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Crystal-size control and characterization of Na-4-mica prepared from kaolinite

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A simple and economical method for the synthesis of high-charge-density Na-4-mica (ideal chemical composition of $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot xH_2O$) from kaolinite was investigated. Synthesis conditions were varied to control crystal size. This novel swelling Na-4-mica was synthesized from a mixture of kaolinite, magnesium nitrate (or ultrafine MgO) and NaF at 850 °C, and characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), particle size analysis by laser diffraction and ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. Decreasing the mass of NaF flux during the crystallization of Na-4-mica reduced the crystallite size from 2 to 0.2 μm. As the crystallite size decreased, the average particle size of the mica decreased from 5 to 2 μm. ^{27}Al MAS-NMR spectra showed that all or nearly all Al is in tetrahedral coordination whereas ^{29}Si MAS-NMR spectra showed that the nearest neighbour environment of Si is mainly in Si(3Al), as expected based on the Si : Al ratio.

Introduction

Naturally occurring and synthetic cation exchangers are useful for separation of hazardous radioactive and non-radioactive cations.[1–4] The synthetic clay mineral, "Na-4-mica", is a sodium fluorophlogopite mica of theoretical chemical composition $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot xH_2O$ with very high charge density.[5–16] This mica has a very high Al(III) content but exhibits unusual swelling behavior and selective cation exchange properties which are potentially useful in hazardous cation separations from solutions. Micas are distinguished from smectites or vermiculites by their higher layer charge density.[17] Due to the high layer charge density, naturally occurring micas do not swell in water, and as a result, ion exchange reactions with the interlayer cations do not readily occur. Synthetic micas, which swell in water, with ion exchange capacities of 200 to 250 mequiv $(100\ g)^{-1}$ have been prepared and these are of considerable interest.[18–21] The Na-4-mica has a theoretical cation-exchange capacity of 468 mequiv $(100\ g)^{-1}$ on an anhydrous basis but readily becomes hydrated on contact with water or even in moist air at ambient conditions.[5–16] Na-4-mica contains an unusually large number of 4 interlayer cations per unit cell. No mica with more than 2 interlayer cations per unit cell had ever been observed before. This unusually high number of four interlayer cations was accommodated in the ditrigonal holes above and below the central plane of the interlayer space as a result of unique offset layer stacking of *b*/3.[6] The unusual layer stacking along with the interlayer Na^+ ions located in the ditrigonal holes leads to the incorporation of one layer of water molecules in the interlayer space.

Gregorkiewitz *et al.*[5–7] first synthesized this special mica as millimeter sized flakes by reacting natural augite crystals in 1 : 1 molar ratio of $NaF–MgF_2$ melt at approximately 900 °C. Paulus *et al.* reported that a very fine and pure phase of microcrystalline Na-4-mica (< 1 μm), which is essential for practical applications, could be prepared by a solution–sol–gel process.[8] They further showed that the microcrystalline mica so produced had high cation-exchange selectivities for many divalent transition-metal ions and for strontium and barium.[9] This synthetic 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 simplified procedure was later developed for the synthesis of this mica using fumed silica instead of TEOS as the silica source.[10] Recently, we have been able to easily and economically synthesize Na-4-mica from NaF, ultrafine MgO (or magnesium nitrate) and kaolinite, the latter serving as a cost-effective aluminosilicate source with the desired 1 : 1 Si to Al molar ratio.[11–16] In the present work, this simple synthetic route using kaolinite is further developed for controlling the crystal size of the Na-4-mica, which controls the diffusion of ions during exchange. Micas were synthesized at the crystallization temperature of 850 °C with different ratios of NaF to kaolinite.

Experimental

Preparation of Na-4-micas

Na-4-micas were prepared from a mixture of naturally occurring kaolinite, magnesium nitrate and NaF at

