

Simplified Synthesis of Swelling Na-4-Mica from Diatomite

ORRANUCH KUNTHIYAJAI^a, PHONGSAK LAOOT^a,
KUNWADEE RANGSRIWATANANON^b and APHIRUK CHAISENA^{a*}

^aDepartment of Applied Chemistry and Center for Innovation in Chemistry,
Faculty of Science, Lampang Rajabhat University, Lampang 52100, Thailand

^bSchool of Chemistry, Institute of Science, Suranaree University of Technology,
Nakhon Ratchasima 30000, Thailand

a_chaisena@hotmail.com

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Abstract: A swelling Na-4-mica (a highly charged fluorophlogopite) has recently attracted much attention because of its unique combination of high charge (four charges per unit cell) and swelling and cation exchange properties. Synthetic mica (ideal composition of $\text{Na}_4\text{Mg}_6\text{Al}_4\text{O}_{20}\text{F}_4 \cdot x\text{H}_2\text{O}$) was prepared by a simplified single-step synthetic process (NaCl-melt method) from diatomite at 900 °C for 5 h. The obtained micas were characterized by powder X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and ²⁹Si and ²⁷Al magic-angle-spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. Powder XRD and FT-IR data showed that the swelling Na-4-mica was obtained from diatomite (which serves as a cost-effective aluminosilicate source) with a small particle size (mean 2 μm) as revealed by SEM. The ²⁹Si and ²⁷Al MAS-NMR revealed the Si and Al nearest neighbor environment as well as the presence of impurities such as glassy phase.

Keywords: Swelling Na-4-mica, Diatomite, Single-step synthetic process, Aluminosilicate

Introduction

Mica is representatives of the 2:1 phyllosilicates and consists of layers, composed of two sheets of Si-Al-O tetrahedral sandwiched between M-O and OH octahedral; the tetrahedral share corners of oxygen atoms. In contrast, two anion sites of the octahedral sheet shared only by other octahedral are oxygen atoms that are bound to hydrogen atoms forming OH groups, when not comprised of other anions such as F and Cl. Micas are distinguished from smectites or vermiculites by their higher layer charge density. The two main categories of micas based on layer charge density are: 1) true micas with 1 negative charges per formula unit and 2) brittle micas with 2 negative charges per formula unit¹. Owing to their high charge density, naturally occurring micas do not normally swell in water and other polar solvents; as a result, exchange reactions with the interlayer cations do not readily occur. Synthetic micas, which swell in water, with cation exchange capacities of more than 200 mequiv (100 g)⁻¹, have been prepared and are of considerable interest²⁻⁷. In particular, Na-4-mica is a very highly charged sodium fluorophlogopite mica of theoretical chemical composition

$\text{Na}_4\text{Mg}_6\text{Al}_4\text{O}_{20}\text{F}_4 \cdot x\text{H}_2\text{O}$, first prepared by Gregorkiewitz and Rausell-Colom in 1978⁸. In the first synthesis, was obtained as a reaction product, among others, after augite powders had been melted in fluoride salts. Two decades later, Paulus *et al.*⁹ employed a multi-step sol-gel method, obtaining higher amounts of the silicate in each experiment, with mica being the main product. However, to leave the product free of insoluble salts, repeated washings in boric acid were necessary. Franklin and Lee¹⁰ succeeded in an “all-in-one” method in which several steps of the sol-gel method were merged together, but the problem of impurities remained unsolved. Park *et al.*¹¹ developed a new route, the so called NaCl-melt method, obtaining a “pure” Na-4-mica for which boric acid washings were not necessary. Thus, synthetic Na-4-mica is usually produced using various methods such as hydrothermal synthesis, topotactic exchange, sol-gel and solid-state methods or all-in-one methods. Raw natural materials such as talc¹², augite⁸, kaolinite^{7,13-16} and fly ash¹⁷ are used. Nevertheless, an unprecedented number of micas are synthesized using diatomite. Diatomite rock is a loose, earthy or loosely cemented porous and lightweight rock of sedimentary origin, which is mainly formed by fragments of the armor (skeletons) of microscopic diatom alga with sizes ranging from 0.75 to 1500 m; sometimes this rock is called infusorial earth, kieselguhr, or mountain meal. The main components of the siliceous armor are silica hydrates of a different degree of water content (opals) $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ¹⁸. Diatomites are mineral deposits of diatomaceous algae and commercially exploited diatomite are being restricted to a relatively modern age, starting from the Miocene. Amorphous silica, a constituent of the diatom frustulae, is the main component of diatomite, although variable quantities of other materials [metal oxides, clays, salts (mainly carbonates) and organic matter] may also be present. Prevailing chemical and environmental conditions are determining factors in the nature and importance of the impurity content of a deposit¹⁹. The high quality of diatomite in the Lampang Basin, Thailand has the following composition: silica (SiO_2) 78-80 wt% alumina (Al_2O_3) 10-12 wt% and iron oxide (Fe_2O_3) < 5.0 wt%²⁰. In the present work, we further simplified the synthesis of the Na-4-micas by a single-step synthetic process from diatomite as the main aluminosilicate source and NaCl as a fluxing agent. In addition, we characterized this synthetic Na-4-mica with different techniques. This naturally occurring diatomite as an inexpensive aluminosilicate source is expected to contribute to the cost-effective synthesis of this mica for wide spread application in the remediation of metal-contaminated soils and ground water or the treatment of metal-containing waste solutions.

