

LOW-TEMPERATURE SYNTHESIS OF MICAS UNDER CONVENTIONAL- AND MICROWAVE-HYDROTHERMAL CONDITIONS

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Abstract—Several micas containing different octahedral and interlayer cations were synthesized at different temperatures under conventional- and microwave-hydrothermal conditions and these phases were characterized by powder X-ray diffraction, solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy, scanning electron microscopy and Fourier transform infrared spectroscopy. A Zn K-mica with Zn in the octahedral sheets and K in the interlayers was synthesized in the temperature range 150–200°C and a novel Zn Rb-mica with Zn in the octahedral sheets and Rb in the interlayers was synthesized at 200°C. The synthesis of either Mg, Co or Ni K-micas, however, was found to be difficult or impossible at these low temperatures. Solid-state ²⁹Si MAS-NMR revealed that the Al in the tetrahedral sites is disordered with several nearest-neighbor Si environments. In general, microwave-assisted hydrothermal conditions led to better crystallization of the Zn K-micas compared with the conventional method.

Key Words—Hydrothermal, Microwave-hydrothermal, Rb-mica, Seeding, Zn Mica.

INTRODUCTION

Synthetic micas have been prepared by hydrothermal (Yoder and Eugster, 1955), topotactic (Komarneni and Roy, 1986) and solid-state (Eppler, 1961) methods. Fluorine-containing micas have been synthesized by numerous researchers using solid-state methods including hot pressing (Comeforo *et al.*, 1953; Eitel *et al.*, 1953), anhydrous fluoride melt or a glass-ceramic process (Eppler, 1961; Hatch, 1961; Beall, 1972; Grossman, 1974), and a fluoride-flux method (Hessinger *et al.*, 1965; Gregorkiewitz, 1972; Gregorkiewitz and Rausell-Colom, 1987; Paulus *et al.*, 1992). Early research on fluoromicas dates back to the 1940s when the goal was to synthesize materials for application as dielectric insulators in electronic equipment. Most of the micas synthesized by the solid-state method are non-swelling, and contain K⁺ ions in the interlayers although a few synthetic micas were prepared with interlayer cations other than K⁺ (Beall *et al.*, 1980, 1986; Daimon and Izawa, 1976; Daimon and Kitajima, 1978; Gregorkiewitz, 1972; Gregorkiewitz and Rausell-Colom, 1987; Paulus *et al.*, 1992). The main advantage of the fluoride melt or glass-ceramic and fluoride-flux techniques is that they can be carried out at high temperatures but at atmospheric pressure, unlike the hydrothermal or hot-pressing methods which require both high temperatures and high pressures. Hydroxyl-containing micas, however, can only be prepared by

hydrothermal methods. Numerous non-hydrating type micas with varying compositions containing hydroxyls have been synthesized hydrothermally (Yoder and Eugster, 1955; Klingsberg and Roy, 1957; Frondel and Ito, 1966; Hazen and Wones, 1972; Comodi *et al.*, 1999; Redhammer *et al.*, 2000). However, the high temperatures, pressures and long durations required to synthesize micas using the hydrothermal technique make it less desirable than the synthesis from melts or fluxes. There are only a few studies in the literature that use low-temperature and low-pressure hydrothermal methods for the synthesis of micas (Perrotta and Garland, 1975) but this process takes many days. The objective of the present study is to demonstrate the value of a microwave-assisted hydrothermal process (Komarneni *et al.*, 1992) in the rapid synthesis of phlogopite-type micas composed of Zn, Mg, Co or Ni in the octahedral sheet and Zn phlogopite micas (referred to hereafter as Zn mica) containing different interlayer cations.

EXPERIMENTAL

Zinc mica syntheses were carried out using various starting chemicals (Tables 1 to 5) by both conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) (Komarneni *et al.*, 1992) methods. A MARS 5 microwave reaction system (CEM corporation, Matthews, North Carolina) was used to carry out all the M-H reactions. Both the temperature and pressure in the vessels can be controlled in this system using an optical temperature probe and a pressure transducer coupled to an on-board computer. The maximum temperature and pressure that can be achieved with this system are 240°C and 350 psi, respectively. The system can operate at various power levels with a

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Table 1. Powder XRD analyses and other characterizations of Zn mica syntheses under M-H and C-H conditions using the same gel composition* and chemicals[#].