850 °C. Ultrafine MgO (supplied by Ube Industries, Ube, Japan) was also used as the magnesium source in some syntheses instead of magnesium nitrate. Naturally occurring kaolinite has the theoretical chemical composition $Al_2Si_2O_5(OH)_4 \cdot nH_2O$. 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, Dept. of Geology, Univ. of Missouri, Columbia, MO 65201, USA), was used as the aluminosilicate source for the synthesis of the Na-4-micas. Appropriate amounts of the kaolinite (3.0 g) and $Mg(NO_3)_2 \cdot 6H_2O$ were mixed to obtain a stoichiometric composition. The water content of the kaolinite was previously determined to be 14.16 wt% by thermal analysis using a TG DTA 2010, Mac Science instrument. Then it was mixed with NaF with the desired molar ratio of NaF/kaolinite $[Al_2Si_2O_5(OH)_4]$. Sodium fluoride not only acts as a flux for the high-temperature crystallization of Na-4-mica but also serves as a source of sodium and fluorine. The amount of NaF was varied and was in excess of the stoichiometric amount. In the present work, control of the Na-4-mica crystal size was attempted by changing the amount of NaF flux to kaolinite. NaF/kaolinite$[Al_2Si_2O_5(OH)_4]$ molar ratios in the range of 4 to 24 were used for the preparation of the precursor mixture. The mixture was thoroughly homogenized using a pestle and mortar, and transferred to an alumina vessel. The precursor mixture was reacted for 24 h at 850 °C in air using a programmed furnace. The resulting solids were gently 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.[8,11] 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.

Characterization of products

Powder X-ray diffraction (XRD) was carried out to check for phase purity and to determine the basal spacings of the mica using a Rigaku RAD-γA diffractometer with CuKα radiation. Sodium, magnesium, aluminium, silicon, iron and titanium contents were determined by X-ray fluorescence analysis (X-ray Fluorescence Spectrometer, RIX3000, RIGAKU Industrial Co.). The water content of the hydrated mica was determined by thermal analysis. Scanning electron microscopy (SEM) was used to determine the crystallite size and shape (EPMA-8705, Shimadzu). The particle size distribution was determined in a 0.3 wt% sodium hexametaphosphate solution using laser diffraction (SALD-3000, Laser Diffraction Particle Size Analyzer, Shimadzu). ^{27}Al and ^{29}Si MAS-NMR spectra were obtained at 103.9 and 79.8 MHz respectively using a Varian Unity 400 spectrometer with a double bearing rotor (5 mm, zirconia).[15] For ^{27}Al resonance the spectrometer operating conditions were: pulse width 1 μs (equivalent to a π/18 pulse, measured on $Al(NO_3)_3$ aqueous solution), spectral width 1 MHz, recycle delay 1.0 s, number of transients 2000, and spinning speed 12 kHz. No line broadening was considered in data processing.[15] Chemical shifts were measured relative to aqueous $Al(NO_3)_3$. The ^{29}Si spectra were acquired by using a 4 μs pulse width, 40 kHz spectral width, recycle delay of 60 s, 1000 transients, and 8 kHz spinning speed.[15] Line broadening of 10 Hz was used in data processing. Chemical shifts were referenced to the signal of tetramethylsilane (TMS).

Results and discussion

The XRD patterns of the resultant solids prepared from a mixture of kaolinite, magnesium nitrate and NaF at various NaF/kaolinite$[Al_2Si_2O_5(OH)_4]$ molar ratios are shown in Fig. 1. In the XRD pattern of the solid prepared at the NaF/kaolinite molar ratio of 24 (referred to as Mica-1), a strong peak for the (001) reflection of the hydrated Na-4-mica with a single sheet of interlayer water was observed at $d = 12.03$ Å (Fig. 1a).[6] Small peaks observed around $d = 6.05$, 4.03 and 3.07 Å are assigned to the (002), (003) and (004) reflections of c-axis spacing of the hydrated Na-4-mica. Other small peaks are consistent with the limited powder XRD data reported previously for the hydrated Na-4-mica.[9–16] Strong peaks of hydrated Na-4-mica with a single interlayer water sheet were also observed in the XRD patterns of the solids prepared at the NaF/kaolinite molar ratios of 8 and 4 (referred to as Mica-2 and Mica-3, respectively) although small peaks due to the unhydrated Na-4-mica phase appeared around $d = 9.94$ and 3.26 Å (Fig. 1b and c). Decreasing the mass of NaF enhanced the formation of the unhydrated phase of Na-4-mica. We also synthesized the mica by using ultrafine MgO instead of magnesium nitrate at the NaF/kaolinite molar ratio of 4