Experimental

Naturally occurring diatomite of the composition, 72.40% SiO_2 , 12.50% Al_2O_3 , 5.80% FeO_3 , 0.40% TiO_2 , 0.23% CaO , 0.52% MgO , 1.34% K_2O and 0.31% Na_2O (supplied by Sriphum Wattana Partnership Limited, MaeTha District, Lampang Province, Thailand) was used to synthesize Na-4-mica. A single-step procedure similar to that described by Park *et al.* was employed to synthesize Na-4-mica¹¹. Near-stoichiometric powder mixture with the molar composition 4SiO_2 , $2\text{Al}_2\text{O}_3$, 6MgF_2 , 8NaCl was used. Diatomite was used as received without any pretreatment. MgF_2 was obtained from Aldrich (CAS.no.20831-0, 98%) and NaCl was obtained from Panreac (CAS.no.131659, 99.5%). All reactant mixtures were ground in an agate mortar, weighted and subsequently heated in Pt crucibles in the temperature range of 700 to 1000 °C for 15 h. To study the effect of time on the formation of Na-4-mica at 900 °C, time periods of 5 h, 10 h, 15 h, 20 h and 25 h were employed. After the above treatment, the samples were repeatedly washed with deionized water to remove all the soluble salts by centrifugation. The solids were dried in an oven at 60 °C prior to characterization. The solid samples were characterized by power X-ray diffraction (XRD)

using a Scintag diffractometer with a Bruker D5005 instrument, operated at 35 kV and 35 mA current with CuK_α radiation ($\lambda=1.54178 \text{ \AA}$). Moreover, Fourier transform infrared spectroscopy (FT-IR) was used to study the structural features. The instrument used for this analysis was a Shimadzu model 8900, measuring samples prepared by the KBr pellet technique. Infrared spectroscopy studies were performed for the mid-infrared region (from 4000 to 400 cm^{-1}), where vibration and rotation bands are observed. The spectra were obtained using an average of 20 scans with 8 cm^{-1} resolution. Some of the samples were characterized by scanning electron microscopy (SEM) using JSM-5410LV with INCA software by oxford to determine the particle size and shape. A few samples were investigated by solid-state ^{29}Si and ^{27}Al MAS-NMR spectroscopy to determine the coordination of Al and the nearest neighbor environment of the Si atoms. ^{29}Si and ^{27}Al spectra were obtained at 78 and 60 MHz respectively using a Bruker Biospin DPX300 spectrometer with double bearing rotor (5 mm, Zirconia). For ^{27}Al resonance the spectrometer operating conditions were as follows: recycle delay 4.05 s, number of transients 800, and spinning speed 5 KHz. Chemical shifts were measured relative to aqueous $\text{Al}(\text{NO}_3)_3$. The ^{29}Si spectrum was acquired using a recycle delay of 6 s, 1600 transients and 5 KHz spinning speed. Chemicals shifts were referenced to the signal of tetramethylsilane (TMS).

