below 800°C. Well-dispersed and highly crystalline Na-4-mica crystals with plate-like and hexagonal shapes, 2–3 μm in size, could be prepared at 800°C. This mica was selective for Cu^{2+} and Pb^{2+}, and had large cation-exchange capacities for these ions. High-level decontamination of Cu and Pb is possible with this easily and economically synthesized ion exchanger. This is an important separation required for the purification of drinking water as well as for industrial wastewater treatment and disposal. This mica was also highly selective for Ba^{2+}. The order of the selectivity for the alkaline earth metals is $\mathrm{Ba}^{2+} >> \mathrm{Sr}^{2+} > \mathrm{Ca}^{2+}$. The smaller hydrated radius of Ba^{2+} ion may facilitate the migration of this cation into the interlayer spacings. For Sr^{2+} and Ca^{2+} ions with their larger hydrated radii, cation exchange seems to occur only at the crystal edges.

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REFERENCES

1. M. Gregorkiewitz, J. F. Alcover, J. A. Rausell-Colom, and J. M. Serratosa, *2eme Reunion des Groupes Europeens d'Argiles*, Strasbourg, 1974, p. 64.
2. R. E. Grim, *Clay Mineralogy*, 2nd ed., McGraw-Hill, New York, NY, 1968, p. 188.
3. M. Gregorkiewitz and J. A. Rausell-Colom, *Am. Mineral.*, *72*, 515 (1987).
4. W. J. Paulus, S. Komarneni, and R. Roy, *Nature* (*London*), *357*, 571 (1992).
5. S. Komarneni, W. J. Paulus, and R. Roy, in *New Developments in Ion Exchange*; *Proceedings of an International Conference on Ion Exchange*, Elsevier, Amsterdam, 1991, p. 51.
6. K. R. Franklin and E. Lee, *J. Mater. Chem.*, *6*, 109 (1996).

7. S. Komarneni, R. Pidugu and J. E. Amonette, *Ibid*., *8*, 205 (1998).
8. T. Kodama and S. Komarneni, *Ibid*., *9*(2), 533 (1999).
9. T. Kodama and S. Komarneni, *Sep*. *Sci*. *Technol*., *34*(12), 2275 (1999).
10. R. M. Barrer and J. Klinowski, *J*. *Chem*. *Soc*., *Faraday Trans*. *I*, *70*, 2080 (1974).
11. F. Helfferich, *Ion Exchange*, Dover, New York, NY, 1995, p. 170.
12. J. Kielland, *J*. *Soc*. *Chem*. *Ind*., *54*, 232T (1935).
13. R. M. Barrer, *Natural Zeolites*, *Occurrence*, *Properties and Use*, Pergamon, Oxford, 1978, p. 385.
14. M. A. Keane, *Microporous Mater*., *3*, 93(1994).
15. E. Ekedahl, E. Högfeldt, and L. G. Sillén, *Acta Chem*. *Scand*., *4*, 556 (1950).
16. G. L. Gaines Jr. and H. C. Thomas, *J*. *Chem*. *Phys*., *21*, 714 (1953).
17. R. M. Barrer and J. D. Falconer, *Proc*. *R*. *Soc*. *London A*, *236*, 227 (1956).
18. M. Tusji and S. Komarneni, *J*. *Mater*. *Res*., *4*(3), 698 (1989).
19. Y. Tanaka and M. Tsuji, *Mater*. *Res*. *Bull*., *32*(4), 461 (1997).

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