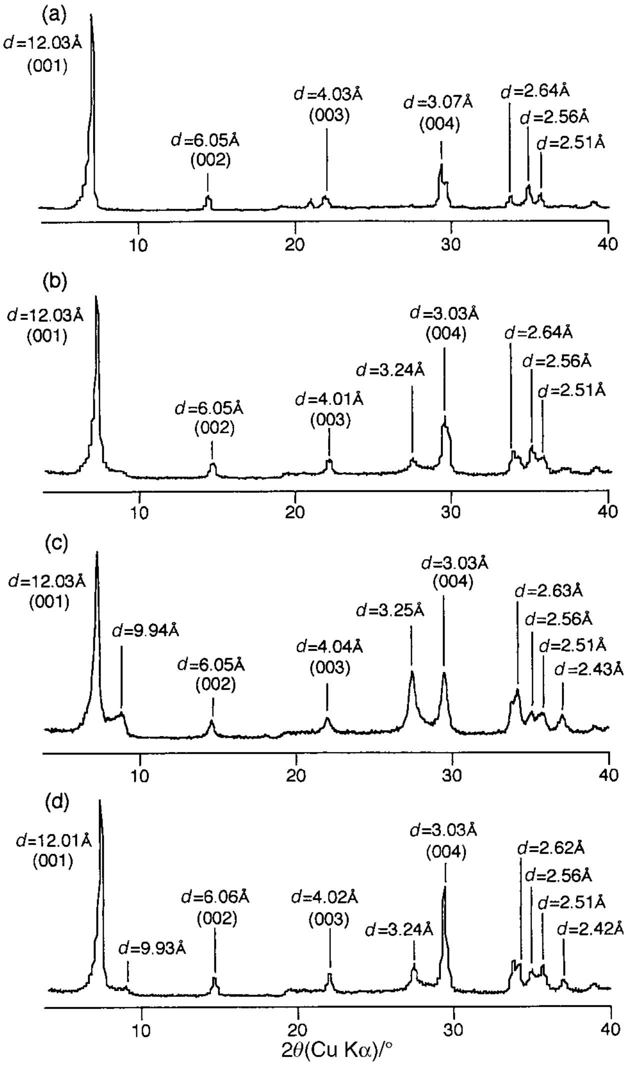

Fig. 1 XRD patterns of Na-4-mica samples prepared at various mass of NaF flux by the synthetic method from kaolinite at 850 °C. The samples were prepared from mixtures of kaolinite, magnesium nitrate and NaF at NaF/kaolinite molar ratios of (a) 24(Mica-1), (b) 8 (Mica-2) and (c) 4 (Mica-3). The sample of (d) Mica-4 was prepared using ultrafine MgO as the magnesium source instead of magnesium nitrate at a NaF/kaolinite molar ratio of 4.

Table 1 Analytical data for mica samples

	Content[a]/wt%						
Mica sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	Na_2O	H_2O
Mica-1	27.87	23.44	1.47	0.68	29.36	13.70	10.65
Mica-2	25.51	21.39	1.33	0.63	26.55	13.84	7.35
Mica-3	27.70	23.34	1.45	0.68	28.40	15.01	6.24
Mica-4	25.89	21.95	1.36	0.64	25.84	12.95	8.18
Mica-5[b]	27.94	22.98	1.53	0.70	27.65	13.18	5.92
Mica-6[b]	22.75	19.66	1.23	0.62	25.78	13.37	12.39
Mica-7[b]	22.33	19.00	1.26	0.59	24.91	14.47	13.49

[a]The metal content was determined by X-ray fluorescence analysis and the water content by thermal analysis. [b]These samples were previously prepared.[16]

(referred to as Mica-4). The resultant solid gave almost the same XRD pattern (Fig. 1d) as that of Mica-3.

Table 2 Chemical compositions of mica samples

Mica sample	Chemical composition[a]
Mica-1	$Na_{3.79}Mg_{6.24}Al_{3.94}Si_{3.98}O_{20}F_4 \cdot 5.7H_2O$
Mica-2	$Na_{4.16}Mg_{6.14}Al_{3.91}Si_{3.96}O_{20}F_4 \cdot 3.8H_2O$
Mica-3	$Na_{4.17}Mg_{6.07}Al_{3.94}Si_{3.97}O_{20}F_4 \cdot 3.2H_2O$
Mica-4	$Na_{3.90}Mg_{5.98}Al_{4.02}Si_{4.02}O_{20}F_4 \cdot 4.2H_2O$
Mica-5[b]	$Na_{3.74}Mg_{6.02}Al_{3.96}Si_{4.08}O_{20}F_4 \cdot 3.0H_2O$
Mica-6[b]	$Na_{4.33}Mg_{6.42}Al_{3.87}Si_{3.80}O_{20}F_4 \cdot 6.8H_2O$
Mica-7[b]	$Na_{4.77}Mg_{6.31}Al_{3.81}Si_{3.80}O_{20}F_4 \cdot 7.5H_2O$