Sample no.	Temperature (°C)	Time (h)	Phase analysis (XRD)	SEM	NMR	FTIR
1	150	2	Poorly crystallized mica			
2	150	4	Well crystallized mica	Yes		Yes
3	150	2/CH	Poorly crystallized mica			
4	150	4/CH	Slightly crystallized mica			
5	175	2	Poorly crystallized mica			
6	175	4	Well crystallized mica			
7	200	2	Poorly crystallized mica	Yes		Yes
8	200	4	Well crystallized mica	Yes	Yes	Yes
9	220	4	Well crystallized mica			
10	200	4/CH	Poorly crystallized mica	Yes		Yes
11	200	24/CH	Well crystallized mica	Yes	Yes	Yes

* Gel composition: 1.92K₂O:0.08Al₂O₃:0.31ZnO:0.42SiO₂:84H₂O[#] Chemical sources used: Al nitrate, Zn sulfate, H₂SiO₃ and KOH

maximum power of 1500 W. Reactions were carried out in Teflon vessels sealed with a lid and surrounded by a high-strength outer vessel constructed of polyetherimide. For comparison with the M-H method, a few C-H experiments were conducted with Parr (Moline, Illinois) hydrothermal reactors. These reactors use Teflon inner vessels for the reactants and surrounded by stainless steel containers. After sealing the reactants in the Teflon vessel, the Parr reactor was then placed in an oven preheated to a particular temperature to carry out the reaction. The temperature of the reaction vessel was assumed to be the temperature of the oven and the pressure was not monitored but assumed to be auto-geneous. After the synthesis reactions, the solid and solution phases were separated by centrifugation and the solids were washed free of any remaining soluble species by repeatedly washing with deionized water. The solids were then dried at ~60°C prior to characterization by powder X-ray diffraction (XRD) using a Philips X'Pert powder diffractometer using CuK α radiation. A few mica samples were characterized for particle size and shape by scanning electron microscopy (SEM) using an Hitachi S-3500N instrument with backscatter and energy dispersive spectroscopy (EDS) capabilities. Several Zn

mica samples were also characterized by infrared (IR) spectroscopy using a Nicolet Magna-IR 560 Spectrometer after pelletizing the samples with KBr.

Some mica samples were characterized by ²⁷Al and ²⁹Si MAS-NMR spectroscopy. The ²⁷Al MAS-NMR spectra were collected at 94.7 MHz using a 360 MHz Tecmag NMR system equipped with a 7 mm CPMAS Doty probe. The operating conditions of the spectrometer included a pulse width of 1.1 μ sec, the solution 90° pulse of 6.5 μ s, a solids 45° pulse of ($I = \frac{1}{2}$), number of transients equal to 2000 and a spinning speed of 10 kHz. We used a relaxation delay of 300 ms, which was large compared to typical relaxation delay for solid Al species which is 50 ms or less. The acquisition time is a few ms. The samples are spun at 10 kHz, so the spinning side bands are weak and small, and not easily observed. Chemical shifts were measured relative to [Al(H₂O)₆]³⁺ using 1 N aqueous Al nitrate solution. The ²⁹Si MAS-NMR spectra were obtained at 53.7 MHz using a 270 MHz Tecmag NMR system using a 7 mm CPMAS Doty probe. The operating conditions of the spectrometer included a pulse width of 4 μ s, 40° pulse, the number of transients in the range 104–300 and a spinning speed of 4 kHz. No proton decoupling was used

in the collection of ^{29}Si spectra. The relaxation delay was 60 s. Chemical shifts were measured relative to tetramethylsilane (TMS).

RESULTS AND DISCUSSION

Micas containing K in the interlayers and Zn in the octahedral sheets

Table 1 shows the powder XRD results of various M-H and C-H syntheses of micas below 220°C using Al nitrate, Zn sulfate, H_2SiO_3 and KOH. Well crystallized micas containing only Zn in the octahedral sheets (referred to here as Zn micas) were obtained in the temperature range $150\text{--}220^\circ\text{C}$ after M-H treatment of 4 h while poorly crystallized Zn mica resulted after treatment for 2 h in the temperature range of $150\text{--}200^\circ\text{C}$ (Table 1). Thus, it appears that at least 4 h are needed for nucleation and growth of this Zn mica phase under M-H conditions. However, only poorly crystallized micas were obtained after 4 h of C-H treatment at both 150 and 200°C although treatment for 24 h at 200°C