Results and Discussion

Natural raw diatomite collected from Lampang contains quite high amount of SiO_2 and Al_2O_3 and some impurities of Fe_2O_3 and K_2O and smaller amounts of TiO_2 , CaO , MgO and Na_2O . The diatomite was a sufficient aluminosilicates sources for the synthesis of Na-4-mica. The synthesis conditions and d -spacing of the (001) peak (\AA) for Na-4-mica samples are provided in Table 1. Figure 1 shows the XRD patterns obtained for the different products synthesized by temperature of 700, 800, 900 and 1000 $^\circ\text{C}$ for 15 h. The XRD pattern of the resultant solid prepared at 700 $^\circ\text{C}$ can be described as containing mostly sodalite (PDF 72-0029). The lattice spacing of the Na-4-micas formed at 800-1000 $^\circ\text{C}$ related to that of the Na-4-mica (PDF 54-1025). As shown in Figure 2, (001) reflection of the hydrated Na-4-mica with a single sheet of interlayer water was observed at 11.33-11.89 \AA . As the temperature increased, the Na-4-mica peaks became sharper, because of crystal growth. The $d(001)$ spacing of 11.62-11.99 \AA can be observed in the XRD patterns of all the samples and the crystalline phase of MgF_2 (PDF 41-1443) is observed in the XRD pattern of the reaction time of 5 h. Impurity peaks attributed to sodalite (PDF 72-0029) and a forsterite (Mg_2SiO_4 , PDF 34-0189) corresponding to those reported by Alba *et al.* were observed²². Thus, the XRD pattern of the product that was heated for 15 h was found to be stable, showing reflections that can be indexed as hydrated mica with a 11.89 \AA basal spacing. Additionally, for $t \geq 5$ h, a new reflection was observed, indexed as sodalite.

Table 1. Synthesis conditions and d -spacing of Na-4-micas synthesized by the NaCl melt method

Sample no.	Temperature, $^\circ\text{C}$	Duration time, h	d -spacing, \AA
D01	700	15	-
D02	800	15	11.33
D03	900	15	11.89
D04	1000	15	11.76
D05	900	5	11.62
D06	900	10	11.91
D07	900	20	11.86
D08	900	25	11.99