[a]Calculated based on $O_{20}F_4$ as expected for a 2 : 1 layer aluminosilicate. [b]These samples were previously prepared.[16]

Table 1 shows the metal oxide and water contents of these mica samples. The chemical formulae were calculated based on $O_{20}F_4$, as expected for a 2 : 1 layer aluminosilicate and are listed in Table 2. Oxides of iron and titanium were not used in the calculation of formulae because these are not expected to occur in the mica structure. These compositions were almost consistent with the ideal composition.

The SEM micrograph of the mica prepared at the NaF/kaolinite molar ratio of 24 (Mica-1) showed plate-like (pseudo hexagonal) crystallites (Fig. 2a). The crystallite size of the mica varied widely between 0.1 and 4 μm. However, many crystallites were around 2 μm in size. It can be seen from the SEM pictures that many crystallites agglomerated to form massive grains. Fig. 3a shows the particle size distributions estimated by laser diffraction. A size distribution from 0.3 to 50 μm was

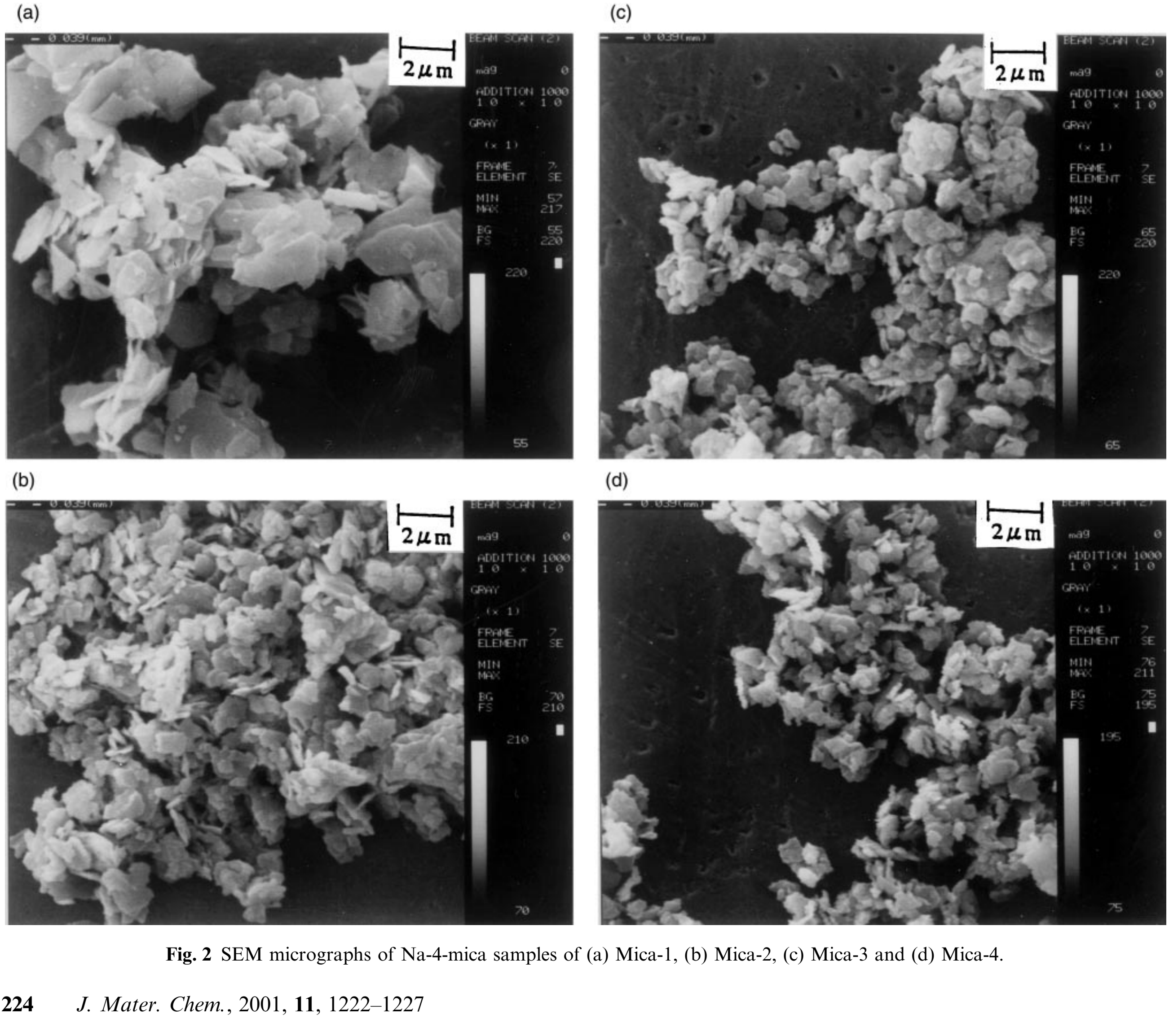

Fig. 2 SEM micrographs of Na-4-mica samples of (a) Mica-1, (b) Mica-2, (c) Mica-3 and (d) Mica-4.

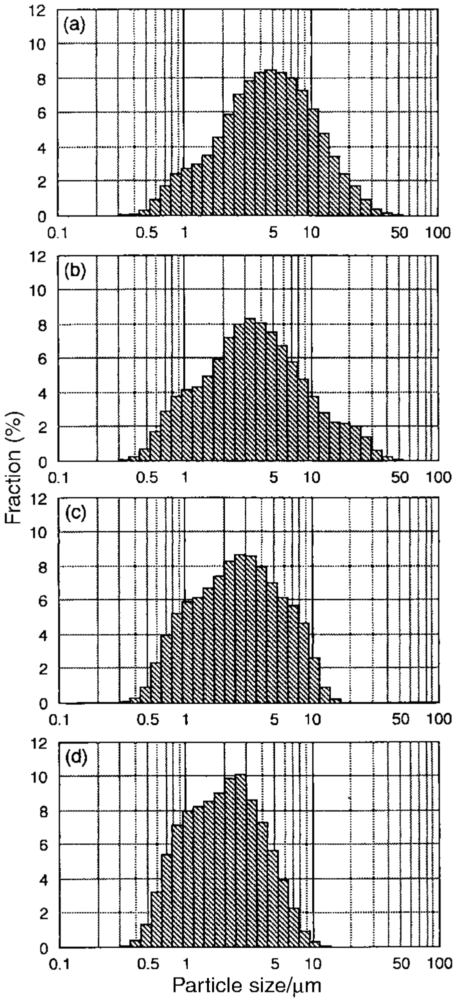

Fig. 3 Particle size distributions of (a) Mica-1, (b) Mica-2, (c) Mica-3 and (d) Mica-4 estimated from laser diffraction.