resulted in a well crystallized phase. Thus, microwave-hydrothermal reactions appear to lead to faster crystallization of Zn micas (Table 1). These results are consistent with earlier findings which suggest that microwave-assisted reactions are faster than conventional reactions because of super heating effects (Baghurst and Mingos, 1992) or generation of localized high temperatures (Neas and Collins, 1988). Two prototypical synthetic Zn micas prepared at 200°C under conventional and microwave-hydrothermal conditions for 4 and 24 h, respectively, were used in further detailed characterization. Figure 1 shows the XRD patterns of the above two synthetic Zn micas and this figure reveals that they are highly crystalline. Figure 2 shows the SEM images of the micas above and these reveal that the synthetic micas are plate-like in nature with a particle size of $\sim 1\text{--}2\ \mu\text{m}$. The microwave-hydrothermally synthesized mica appears to be slightly larger (Figure 2a) than the conventional hydrothermally synthesized material (Figure 2b). Solid-state ^{27}Al MAS-NMR shows that most of the Al is substituted in tetrahedral sites as revealed by strong resonances around 59.4 ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in both these samples (Figure 3). A small resonance around 2.6 ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in both of these samples reveals the

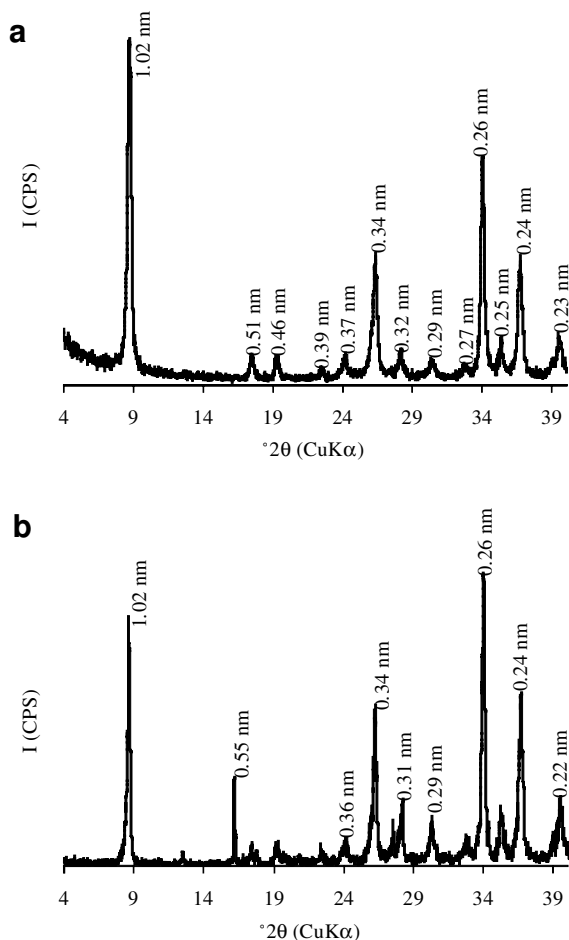


Figure 1. XRD patterns for Zn micas prepared under (a) microwave-hydrothermal, and (b) conventional-hydrothermal conditions at 200°C for 4 and 24 h, respectively.

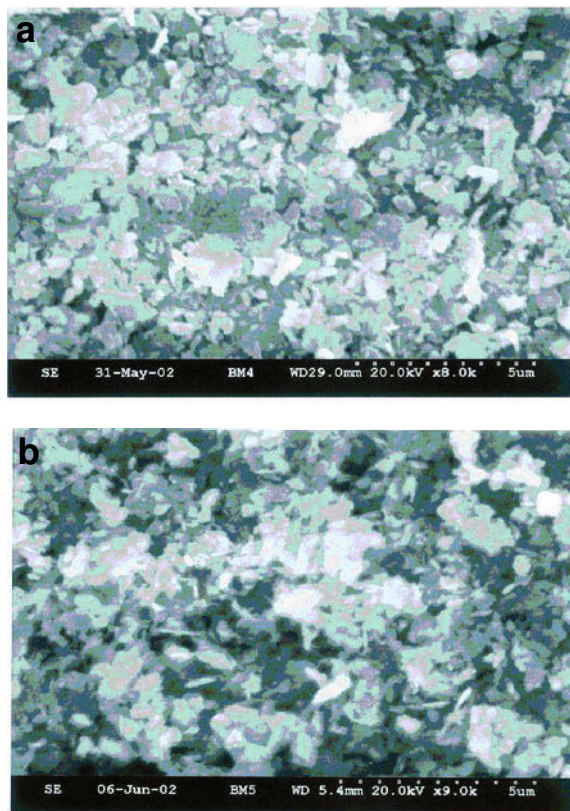


Figure 2. SEM images for Zn micas prepared under (a) microwave-hydrothermal, and (b) conventional-hydrothermal conditions at 200°C for 4 and 24 h, respectively.