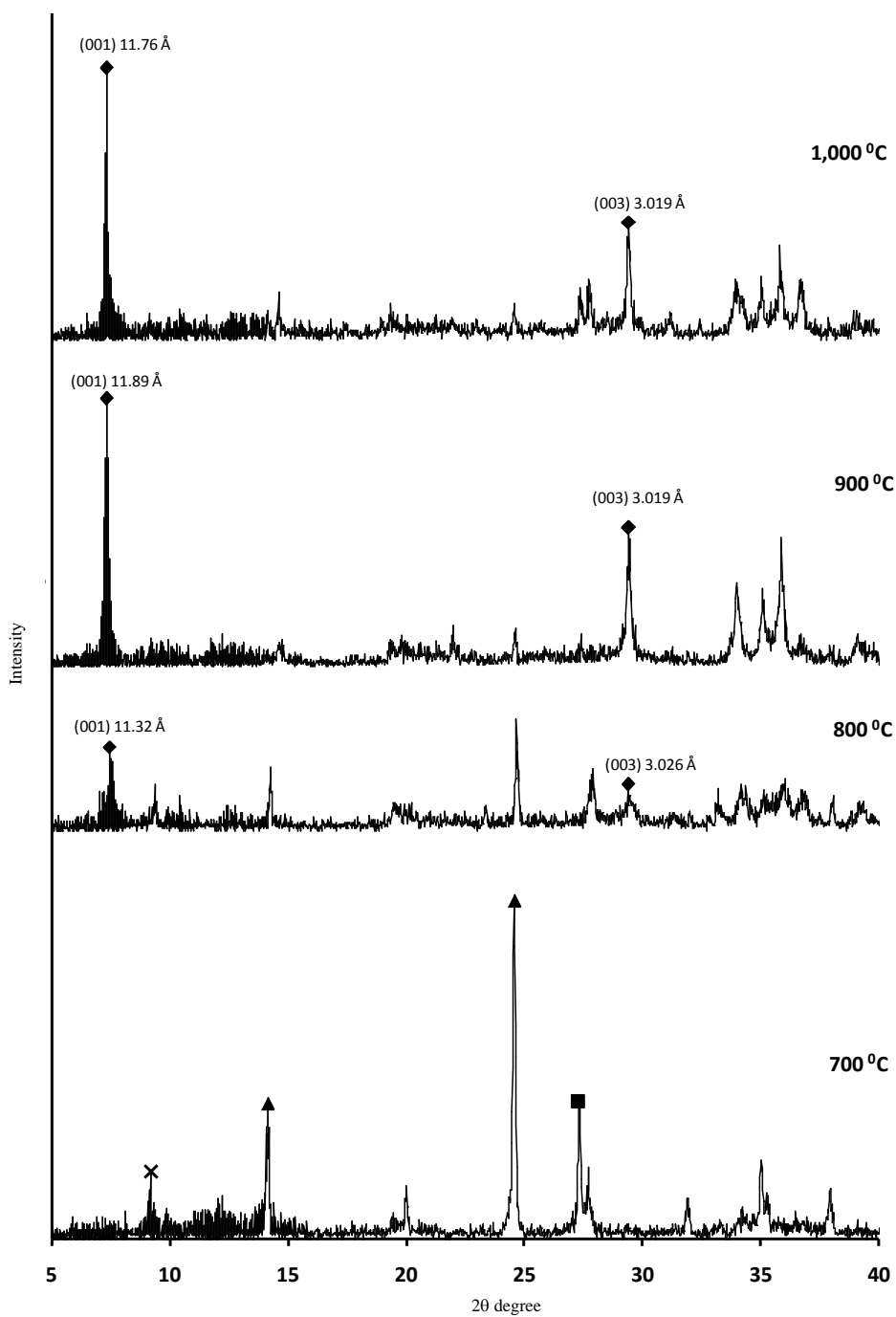


Figure 1. XRD pattern of the samples as a function of temperature calcinations at 700 °C, 800 °C, 900 °C and 1000 °C (◆): Na-4-Mica, (X): anhydrous mica, (▲): sodalite, (■): MgF₂