found with an average particle size of 4.3 μm. For the mica prepared with the NaF/kaolinite molar ratio of 8 (Mica-2), the crystallite size was reduced to around 0.2–0.5 μm (Fig. 2b). The particle size distribution similarly ranged from 0.3 to 50 μm but the average particle size was reduced to 3.4 μm (Fig. 3b). With the NaF/kaolinite molar ratio of 4 (Mica-3), the crystallite size was somewhat reduced and most crystallites appear to be about 0.2 μm in size (Fig. 2c). In this case, a narrower size distribution from 0.3 to 20 μm was observed and the average particle size decreased to 2.4 μm (Fig. 3c). In the case of ultrafine MgO instead of magnesium nitrate as the magnesium source with a NaF/kaolinite molar ratio of 4 (Mica-4), the formation of crystallites of about 0.2 μm in size can be also observed in the SEM micrograph (Fig. 2d). The particle size distribution, however, was somewhat reduced to a range of 0.3 to 10 μm and a smaller average particle size (1.9 μm) was obtained (Fig. 3d). Kaolinite and Na-4-mica have different crystal structures, the former is the 1 : 1 phyllosilicate and the latter the 2 : 1 phyllosilicate. Kaolinite has octahedral sheets composed of Al^{3+} ions but Na-4-mica has sheets composed of Mg^{2+} ions. Therefore, the formation of Na-4-mica from kaolinite is considered to involve dissolution and crystallization processes in the molten NaF flux at a high temperature. Decreased mass of NaF flux to kaolinite mass may favor the supersaturation and accelerate the nucleation rate of Na-4-mica crystallites in the dissolution–crystallization process, which results in the formation of smaller crystallites of mica.

