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# Synthesis of Na-4-mica from metakaolinite and MgO: characterization and $Sr^{2+}$ uptake kinetics

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Na-4-mica, a high-charge-density sodium fluorophlogopite mica of ideal chemical composition $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot xH_2O$ has been prepared from a mixture of NaF, MgO and metakaolinite (the latter serving as an inexpensive aluminosilicate source). Highly crystalline Na-4-mica can be easily and economically synthesized from the above precursors in the temperature range 850–890 °C. $^{27}Al$ and $^{29}Si$ MAS NMR spectroscopy revealed that the Na-4-mica synthesized from metakaolinite is more close to the ideal nearest neighbor distribution of Al and Si compared to that prepared from magnesium aluminosilicate gel. Selective Sr exchange kinetic studies showed that the uptake was slow because of the somewhat large particle size as determined by scanning electron microscopy as well as restricted interlayer spacing.

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.[1] during a series of experiments dealing with the synthesis of mica-type silicates from fluoride melts. In a subsequent paper Gregorkiewitz and Rausell-Colom[2] reported the detailed characterization and properties of this new synthetic silicate with highly charged mica-type layers. They informally named this phase as Na-4-mica because it contains four Na ions per unit cell. The presence of four interlayer cations per unit cell has never been observed before in micas. This unusually high number of four interlayer cations was apparently accommodated in the ditrigonal holes above and below the central plane of the interlayer space as a result of unique layer stacking with displacement in the (001) plane.[2] This unusual layer stacking along with a large number of cations leads to the incorporation of one layer of water molecules in the interlayer space upon exposure to humidity after high-temperature melt synthesis. The incorporation of water molecules leads to an open interlayer space where cation exchange and other reactions can be carried out. Preliminary cation exchange experiments were reported[2] on millimeter-sized flakes. Recognizing the special features of this mica and its potentialities for cation exchange separations, we have previously developed a method to synthesize ultrafine powders of this phase in order to achieve high reactivity for cation exchange.[3–5]

This method involved powders from solution-sol–gel processing using tetraethoxysilane, aluminium nitrate and magnesium nitrate.[3,4] A somewhat simplified procedure was recently reported[6] for the synthesis of Na-4-mica using fumed silica as the silica source. For large-scale use of Na-4-mica in cation exchange separations or waste disposal, it is useful to have a cost-effective process for its synthesis.

Here we report the synthesis of Na-4-mica using calcined kaolinite (metakaolinite) as a very cheap aluminosilicate source with the desired 1 : 1 Si to Al molar ratio and the components mixed on the nano-scale. We also report that the Na-4-mica synthesized by this new method appears to be very close to the theoretical nearest neighbor distribution of Al and Si as determined by $^{27}Al$ and $^{29}Si$ MAS NMR spectroscopy.

## Experimental

A poorly crystallized kaolinite of composition,[7] 43.9% $SiO_2$, 38.5% $Al_2O_3$, 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), fine MgO (supplied by Ube Industries, Ube, Japan) and NaF were the starting precursors for the synthesis of Na-4-mica. The kaolinite was first calcined at 700 °C for

