

SYNTHESIS OF EXPANDABLE FLUORINE MICA FROM TALC

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Abstract—Expandable fluorine micas were synthesized using talc and Na₂SiF₆ at 800°C for 2 hours in air, nitrogen, argon, and under vacuum. Gaseous SiF₄, generated from Na₂SiF₆, and the resultant amorphous sodium silicofluoride formed during the reaction between talc and Na₂SiF₆ below 900°C are taking active part in the formation of expandable micas because the intensity of the 12.5 Å reflection of expandable micas decreases as the gas flow increases in the furnace. Expandable micas seem to be formed by the transformation from talc taking place without the entire disruption of the original atomic arrangement. This takes place with the loss of one Mg²⁺ from an octahedral site and by the intercalation of every two Na⁺ into the interlayer site of talc. Infrared absorption and thermal analyses show that expandable micas include a small amount of OH⁻ in their structures.

Key Words—Expandable mica, Fluorine, Intercalation, Synthesis, Talc.

INTRODUCTION

Fluorine micas have been synthesized from melts at 1200°–1500°C or by solid state reactions at 900°–1200°C (Daimon, 1952; Hatch *et al.*, 1957; Matsushita, 1960; Shell and Ivey, 1969; Sugimori, 1986). Fluorhectorites (Li-smectites) were synthesized in the solid state at 800°C within 24 hours, or in melts at 850°C within 2 hours, using reagent-grade chemicals such as pure silica, MgO, MgF₂, LiF, and Na₂CO₃ (Barrer and Jones, 1970). However, pure Na-smectites could not be synthesized in these experiments. Tateyama *et al.* (1990) reported expandable and nonexpandable micas synthesized at 700°–900°C for one hour using talc and alkali silicofluoride. In the present study, the formation of expandable micas from talc and the properties of these micas were investigated by thermal, X-ray powder diffraction, infrared absorption and nuclear magnetic resonance techniques. The synthetic products are called expandable micas because they are chemically similar to sodium tetrasilicic micas (Shell and Ivey, 1969). The expandable properties of the synthetic micas will be discussed in a subsequent paper.

EXPERIMENTAL METHODS

The talc used in this study is from the Kanshi deposit in China. The chemical composition of the talc is given in Table 1. The Na₂SiF₆ used was a reagent-grade chemical. Milled in a vibrating ball mill, the weighed talc [Mg₃Si₄O₁₀(OH)₂] and Na₂SiF₆ were mixed as shown in Table 2, and then placed in a platinum crucible with a lid to minimize volatilization. The crucible was heated at 700°–900°C in an electric furnace having a cylindrical shape 330 mm in diameter by 400 mm in length, into which a cylindrical, aluminum-oxide pipe 40 mm in diameter and 700 mm long was placed.

The experimental conditions were as follows: heating rate, 10°C/min; holding time, 2 hours. The atmosphere in the electric furnace was in air without current, or in air, argon, or nitrogen with a flow rate of 40–200 ml/min. A vacuum condition at 20 Pascal was used.

The mixtures were analyzed by thermogravimetric (TGA) and differential thermogravimetric analysis (DTG). They were placed in a Pt capsule with a lid under the same heating conditions as the experiments in the electric furnace. All the products were analyzed with Cu radiation by X-ray powder diffraction at 70% (±5%) relative humidity. Infrared absorption spectra of the products were measured by the KBr method. All the ²⁹Si-NMR spectra of talc and synthetic micas were recorded in a 47-SCG field at 39.75 MHz equipped with a widebore superconducting magnet. High-power ¹H spin decoupling and rapid (~3.25 SCHz) sample spinning at the magic angle to the external magnetic field were used.

RESULTS AND DISCUSSION

Synthesis of expandable micas from talc

Batch TM-3 in Table 2 was analyzed by TGA and DTG as shown in Figure 1. Two prominent weight-loss events were encountered. The first event, at roughly 400°–620°C, marked a rapid weight loss, and the second event was a gradual weight loss between 620° and 920°C.