The ^{29}Si MAS-NMR spectra of the micas prepared at various NaF/kaolinite molar ratios are presented in Fig. 4. Table 3 shows the chemical shifts δ and the normalized intensities. Complete Si/Al ordering in the Na-4-mica of ideal composition would give only one resonance due to the Si(3Al) environment. These spectra, however, show the presence of two Si(3Al) resonances at δ −78 and −75 which represent two types of environments. For the hydrated Na-4-micas which had been prepared before, the resonance for Si(3Al) predominantly appeared around δ −78.[7,9,11,15,16] Frequently, however, a small Si(3Al) resonance was also observed around δ −75.[11,15,16] Slight changes in the chemical shifts of resonances corresponding to the same tetrahedral environment have been previously attributed to differences in the octahedral and interlayer environment of silicon.[22] Komarneni *et al.* suggested that the resonance around δ −75 would be due to the Si(3Al) resonance of the unhydrated Na-4-mica phase because the completely unhydrated mica prepared by solution–sol–gel processing at 850 °C showed predominantly a resonance at δ −74.7 with a minor resonance at −78.3.[15] This suggestion would be true for our mica samples of Mica-1, 2 and 3 where the normalized intensity for a resonance at δ −75 (Table 3) increased with an increase in the proportion of unhydrated phase in the Na-4-mica as indicated by the XRD patterns (Fig. 1).

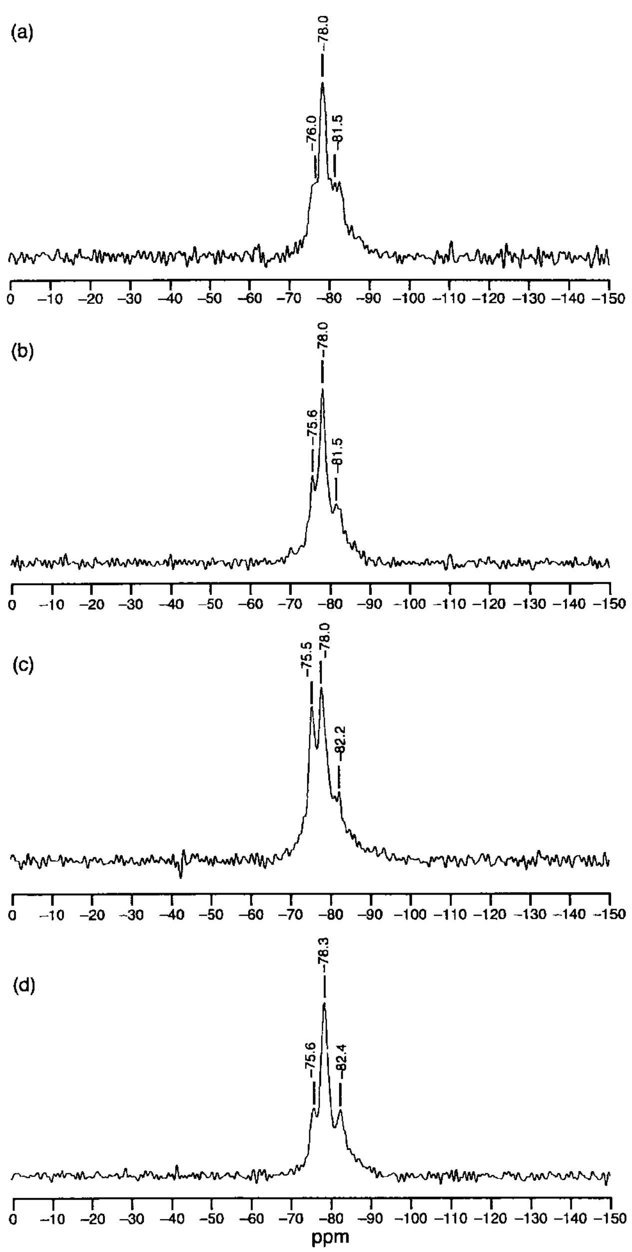

Fig. 4 ^{29}Si MAS-NMR spectra (ref. TMS) of Na-4-mica samples of (a) Mica-1, (b) Mica-2, (c) Mica-3 and (d) Mica-4.