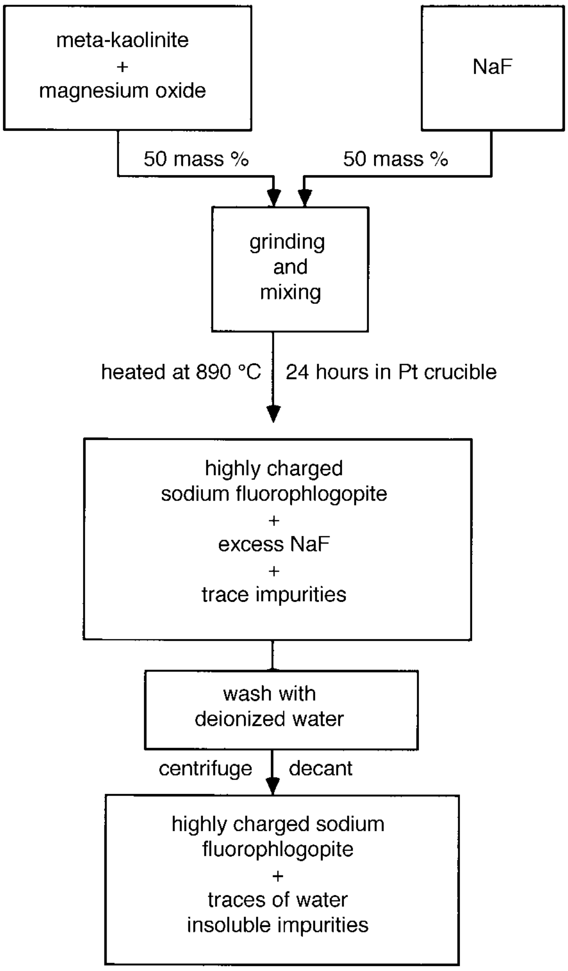

**Fig. 1** Preparation of Na-4-mica from metakaolinite using the NaF flux method

18 h to transform it to metakaolinite. The preparation and purification of Na-4-mica using this metakaolinite are shown in Fig. 1 and 2. Two Na-4-micas were prepared, one with exact stoichiometry and another with a 2 mass% excess of MgO than is required for stoichiometry. Excess MgO was used hoping that it would completely prevent Al substitution in the octahedral sheet. Both the samples were prepared by heat treatment at 890 °C for 24 h (Fig. 1). A temperature of 850 °C was also found to be suitable for Na-4-mica synthesis using the above procedure. After washing with boric acid and water (Fig. 2), the samples were dried at 60 °C and characterized by a variety of techniques. Powder X-ray diffraction (XRD) was used to check for phase purity. A Scintag diffractometer with Ni-filtered Cu-K$\alpha$ radiation was used for XRD. Scanning electron microscopy (SEM) was used to determine particle size and shape. An ISI-DS 130 instrument was used for SEM. $^{27}$Al and $^{29}$Si MAS NMR spectra were obtained using Bruker instruments. The $^{27}$Al MAS NMR spectra were recorded using a 15° pulse angle, a recycle delay of 300 ms and a spinning speed of 9.4–10.0 kHz. These data were collected on the SDS 360-1 instrument, operating at a $^{27}$Al Larmor frequency of 94.669 MHz. The $^{29}$Si MAS NMR spectra were recorded using 90° pulse, a recycle delay of 60 s and spinning speed of 4.0 kHz. These data were collected on the SDS 270 instrument, operating at a Larmor frequency of 53.762 MHz. The $^{27}$Al chemical shift values were recorded with respect to 1 M aqueous $Al(NO_3)_3$ solution ($\delta = 0$) as a reference while the $^{29}$Si chemical shift values were assigned with respect to the external standard of tetramethylsilane. The deconvolutions were performed with the Nicolet NMC program NMRCAP.

Strontium ion exchange kinetics were determined on both the above micas by equilibrating 20 mg of sample with 25 ml of 0.5 M NaCl containing 0.0001 M $SrCl_2$ for different periods in a batch experiment. Three replicates were used for each duration. After equilibration, the solid and solution phases were separated by centrifugation. The solutions were analyzed for $Sr^{2+}$ remaining in solution by atomic emission spectroscopy.

## Results and Discussion

Powder X-ray diffraction (Fig. 3) revealed that highly crystalline Na-4-micas were obtained by using metakaolinite as the aluminosilicate source. The resultant Na-4-micas with stoichiometric amount of Mg and 2% excess MgO exhibited very similar XRD patterns. Several higher integral orders such as 002, 003, 004 and 005 of the 001 peak are clearly seen in the XRD peaks with the 001 peak being the strongest. A small intensity peak at *ca.* 9.8 Å in both XRD patterns indicates the presence of anhydrous (unhydrated) Na-4-mica.[1–4] There is also a small peak at *ca.* 10.97 Å in one XRD pattern (Fig. 3A) which may have resulted from mixed layering of hydrated (12 Å) and unhydrated (9.8 Å) phases.