To analyze the formation of expandable micas from talc, batch TM-3 was air-quenched from 300° to 1000°C at each 50°C interval. X-ray powder diffraction patterns of the air-quenched samples are shown in Figure 2. The reflections from Na₂SiF₆ remained until the structure collapsed at about 600°C when the reflections disappeared and those of NaF appeared. The 3.8%

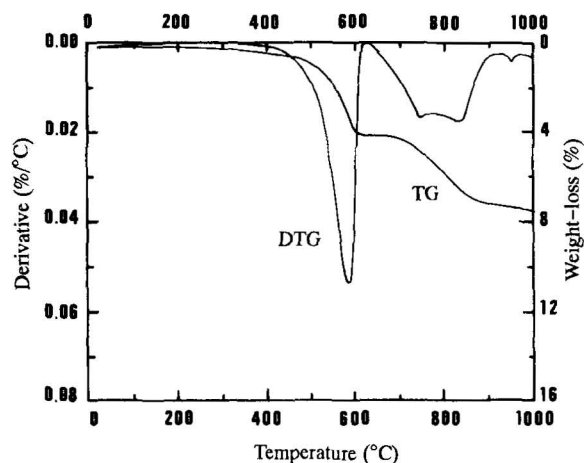


Figure 1. Thermogravimetric data for the mixture (TM-3).

weight loss between 400° and 620°C was due to the decomposition of Na_2SiF_6 . However, the total weight loss of Na_2SiF_6 , which is supposed to be completely collapsed below 620°C, was calculated to be 9.1%. The calculated weight loss did not correspond to the observed loss.

The peak intensity of the (001) reflection of talc at each reaction temperature is shown in Figure 3. The peak intensity of talc decreased from about 8000 cps at 20°–400°C to about 4000 cps at 600°C. These results indicate that the partial removal of the structural water in talc may occur between 400°C and 600°C. Continued heating up to 800°C leads to a reaction of NaF with talc, which yields mainly nonexpandable materials with a *c*-dimension spacing of 9.6 Å and a small amount of expandable micas with a spacing of 12.5 Å. (Nonexpandable materials are here defined to lack the property of being readily expanded by the incorporation of moisture in the air into the phyllosilicate at room temperature. The properties of nonexpandable materials will be discussed in a subsequent paper.) The X-ray powder diffraction pattern of the mixture heated at 900°C shows that talc transformed into expandable micas from nonexpandable materials. The formation of expandable micas indicates that OH^- in the talc structure is replaced by F^- in the mica structure, whereas Na^+ intercalates in the interlayer site of talc. The charge balance of the expandable micas would require the loss of one Mg^{2+} from an octahedral site for every two Na^+ in the interlayer site (Tateyama *et al.*, 1990).

The total weight loss of talc in the mixture was calculated to be (ideally) 4.0% on the basis of the empirical formula of talc. This value did not correspond to the measured 3.1% weight loss between 620° and 920°C. The difference between the observed and calculated values (0.8%) seems to be the amount of talc dehydration below 620°C. Richterite first formed at 950°C, and