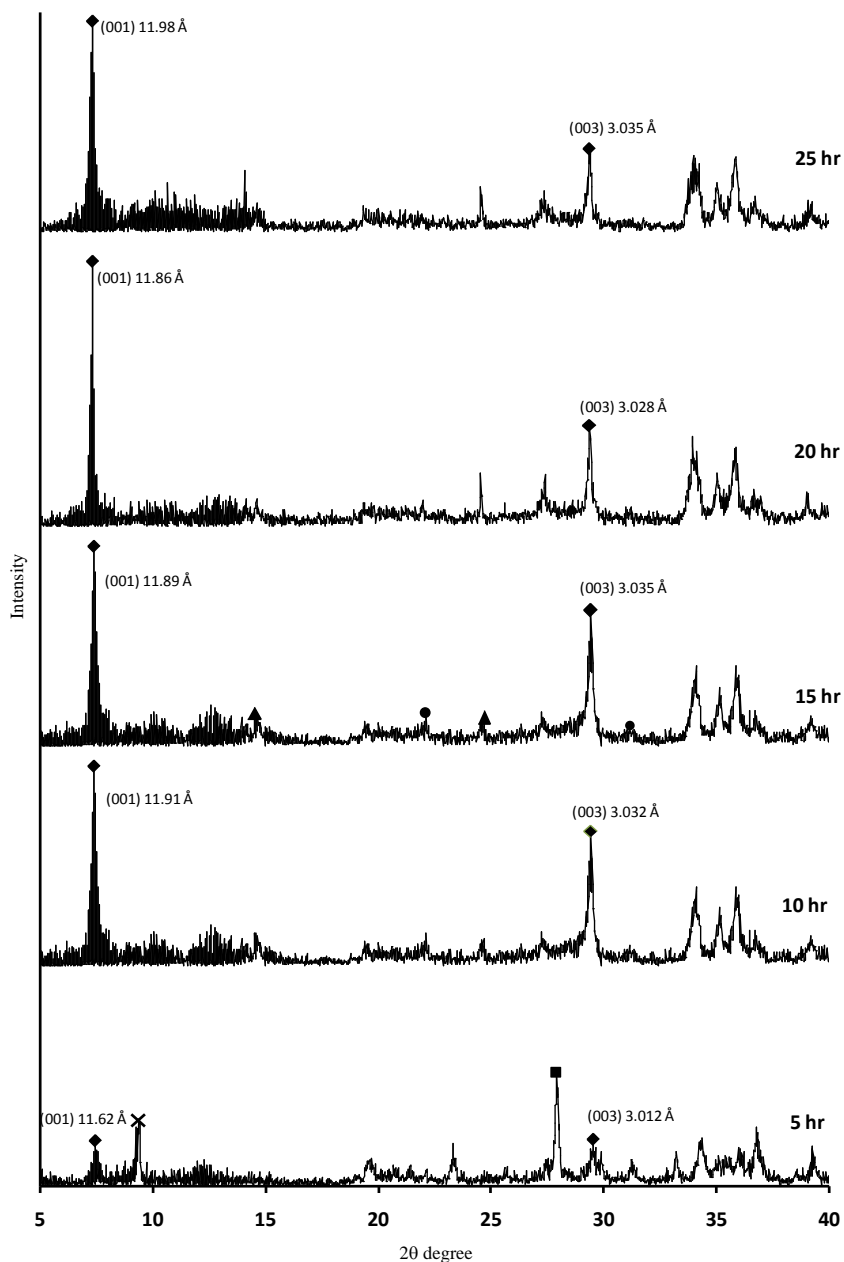


Figure 2. XRD pattern of the samples as a function of reaction time at 5 h, 10 h, 15 h, 20 h, and 25 h. (◆): Na-4-Mica, (X): anhydrous mica, (▲): sodalite, (■): MgF_2 (●): forsterite

The infrared spectra of diatomite and the synthesized Na-4-mica (15 h) are presented in Figure 3. The major composition of diatomite is SiO_2 and the IR spectra exhibit a series of expected transmission bands. The FT-IR spectral band positions of the diatomite sample were 1649, 1096, 1016, 914, 799, 673, 535 and 469 cm^{-1} . The band at 1649 cm^{-1} is assigned

to the bending vibration of adsorbed water. In the low wave numbers region, there were up to 7 characteristic bands of natural diatomite and the band at 1096 cm^{-1} was mainly attributed to siloxane (Si-O-Si) stretching of amorphous silica.

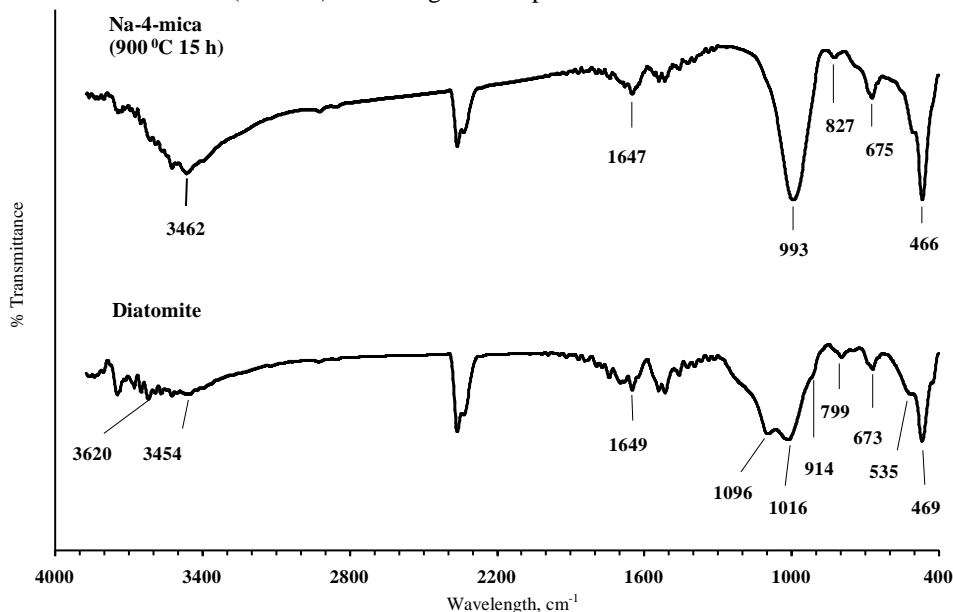


Figure 3. IR transmission spectrum of diatomite as compared with synthetic Na-4-mica ($900\text{ }^{\circ}\text{C}$ 15 h)