presence of some octahedrally coordinated Al along with Mg (Figure 3). In order to investigate the ordering of Al in the tetrahedral sheet, solid-state ^{27}Al MAS-NMR was used and the results presented in Figure 4 show that the Al exists in several different environments and hence it is disordered. The Zn mica synthesized under M-H conditions shows three main resonances at -92.5 , -88.3 and -84.9 ppm from TMS (Figure 4a) and these can be assigned to Q3(OAl), Q3(1Al) and another Q3(1Al) environments, respectively. These assignments are based on previous studies with natural and synthetic clays (Sanz and Serratosa, 1984; Komarneni *et al.*, 1986, 1999). The Zn mica synthesized under C-H conditions also shows three main resonances at -92.3 , -88.5 and -84.6 ppm from TMS (Figure 4b) and these can also be assigned to Q3(OAl), Q3(1Al) and another Q3(1Al) environments, respectively. Thus, it appears that there is more than one environment for Q3(1Al) sites in both types of hydrothermally synthesized samples. Infrared spectra of the two synthetic micas (not illustrated) also confirm the synthesis of Zn micas although a small water band is present at 1670 cm^{-1} that can be attributed to the adsorbed water on the surface.

Micas containing different alkali ions in the interlayers and Mg or Zn in the octahedral sheets

Table 2 shows the various attempts in synthesizing micas containing different interlayer and octahedral

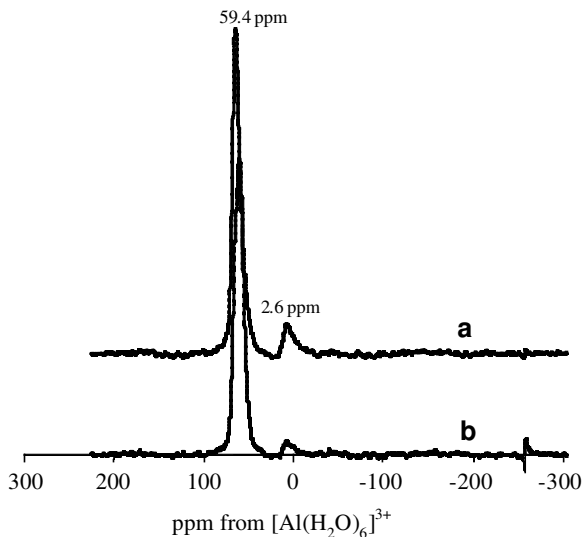


Figure 3. ^{27}Al MAS-NMR spectra for Zn micas prepared under (a) microwave-hydrothermal, and (b) conventional-hydrothermal conditions at 200°C for 4 and 24 h, respectively.

cations. Attempts at synthesizing Mg- rather than Zn-containing micas with K in the interlayers yielded 1.16 and 1.09 nm phases with poor crystallinity (Table 2) at 200 and 220°C . Thus, Mg phlogopite micas appear to be harder to synthesize than Zn micas as has already been found with hectorites (Higashi *et al.*, 2002). We also

Table 2. Powder XRD analyses of Zn and Mg phlogopite micas with different interlayer cations.