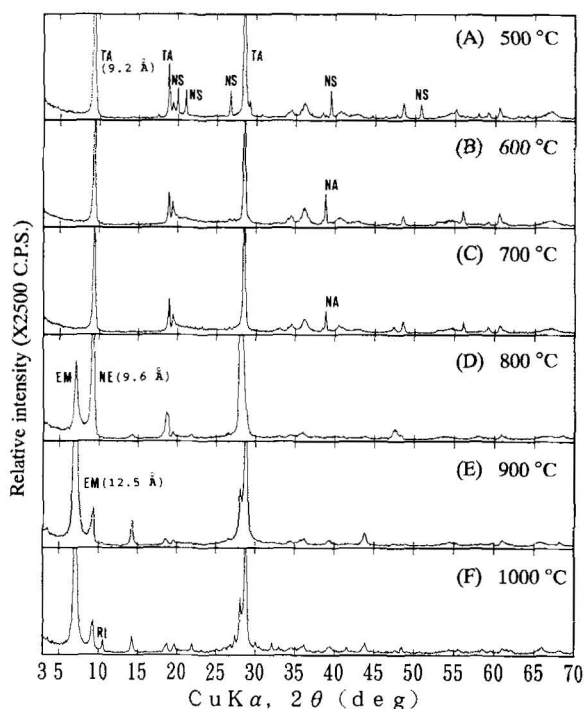


Figure 2. X-ray powder diffraction patterns of air-quenched samples. TA, Talc; NS, Na_2SiF_6 ; NA, NaF; NE, nonexpandable materials; EM, expandable micas; RI, richterite.

at 1000°C its X-ray pattern became much clearer. The intensity of the (001) reflections of both products decreased, indicating the partial decomposition of expandable micas and nonexpandable materials.

Synthesis of expandable micas in different atmospheres

Figure 4 (A) shows the X-ray diffraction pattern of the product after heating at 800°C for 2 hours in static air. It is similar to that of the product in Figure 2 (E). The X-ray powder diffraction pattern of the product synthesized in a slow air current (40 ml/min) is shown in Figure 4 (B). The air-flow treatment will have a negative effect on the formation of expandable micas. Figures 4 (C) and (D) show X-ray powder diffraction patterns of the products synthesized in the slow currents of nitrogen and argon, respectively. The peak intensities of the expandable micas decreased as compared with those of the expandable micas in Figure 4 (A). The decrease in the intensity of expandable micas became more prominent as the gas flow current increased from 40 to 200 ml/min. Figure 4 (E) shows the X-ray powder diffraction pattern of the product synthesized under vacuum. The intensities of both the expandable micas and nonexpandable materials decreased. These results indicate that the removal of gaseous SiF_4 from the crucible has a negative effect on the formation of expandable micas because the elemental

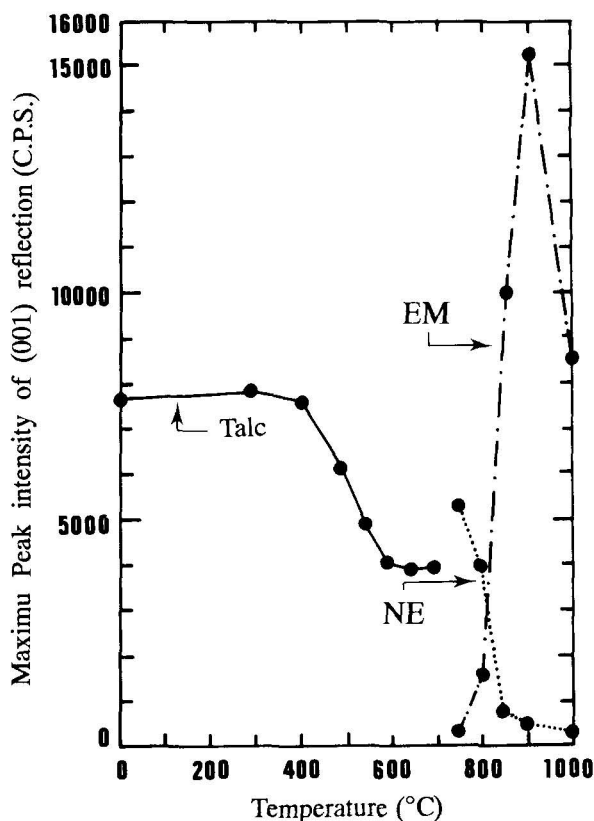


Figure 3. The maximum peak intensity of the (001) reflection of talc, expandable micas and nonexpandable materials plotted against reaction temperature. Talc, 9.2 Å reflection; EM, 12.5 Å reflection of expandable micas; NE, 9.6 Å reflection of non-expandable materials.

compositions of the resultant amorphous sodium silicofluoride alter according to the atmosphere in the furnace. To clarify the role of SiF_4 in the formation of expandable micas, 2NaF instead of Na_2SiF_6 was mixed with talc and the mixture heated at 800°C for 2 hours. Expandable micas were not formed, and impurities were obtained as shown in Figure 5 (A). This fact also implies that diffusion of SiF_4 out of the crucible is important since the concentration of SiF_4 in the gas phase over the solid reactants should influence the formation of the expandable micas.