The band at 535 cm^{-1} was due to Si-O-Al bending. The band at 799 cm^{-1} corresponds to an inter tetrahedral Si-O-Si bending vibration and the 673 and 469 cm^{-1} bands were due to O-Si-O bending. The 914 cm^{-1} band may be due to Si-OH stretching and Al-Al-OH bending²³⁻²⁶. For the hydrated form of Na-4-mica ($d=11.89\text{ \AA}$), there are strong peaks at 3462 and 1647 cm^{-1} that corresponding to the frequencies of H_2O stretching and bending, respectively. The lower part of the spectrum ($1200\text{-}400\text{ cm}^{-1}$) corresponds to lattice vibrations of (Si, Al)-O and Mg-O. The characteristic bands of SiO_4 tetrahedral units were observed at 466 cm^{-1} (Si-O-Si) bending, 675 cm^{-1} (M-O-Si) stretching and 993 cm^{-1} (Si-O) stretching²⁷.

The SEM micrograph of Na-4-mica that had been heated $900\text{ }^{\circ}\text{C}$ for 15 h (Figure 4) reveals hexagonal crystallites that are typical of the mica morphology with a mean crystal size of $2\text{ }\mu\text{m}$. The ^{29}Si MAS-NMR spectrum revealed that this mica has a similar nearest neighbor environments to that of a Na-4-mica⁵. It exhibited two major and three minor ^{29}Si resonances of Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al) at -74.5 , -78.1 , -81.3 , -85.4 , and -90.0 ppm from TMS. A complete Si/Al ordering in a Na-4-mica of ideal composition would give only one resonance corresponding to a Si(3Al) environment. These spectra, however, showed the presence of two resonances at δ -78.1 and -74.5 ppm , which represent two different types of environments. For the hydrated Na-4-micas that had been prepared before, the resonance for Si(3Al) predominantly appeared at about δ -78 ppm ^{2,5,8}. Frequently, however, the small Si(3Al) resonance was also observed at about δ -75 ppm ^{2,5}. 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 silicon²⁸.

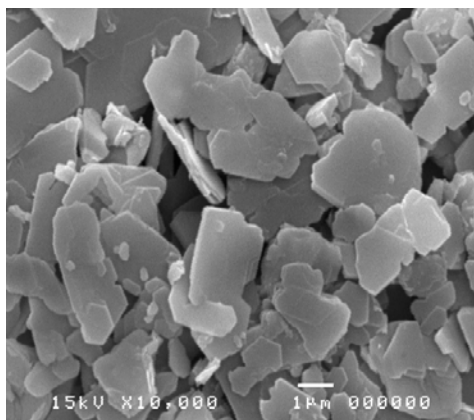


Figure 4. SEM micrographs of Na-4-mica after 900 °C for 15 h of heating

Komarneni *et al.* suggested that the resonance at about δ -75 ppm may be due to the Si(3Al) of the anhydrous Na-4-mica phase because the completely anhydrous mica prepared by the NaCl melt method at 900 °C showed predominantly a resonance at δ -74.5 ppm with a minor resonance at δ -78.1 ppm²⁹. These micas prepared here may contain a very small portion of an anhydrous phase or a poorly hydrated phase, although it was not detected by the XRD analysis (Figure 1, 2). The synthetic micas also showed a significant resonance at -81.3 ppm, which can be assigned to Si(2Al) based on previously reported assignments^{2,5,6,28,30}. The spectrum shows a strong resonance due to Al in a tetrahedral coordination at δ ca. 53.5 ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. Thus, this spectrum indicated that nearly the entire Al was incorporated into tetrahedral sites. A shoulder resonance at about 40 ppm was observed, however, which represented a second Al tetrahedral environment. It is not clear at this point what this environment is, but a second Al tetrahedral environment has been frequently observed in the ²⁷Al MAS-NMR spectra of Na-4-micas^{5,6}. Komarneni *et al.* previously concluded that the shoulder was probably from a glassy impurity phase⁵. This impurity glassy phase must contain large amounts of sodium to increase the sodium content of Na-4-mica here, as mentioned above. The fraction of the impurity phase must be very small because only a small shoulder resonance was observed at 40 ppm.

Conclusion

A cost-effective method for the synthesis of swelling Na-4-mica has been developed using diatomite as an economical aluminosilicate source and NaCl as a melting agent. This NaCl-melt method can be considered a general procedure for the synthesis of high layer charge silicates. The method consists of a single-step synthetic process that involves mixing and calcinations in a Pt crucible. ²⁹Si and ²⁷Al MAS-NMR spectroscopy revealed that the Na-4-micas prepared here have Si and Al distributions that are much closer to those of ideal Na-4-mica compared with those prepared by other procedures at lower crystallization temperatures.