$^{27}$Al MAS NMR spectra of the two synthetic Na-4-micas are shown in Fig. 4. These spectra clearly show that almost all Al was incorporated in the tetrahedral sites as indicated by resonances at $\delta$ *ca.* 66.5 and 67.4 from $[Al(H_2O)_6]^{3+}$. A small amount of Al was, however, incorporated in octahedral sheets as indicated by weak resonances at $\delta$ *ca.* $-1.15$ and $-2.16$. Deconvolution of the peaks followed by intensity calculations showed 97.44 and 97.67% tetrahedral Al in these two micas with the remainder in the octahedral positions (Fig. 4). This amount of tetrahedral Al is higher than the amounts previously

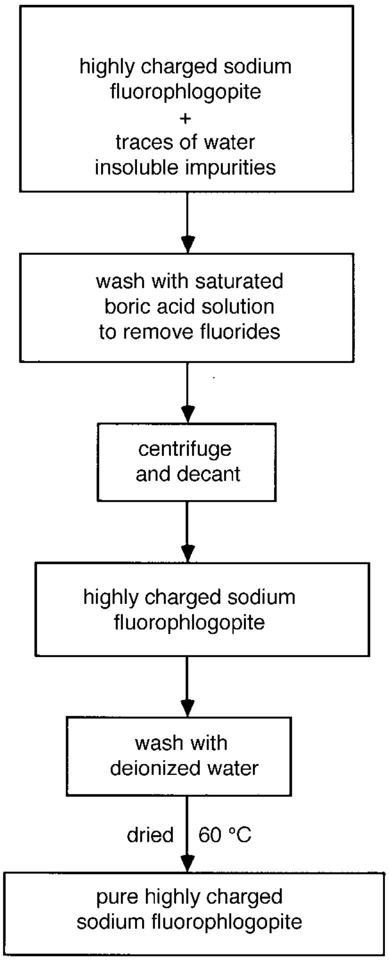

**Fig. 2** Selective dissolution process for removal of water insoluble fluoride impurity phases from reaction products

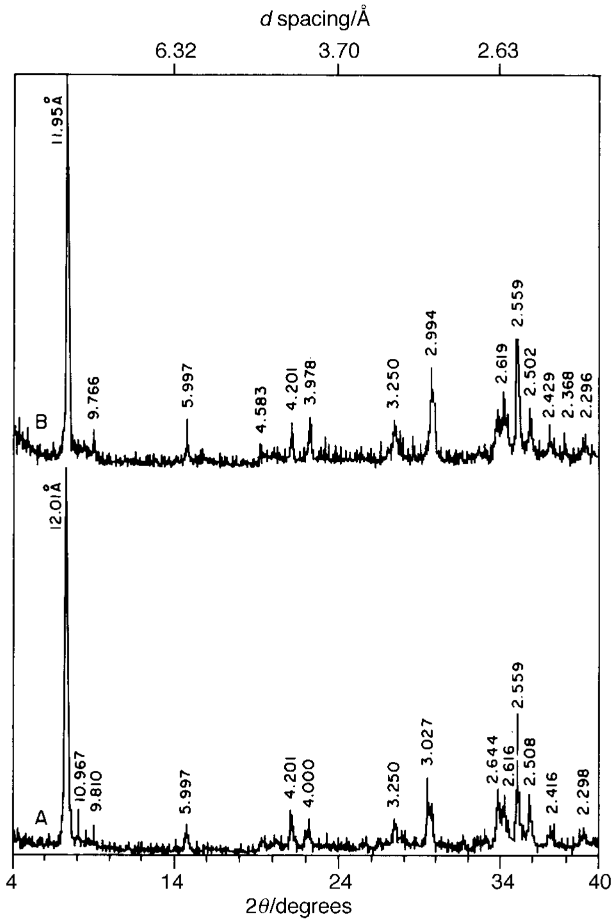

**Fig. 3** Powder X-ray diffraction patterns of Na-4-micas synthesized (A) with stoichiometric MgO and (B) with 2% excess MgO compared to stoichiometry