To compare a solid state reaction using chemicals with the present reaction, a mixed sample in the mole ratio of 3MgO and 4SiO_2 (amorphous silica) was artificially prepared to have the same empirical composition as talc. After mixing the sample ($3\text{MgO} +$

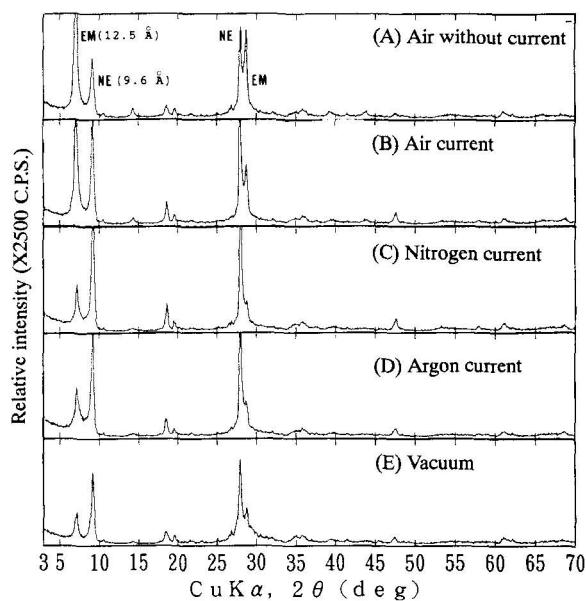


Figure 4. X-ray powder diffraction patterns of micas synthesized at 800°C for 2 hours in several atmospheres. EM, expandable micas; NE, nonexpandable materials.

4SiO_2) with $0.4\text{Na}_2\text{SiF}_6$ in the exact mole ratio, it was heated at 800°C for 2 hours. The X-ray powder diffraction pattern of the product is shown in Figure 5 (B). Expandable micas were not synthesized and the amorphous silica remained in the product as an unreacted substance, but nonexpandable materials were formed. The expandable micas seem to be easily formed from talc at a relatively low temperature, which indicates that the transformation from talc to mica takes place without complete disruption of the original atomic arrangement, and with the loss of one Mg^{2+} from an octahedral site and by the intercalation of two Na^+ into the interlayer site of talc.

Synthesis of expandable micas with variable Na_2SiF_6

Talc was mixed with Na_2SiF_6 as shown in Table 2 in order to investigate the effect of varying the amount of Na_2SiF_6 on the formation of expandable micas and nonexpandable materials. Figure 6 shows the weight loss in each temperature range measured from the thermogravimetric analysis data. The weight loss in the region of $400^\circ\text{--}620^\circ\text{C}$ increased as the amount of Na_2SiF_6 increased. The weight loss by dehydration of talc between 620° and 920°C , however, was almost constant and independent of the amount of Na_2SiF_6 .

Table 1. Composition of Kanshi talc.

Chemical composition								
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	L.O.I.	Total
61.10	0.12	0.19	0.37	32.04	0.01	0.05	6.09	99.97