Table 3 ^{29}Si MAS-NMR data (chemical shift δ relative to TMS and normalized intensity *I*) for Na-4-micas

				Tetrahedral environments of Si[a]				
Mica sample	Composition of precursor mixture	Calcination temperature/°C		Si(3Al)		Si(2Al)	Si(1Al)	Si(1Al) or Si(0Al)
Mica-1	kaolinite + 24NaF + 3Mg(NO$_3$)$_2$	850	δ	−76.0	−78.0	−81.5	—	—
			I (%)	22.8	53.6	23.6	—	—
Mica-2	kaolinite + 8NaF + 3Mg(NO$_3$)$_2$	850	δ	−75.6	−78.0	−81.5	—	—
			I (%)	27.3	54.1	18.6	—	—
Mica-3	kaolinite + 4NaF + 3Mg(NO$_3$)$_2$	850	δ	−75.5	−78.0	−82.2	—	—
			I (%)	38.9	43.7	17.4	—	—
Mica-4	kaolinite + 4NaF + 3MgO	850	δ	−75.6	−78.3	−82.4	—	—
			I (%)	22.3	56.1	21.6	—	—
Mica-5[b]	kaolinite + 24NaF + 3Mg(NO$_3$)$_2$	800	δ	−74.6,	−77.7	−81.2	−85.4	—
			I (%)	18.6	46.3	25.0	10.1	—
Mica-6[b]	kaolinite + 24NaF + 3Mg(NO$_3$)$_2$	750	δ	−75.3,	−77.9	−81.6	−85.3	−87.1
			I (%)	7.7	46.9	24.8	10.8	9.8
Mica-7[b]	kaolinite + 24NaF + 3Mg(NO$_3$)$_2$	700	δ	−74.6,	−77.5	−81.2	−84.4	−87.6
			I (%)	8.5	37.9	23.8	11.7	18.1

[a]Assignment of the chemical shifts was based on refs. 7, 11, 15 and 22. [b]Data were taken from ref. 16. These samples were prepared from a mixture of kaolinite, magnesium nitrate and NaF at a kaolinite/NaF molar ratio of 24.[16] The XRD analyses showed that these samples were almost the pure phases of the hydrated Na-4-mica.[16]

The micas also showed a significant resonance at 82 ppm which can be assigned to Si(2Al), based on previously reported assignments.[7,11,15,16,22] The ^{29}Si MAS-NMR data for these Na-4-micas showed that the nearest neighbor environment of Si was mainly Si(3Al): from the normalized intensity of the resonance, 76–83% of the environment of Si was determined to be Si(3Al). The ^{29}Si MAS-NMR data obtained here were compared to those of the Na-4-mica samples previously prepared by a similar procedure at different temperatures of 700, 750 and 800 °C.[16] These samples (referred to as Mica-5, 6 and 7) had been prepared from a mixture of kaolinite, magnesium nitrate and NaF at the kaolinite/NaF molar ratio of 24. The XRD analyses showed that these samples were almost the pure phases of the hydrated Na-4-mica.[16] The metal oxide and water contents and the estimated chemical formulae are also given in Tables 1 and 2. In the ^{29}Si MAS-NMR spectra of these samples, small resonances at δ 84–87, which can be assigned to Si(1Al) or Si(0Al), were observed along with those due to Si(3Al) and Si(2Al), as shown in Table 3. The lower temperature crystallization of the Na-4-mica decreased the proportion of the idealized Si(3Al) environment to 46–65%.

^{27}Al MAS-NMR spectra of Mica-1, 2, 3 and 4 are shown in Fig. 5. The spectra, except for that of Mica-1, show a single resonance due to Al in tetrahedral coordination at δ *ca.* 67 from $[Al(H_2O)_6]^{3+}$.[22] In the spectrum of Mica-1, a very small resonance due to octahedral coordination appeared at around δ 5.[22] In these mica samples, all or nearly all Al was incorporated in the tetrahedral sites. The ^{27}Al MAS-NMR spectra of Mica-5, 6 and 7 were given in an earlier paper[16] and these results showed that the resonance due to the octahedral Al became more intense as the crystallization temperature was lowered.