Sample no.	Gel composition	Sources used	Temp. ($^\circ\text{C}$)	Time (h)	Phase (XRD)	SEM	NMR	FTIR
1	1.92K ₂ O:0.08Al ₂ O ₃ : 0.31MgO:0.42SiO ₂ :84H ₂ O	Al nitrate, Mg sulfate, H ₂ SiO ₃ KOH	220	4	Poorly crystallized 1.16 nm phase			
2	3.84K ₂ O:0.08Al ₂ O ₃ : 0.31MgO:0.42SiO ₂ :84H ₂ O	Al nitrate, Mg sulfate, H ₂ SiO ₃ KOH	200	4	Poorly crystallized 1.09 nm phase	yes		yes
3	1.92Na ₂ O:0.08Al ₂ O ₃ : 0.31ZnO:0.42SiO ₂ :84H ₂ O	Al nitrate, Zn sulfate, H ₂ SiO ₃ NaOH	220	4	No mica phase; UP*			
4	1.92Na ₂ O:0.08Al ₂ O ₃ : 0.31ZnO:0.42SiO ₂ :84H ₂ O	Al nitrate, Zn sulfate, H ₂ SiO ₃ NaOH	150	4	No mica phase; UP*			
5	1.92Na ₂ O:0.08Al ₂ O ₃ : 0.31ZnO:0.42SiO ₂ :84H ₂ O	Al nitrate, Zn sulfate, H ₂ SiO ₃ NaOH	100	4	No mica phase; amorphous hump			
6	1.92Na ₂ O:0.08Al ₂ O ₃ : 0.31ZnO:0.42SiO ₂ :84H ₂ O	Al nitrate, Zn sulfate, H ₂ SiO ₃ NaOH	200	4	No mica phase; UP*			
7	1.92Cs ₂ O:0.08Al ₂ O ₃ : 0.31ZnO:0.42SiO ₂ :84H ₂ O	Al nitrate, Zn sulfate, H ₂ SiO ₃ CsOH	200	4	Pollucite; no mica phase			
8	1.92Rb ₂ O:0.08Al ₂ O ₃ : 0.31ZnO:0.42SiO ₂ :84H ₂ O	Al nitrate, Zn sulfate, H ₂ SiO ₃ RbOH	200	4	Rb-mica phase		yes	yes
9-CH	1.92Rb ₂ O:0.08Al ₂ O ₃ : 0.31ZnO:0.42SiO ₂ :84H ₂ O	Al nitrate, Zn sulfate, H ₂ SiO ₃ RbOH	200	3 days/ C-H	Rb-mica phase			

* UP = unidentified phases

Table 3. Powder XRD analyses and other characterizations of Zn and Mg mica syntheses using metakaolin under M-H and C-H conditions.

Sample no.	Expected mica	Sources used; K content varied with excess in most cases	Temp (°C)	Time (h)	Phase analysis (XRD)	SEM	NMR	FTIR
1	$\text{KSi}_3\text{AlZn}_3\text{O}_{10}(\text{OH})_2$	$\text{Si}_2\text{Al}_2\text{O}_7$, 0.36 g KOH, 2.58 g Zn sulfate	200	4	No Zn mica phase; poorly crystallized kaolinite			
2	$\text{KSi}_3\text{AlZn}_3\text{O}_{10}(\text{OH})_2$	$\text{Si}_2\text{Al}_2\text{O}_7$, 1.58 g KOH, 2.58 g Zn sulfate	200	4	Broad Zn mica phase; kaolinite			
3	$\text{KSi}_3\text{AlZn}_3\text{O}_{10}(\text{OH})_2$	$\text{Si}_2\text{Al}_2\text{O}_7$, 3.08 g KOH, 2.58 g Zn sulfate	200	4	Broad Zn mica peaks	yes		yes
4	$\text{KSi}_3\text{AlZn}_3\text{O}_{10}(\text{OH})_2$	$\text{Si}_2\text{Al}_2\text{O}_7$, 6.16 g KOH, 2.58 g Zn sulfate	200	4	Broad 1.22 nm phase; KAlSiO_4 ?			
5	$\text{KSi}_3\text{AlMg}_3\text{O}_{10}(\text{OH})_2$	$\text{Si}_2\text{Al}_2\text{O}_7$, KOH, 2.22 g Mg sulfate	200	4	No crystalline phase			
6	$\text{K}_2\text{Si}_2\text{Al}_2\text{Zn}_3\text{O}_{10}(\text{OH})_2$	$\text{Si}_2\text{Al}_2\text{O}_7$, 4.6 g KOH, 3.88 g Zn sulfate	200	4	Broad mica phase	yes	yes	yes
7	$\text{K}_2\text{Si}_2\text{Al}_2\text{Zn}_3\text{O}_{10}(\text{OH})_2$	$\text{Si}_2\text{Al}_2\text{O}_7$, 4.6 g KOH, 3.88 g Zn sulfate	200	3 days/ C-H	Broad mica phase			
8	$\text{K}_2\text{Si}_2\text{Al}_2\text{Mg}_3\text{O}_{10}(\text{OH})_2$	$\text{Si}_2\text{Al}_2\text{O}_7$, 4.6 g KOH, 3.33 g Mg sulfate	200	4	No crystalline phase			

tried to synthesize Zn micas containing Na in the interlayers in the temperature range 100–220°C but these attempts did lead to mica-type phases. However, some amorphous or unidentified crystalline phases formed under the M-H conditions used. Attempts to synthesize Zn mica containing Cs in the interlayers yielded pollucite, $\text{CsAlSi}_2\text{O}_6$, which is the most stable Cs phase under hydrothermal conditions at 200°C (Komarneni and White, 1981).