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References

1. Grim R E, Clay Mineralogy, 2nd Edn., McGraw-Hill; New York., 1968.
2. Komarneni S, Pidagu R and Amonette J E, *J Mater Chem.*, 1998, **8**, 205-208.
3. Kodama T and Komarneni S, *J Mater Chem.*, 1999, **9**, 533.
4. Kodama T and Komarneni S, *J Mater Chem.*, 1999, **9**, 2475-2480.
5. Komarneni S, Pidugu R, Hoffbauer W and Schneider H, *Clays Clay Miner.*, 1999, **47(4)**, 410-416.
6. Kodama T, Komarneni S, Hoffbauer W and Schneider H, *J Mater Chem.*, 2000, **10**, 1649-1653.
7. Kodama T and Komarneni S, *Sep Sci Technol.*, 2000, **35**, 1133-1152.
8. Gregorkiewitz M and Rausell-Colom J A, *Am Miner.*, 1987, **72**, 515.
9. Paulus W J, Komarneni S and Roy R, *Nature (London)*, 1992, **357**, 571-573.
10. Franklin K R and Lee E, *J Mater Chem.*, 1996, **6**, 109-115.
11. Park M, Lee D H, Choi C L, Kim S S, Kim K S and Choi J, *J Chem Mater.*, 2002, **14**, 2582-2589.
12. Taleyama H, Noma H, Nishimura S, Adachi Y, Ooi M and Urabe K, *Clays Clay Miner.*, 1998, **46**, 245-255.
13. Kodama T, Harada Y, Ueda M, Shimizu K, Shuto K and Komarneni S, *Langmuir*, 2001, **17(16)**, 4881-4886.
14. Kodama T, Nagai S, Hasegawa K, Shimizu K I and Komarneni S, *Sep Sci Technol.*, 2002, **37(8)**, 1927-1942.
15. Kodama T, Hasegawa K, Shimizu K I and Komarneni S, *Sep Sci Technol.*, 2003, **38(3)**, 679.
16. Kodama T, Komarneni S, Higuchi T, Hoffbauer W, Shimizu T, Shimizu K I and Schneider H, *J Mater Chem.*, 2001, **11**, 2072-2077.
17. Park M, Lee D H, Choi C L, Lim W T, Lee S K, Heo N H, Komarneni S and Choi J, *J Porous Mater.*, 2002, **9(4)**, 291-298.
18. Arik H, *J Eur Ceramic Soc.*, 2003, **23**, 2005-2014.
19. Mendioroz S, Belzunce M J and Pajares J A, *J Thermal Anal Calorimetry.*, 1989, **35**, 2097-2104.
20. Inglethorpe S D J, Utha-a-room C and Chanyavanich C, The International Conference on Stratigraphy and Tectonic Evolution of Southeast Asia and the South Pacific, Bangkok, Thailand, 1997, August 19-27, 669-685.
21. Maria D A, Miguel A C, Moises N and Esperanza P, *Chem Mater.*, 2006, **18**, 2867-2872.
22. Alba M D, Castro M A, Naranjo M, Orta M M, Pavon E and Pazos M C, *J Phys Chem. C*, 2011, **115**, 20084-20090.
23. Lyng S, Markali J, Krogh-Moe J and Lundberg N H, *Phys Chem Glasses*, 1970, **11**, 6-10.
24. Nayak P S and Singh B K, *Bull Mater Sci.*, 2006, **60**, 464-466.
25. Gendron-Badou A, Coradin T, Maquet J, Frohlich F and Livage J, *J Non-Cryst Solids.*, 2003, **316**, 331.
26. Laoot P, Rangsriwatananon K and Chaisena A, *J Ceram Process Res.*, 2011, **12(3)**, 273-278.
27. Dawy M, *Egypt J Sol.*, 2002, **25(1)**, 137.
28. Herrero C P, Gregorkiewitz M, Sanz J and Serratos J M, *Phys Chem Miner.*, 1987, **15**, 84.
29. Kuo S and Lotse E G, *Soil Sci.*, 1974, **116**, 400-406.
30. Sanz J and Serratos J M, *J Am Chem Soc.*, 1984, **106**, 4790-4793.