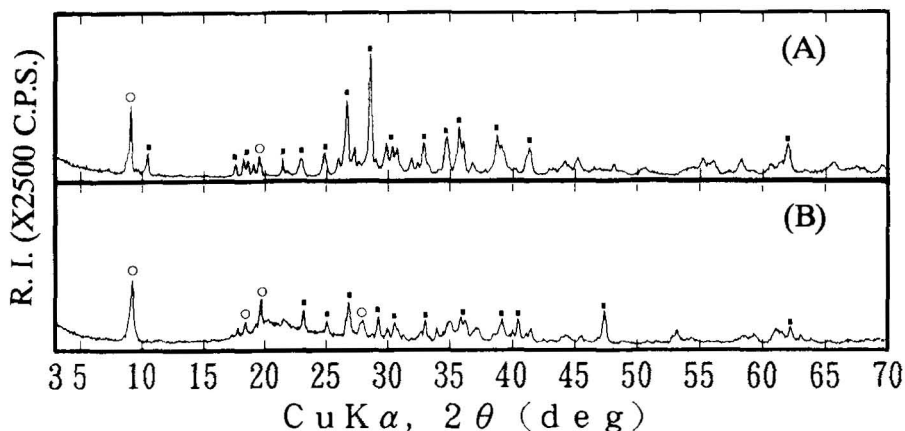


Figure 5. X-ray powder diffraction patterns of the products heated at 800°C for 2 hours. (A) mixture of talc and 2NaF, (B) mixture of 4SiO₂, 3MgO, and 0.4Na₂SiF₆, ○ nonexpandable materials; ■ impurities.

The products synthesized using batches TM-1 and TM-5 included a small amount of cristobalite and enstatite, respectively. The other products did not contain impurities. X-ray analysis of the products (Figure 7) indicates that the amount of Na₂SiF₆ has an effect on the formation of expandable micas and the products consist mainly of expandable micas. The intensity of the 9.6 Å reflection of the nonexpandable materials decreased, and that of the 12.5 Å reflection of the expandable micas increased as the amount of Na₂SiF₆ increased. This result shows that an excess amount of Na₂SiF₆ promotes the formation of expandable micas.

Infrared absorption spectra in the range of 3000–3800 cm⁻¹ are shown in Figure 8. There is a small peak at the shoulder of the H₂O-stretching band at about

3450 cm⁻¹. In the spectra of natural and synthetic micas, the OH-stretching frequency varies with defects and substitutions in the octahedral and tetrahedral sheets (Farmer, 1974). The absorption band at 3630 cm⁻¹ is due to the OH-stretching vibration being a result of the association of OH with vacancies in the octahedral sheet (Vedder, 1964; Tateyama *et al.*, 1976). The peak at 3630 cm⁻¹ for expandable micas in the products of TM-3 and TM-5 may also be assigned to the OH-stretching vibration. The weight loss in the range of 400°–800°C is shown in Table 3. Infrared and thermal analyses show that expandable micas include a small amount of OH⁻ in their structure. The frequency at 3680 cm⁻¹ corresponds to that of talc, which indicates that a small amount of talc still remained in the products of batch TM-1.

The ²⁹Si-NMR spectra of talc and expandable micas are shown in Figure 9. The ²⁹Si chemical shifts of natural aluminosilicates depend mainly on the number of Al atoms in the second coordination sphere of the Si atoms (Lippmaa *et al.*, 1980). The ²⁹Si spectrum of talc

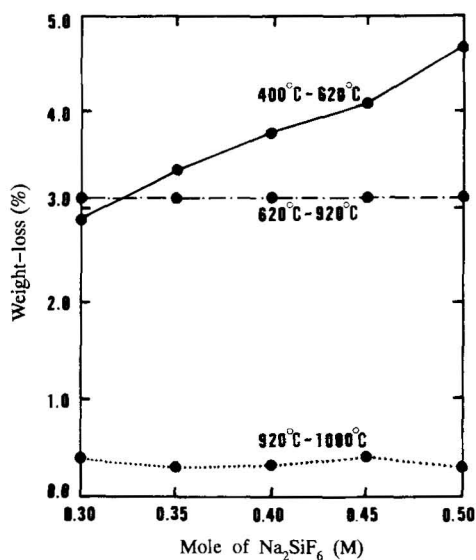


Figure 6. Weight loss (%) of the mixtures from TM-1 to TM-5 at each temperature range plotted against moles of Na₂SiF₆.

Table 2. Batch compositions.

	Batch formulation (moles)		Mixing ratio (wt. %)	
	Talc	Na ₂ SiF ₆	Talc	Na ₂ SiF ₆
TM-1	1	0.30	87.04	12.96
TM-2	1	0.35	85.20	14.80
TM-3	1	0.40	83.44	16.56
TM-4	1	0.45	81.74	18.26
TM-5	1	0.50	80.12	19.88

Table 3. Weight loss (%) of expandable micas at each temperature range.