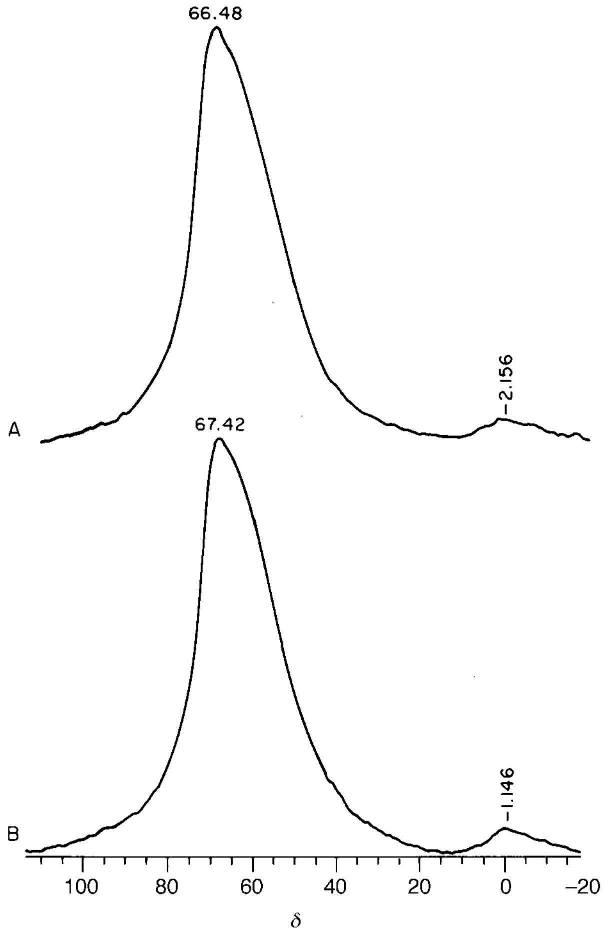

**Fig. 4** $^{27}$Al MAS NMR spectra (ref. $[Al(H_2O)_6]^{3+}$) of Na-4-micas synthesized (A) with stoichiometric MgO and (B) with 2% excess MgO

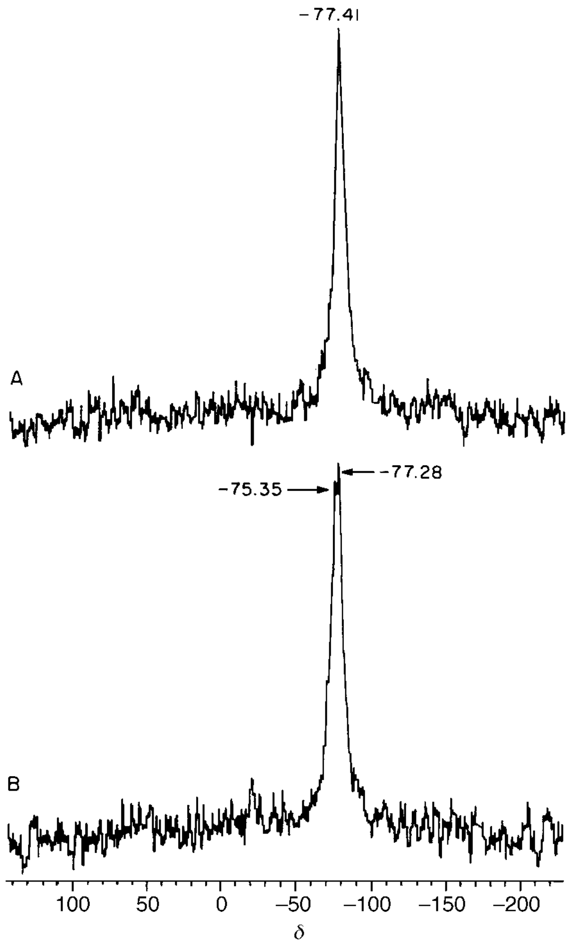

**Fig. 5** $^{29}$Si MAS NMR spectra (ref. TMS) of Na-4-micas synthesized (A) with stoichiometric MgO and (B) with 2% excess MgO

reported by us and others.[2,3,5] In order to achieve high charge density on the Na-4-mica, the tetrahedral Al should be maximum while the octahedral Al should be minimum in these trioctahedral mica phases. $^{29}$Si MAS NMR spectra are presented in Fig. 5 for both the mica preparations and these data are compared to those that were reported previously (Table 1).[2,3] The two synthetic micas prepared here from metakaolinite exhibit complete ordering of Si and Al as indicated by only the Si(3Al) tetrahedral environment of Si *i.e.*, each Si is surrounded by 3Al and each Al is surrounded by 3Si. Na-4-micas synthesized previously[2,3] contained various extents of Si(1Al), Si(2Al) and Si(3Al) as can be seen from Table 1. These $^{29}$Si MAS NMR data clearly show that the charge density in the Na-4-micas synthesized from metakaolinite was uniform while in the previous syntheses the charge density was non-uniform. The uniformity of charge density or otherwise is expected to have an effect on cation exchange and selectivity properties of these micas.