The resonances due to the tetrahedral Al in the ^{27}Al MAS-NMR spectra show a shoulder near δ 60 representing a second Al tetrahedral environment. Komarneni *et al.* previously suggested that the shoulder was probably due to the glassy phase.[15] As the crystallization temperature was lowered, this resonance around δ 60 became more intense (see Fig. 4 in reference 16). SEM micrographs of Mica-5, 6 and 7[16] showed that the edges of the hexagonal crystallites became less sharp and more undifferentiated plate-like crystals were formed as the crystallization temperature was reduced (see Fig. 2 in reference 16). These results indicate that the poorly crystallized or glassy phase was increased at lower crystallization temperatures.

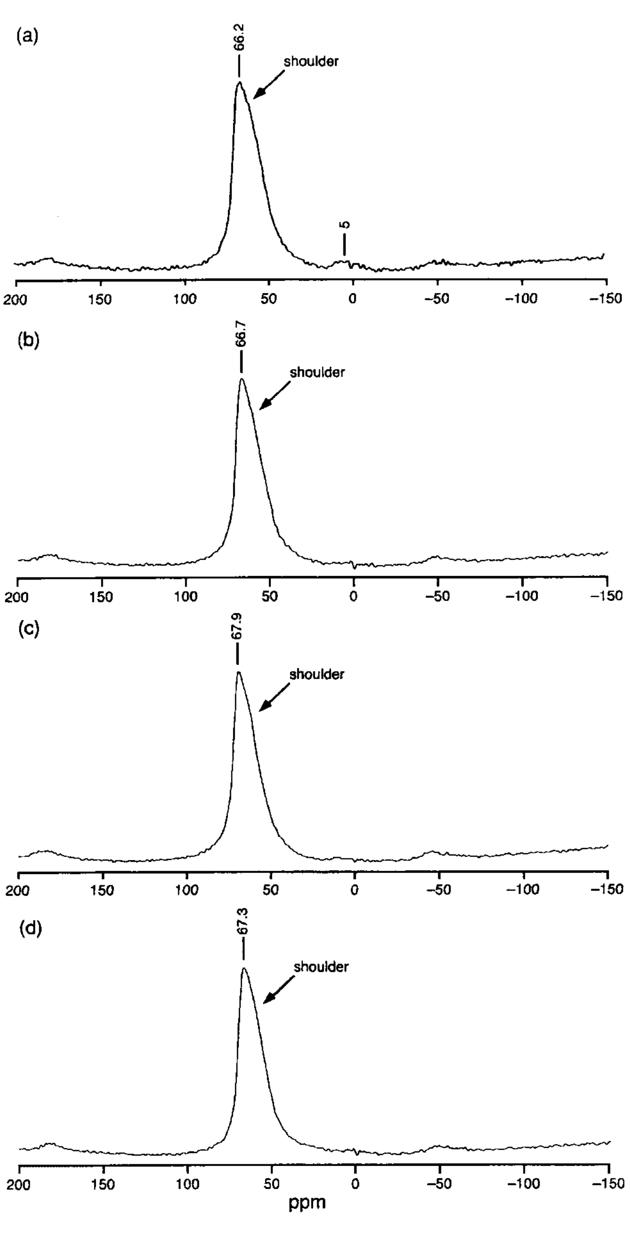

Fig. 5 ^{27}Al MAS-NMR spectra (ref. $[Al(H_2O)_6]^{3+}$) of Na-4-mica samples of (a) Mica-1, (b) Mica-2, (c) Mica-3 and (d) Mica-4.

Conclusions

Na-4-micas of controlled crystal size were prepared from kaolinite at the crystallization temperature of 850 °C. Crystal growth of the mica was reduced by decreasing the mass of NaF flux, resulting in the formation of smaller crystallites of mica. Very fine Na-4-mica with a crystallite size of about 0.2 μm and with a narrow particle size distribution of 0.3–10 μm (average particle size of 1.9 μm) was synthesized from the precursor mixture of kaolinite, ultrafine MgO and NaF flux using a NaF/kaolinite molar ratio of 4. ^{27}Al and ^{29}Si MAS-NMR spectroscopy revealed that the Na-4-micas prepared here have Al and Si distributions much closer to those of ideal Na-4-mica compared to those prepared by the same procedure at lower crystallization temperatures (700–800 °C). The synthesis of size-controlled micro- or nano-crystalline Na-4-mica using kaolinite is expected to be useful in the decontamination and disposal of nuclear and other industrial wastes.[23]

Acknowledgement

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