Batch	400°–800°C	800°–1000°C
TM-1	0.18	0.50
TM-3	0.32	0.54
TM-5	0.39	0.59

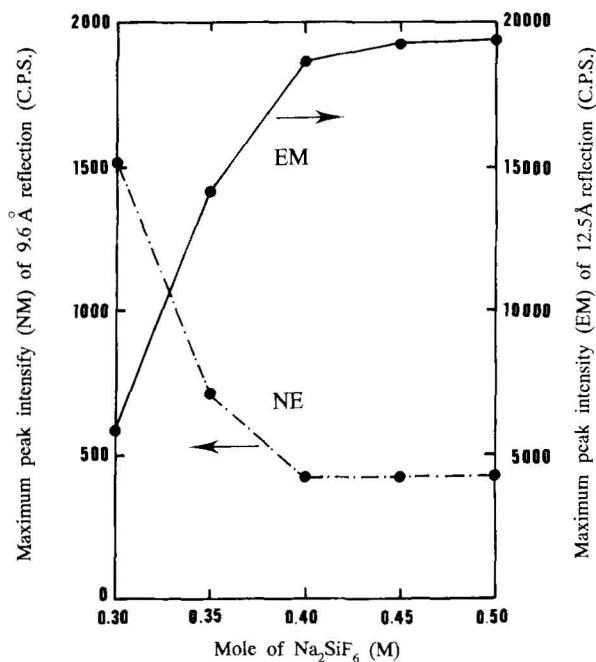


Figure 7. The maximum (001) peak intensity (counts per second) of expandable micas and nonexpandable micas plotted against moles of Na_2SiF_6 .

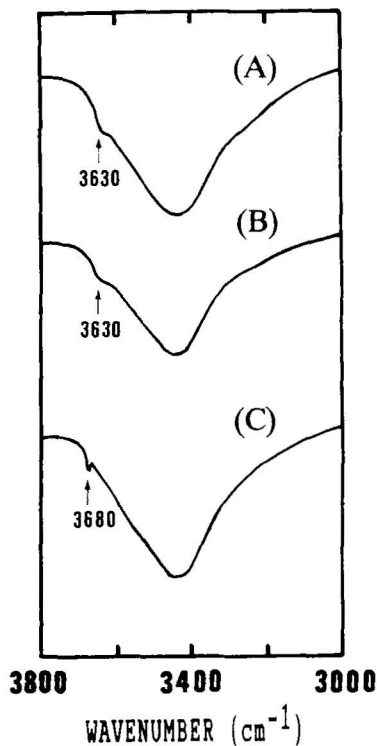


Figure 8. Infrared absorption spectra of synthetic micas in the range of 3000–3800 cm^{-1} . (A) expandable micas (TM-5), (B) expandable micas (TM-3), (C) expandable micas (TM-1).