The Na-4-micas exhibit not only Sr selectivity but also fixation as has been reported previously.[4] Kinetics of selective Sr uptake is an important aspect in any practical application, *i.e.*, radioactive Sr separation from nuclear waste solutions. Table 2 shows the Sr exchange kinetics of the two synthetic micas. Both the micas exhibit slow uptake of Sr. About 30% of the added Sr was taken up by both the micas in a matter of few hours but the selective uptake from a 0.5 M NaCl background solution was not complete even after 184 days (Table 2). This slow uptake and lack of equilibrium may be attributed to the somewhat large crystal size of these synthetic micas (Fig. 6) and the restricted interlayer spacing of *ca.* 2.2 Å. The crystal size of these synthetic micas ranges between 2 and 5 µm although many particles are around 5 µm in size. This is

**Table 1** $^{29}$Si MAS NMR data (chemical shift δ relative to TMS) for Na-4 micas previously reported[2,3] and of this study

| sample | | tetrahedral environments of Si | | | |
|---|---|---|---|---|---|
| | | Si (3Si) | Si (1Al) | Si (2Al) | Si (3Al) |
| I[a] | δ | — | −85.1 | −82.1 | −77.1 |
| | $I^b$ (%) | 0 | 21 | 28 | 51 |
| II[c] | δ | −88 | −85 | −81 | −77 |
| | I (%) | 1.0 | 13.8 | 38.0 | 47.2 |
| III[d] | δ | — | — | — | −77.4 |
| | I (%) | 0 | 0 | 0 | 100 |
| IV[e] | δ | — | — | — | −75.4, −77.3 |
| | I (%) | 0 | 0 | 0 | 100 |

[a]Ref. 3. [b]Normalized intensity. [c]Ref. 2. [d]Na-4-mica prepared with stoichiometric MgO (this work). [e]Na-4-mica prepared with excess MgO (this work).

**Table 2** Sr uptake kinetics by Na-4-mica from a 0.5 M NaCl containing 0.0001 M $SrCl_2$

| time | % Sr update | |
|---|---|---|
| | mica with stoichiometric amount of MgO | mica with 2% excess MgO |
| 2 h | 28±0.9 | 25±1.4 |
| 4 h | 25±4.6 | 29±2.5 |
| 8 h | 28±2.5 | 28±5.9 |
| 1 d | 29±3.1 | 28±1.2 |
| 14 d | 76±1.4 | 79±2.2 |
| 90 d | 98±0.1 | 98±0.2 |
| 184 d | 99±0.05 | 99±0.05 |

one reason for the slow Sr uptake kinetics. Previously synthesized Na-4-mica from gels exhibited better kinetics[3] because of its smaller particle size of only 1 μm. Thus it is imperative to obtain a small particle size by changing the synthesis parameters such as time and temperature in order to achieve faster kinetics of ion uptake. Cation saturation of the mica may also affect the ion exchange kinetics because the interlayer distance is dependent upon the nature of the charge balancing cation. Such studies are in progress.

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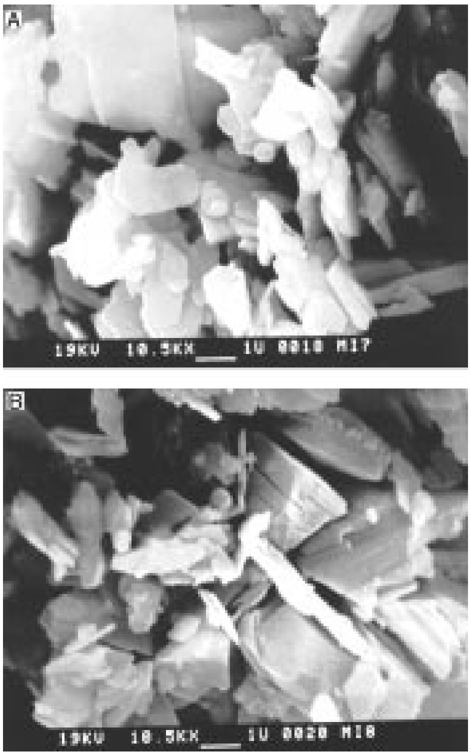

**Fig. 6** Scanning electron micrographs of Na-4-micas synthesized (A) with stoichiometric MgO and (B) with 2% excess MgO

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