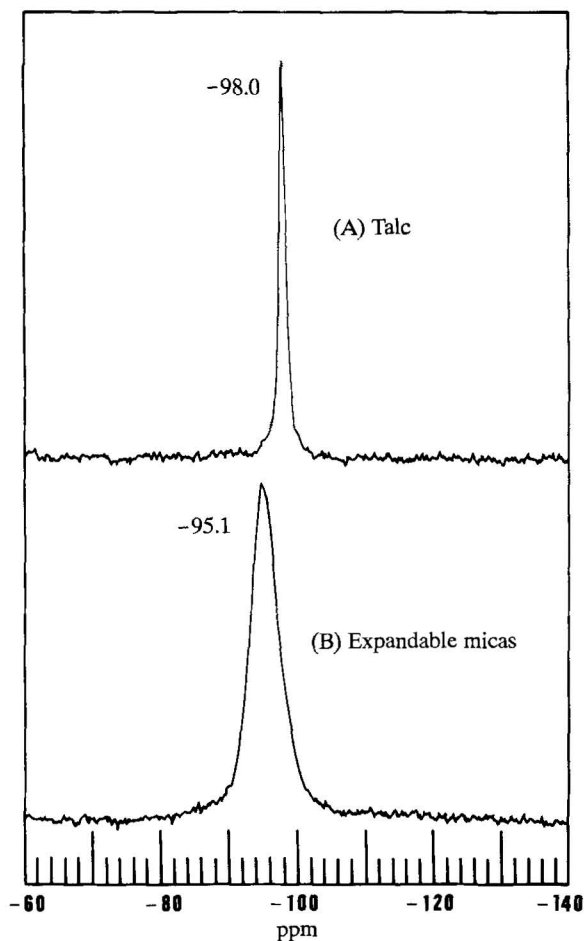


Figure 9. The ^{29}Si -NMR spectra of talc and expandable micas (TM-3).

contains a very sharp line and lies at -98.0 ppm, which is in complete agreement with that of previous studies (Mägi *et al.*, 1984; Smith *et al.*, 1983). The intensity distribution of the ^{29}Si -NMR line of expandable micas corresponding to the unsubstituted Si(OAl) units becomes broad as compared with that of talc. The ^{29}Si chemical shifts of expandable micas (Figure 10) were close to that (-95.3 ppm) of hectorite (Kinsey *et al.*, 1985) rather than that (-93.3 ppm) of sodium tetrasilic mica (Sakurai *et al.*, 1990), and decreased in accordance with the increased Na_2SiF_6 content.

CONCLUSIONS

Expandable fluorine micas were synthesized using talc and Na_2SiF_6 at 800°C for 2 hours in air, nitrogen, argon, and under vacuum. The mixture of talc and Na_2SiF_6 was analyzed by thermogravimetric and X-ray powder diffraction methods. Na_2SiF_6 was partially decomposed into NaF and amorphous sodium silicofluoride, and the partial removal of the structural water in talc occurred between 400° and 600°C . Continued

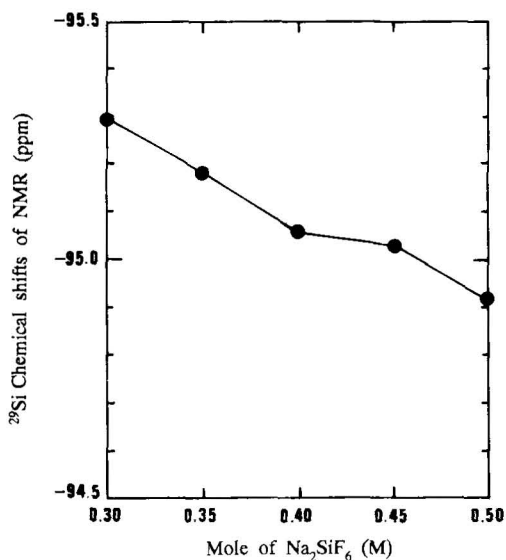


Figure 10. The ²⁹Si chemical shifts of synthetic micas plotted against moles Na₂SiF₆.

heating up to 800°C leads to a reaction with NaF, which mainly yields nonexpandable materials with a *c*-dimension spacing of 9.6 Å and a small amount of expandable mica with a spacing of 12.5 Å. The X-ray powder diffraction pattern of the mixture heated at 900°C shows that talc is transformed into expandable micas from nonexpandable materials. The formation of micas indicates that OH⁻ in the talc structure is replaced by F⁻ in the mica structure, while the sodium ion intercalates in the interlayer site of talc. The charge balance of expandable micas would require the loss of one Mg²⁺ from an octahedral site for every two Na⁺ in the interlayer positions.

SiF₄ generated from Na₂SiF₆ and the resultant amorphous silicofluoride formed during the reaction between talc and Na₂SiF₆ below 900°C play an important role in the formation of expandable micas because the intensities of the 12.5 Å reflection of expandable micas decreased under the flowing gas in the furnace. The infrared absorption and thermal analyses indicate that expandable micas include OH⁻ in their structure.

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