Zinc micas containing Rb in the interlayers (referred to hereafter as Zn Rb-mica) formed under both M-H and C-H conditions (Table 2; Figure 5) at 200°C. The powder XRD pattern clearly shows a *c* axis spacing of 1.05 nm which is expected for this mica based on the ionic size of Rb (Komarneni and Roy, 1986). The XRD pattern also shows some amorphous background (Figure 5). To the best of the authors' knowledge, no

such mica has ever been synthesized. This novel phase is further characterized by solid-state ^{27}Al and ^{29}Si MAS-NMR spectroscopy. The ^{27}Al NMR of this Zn Rb-mica clearly shows that most of the Al is in tetrahedral coordination as indicated by a resonance at 62.7 ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and with a trace amount in the octahedral coordination at -0.05 ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (Figure 6). The Zn Rb-mica synthesized under M-H conditions shows three main resonances at -92.5 , -89.6 and -85.1 ppm from TMS (Figure 7) and these can be assigned to Q3(0Al), Q3(1Al) and another Q3(1Al) environments, respectively. These assignments are the same as above with Zn micas. These results show that the novel Zn Rb-mica is similar to the Zn micas in terms of the Al nearest-neighbor environment in the tetrahedral sheet. Investigation with Fourier transform infrared (FTIR) spectroscopy (Figure 8) showed that this

Table 4. Powder XRD analyses of mica synthesis with and without mica seeds under CH and MH conditions.

Sample no.	Gel composition	Sources used	Temp. (°C)	Time (h)	Phase analysis (XRD)
1	1.92K ₂ O:0.08Al ₂ O ₃ :0.31MgO:0.42SiO ₂ :84H ₂ O; gel seeded with 1% Zn mica	Al nitrate, Mg sulfate, H ₂ SiO ₃ , KOH	200	4/M-H	Broad Mg mica phase
2	1.92K ₂ O:0.08Al ₂ O ₃ :0.31MgO:0.42SiO ₂ :84H ₂ O; gel seeded with 1% Zn mica	Al nitrate, Mg sulfate, H ₂ SiO ₃ , KOH	200	3 days/C-H	Slightly better crystallized mica phase
3	1.92K ₂ O:0.08Al ₂ O ₃ :0.31MgO:0.42SiO ₂ :84H ₂ O; unseeded	Al nitrate, Mg sulfate, H ₂ SiO ₃ , KOH	200	3 days/C-H	Broad Mg mica phase

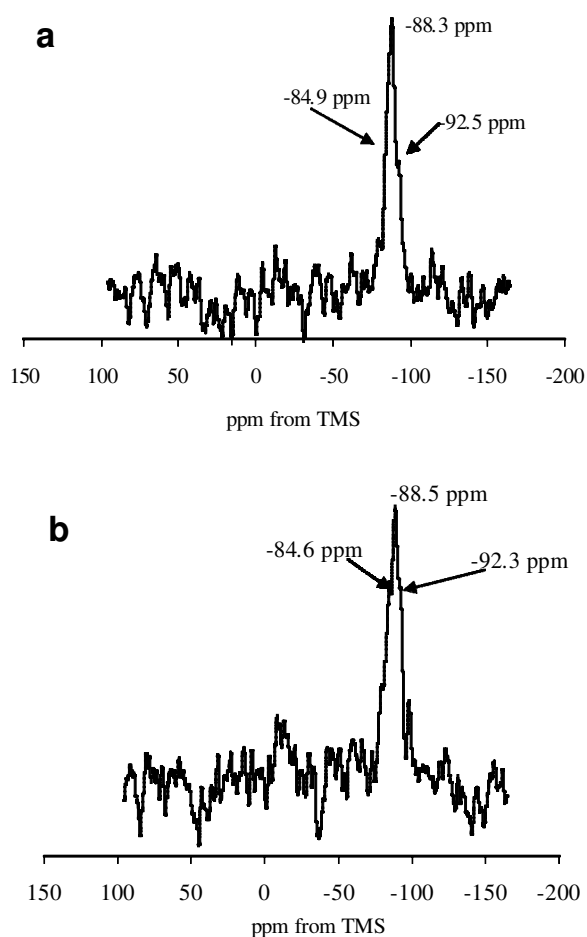


Figure 4. ^{29}Si MAS-NMR spectra for Zn micas prepared under (a) microwave-hydrothermal, and (b) conventional-hydrothermal conditions at 200°C for 4 and 24 h, respectively.

material is not a pure phase as revealed by a peak at 1382 cm^{-1} which can be assigned to nitrate. This nitrate obviously arises from an impurity.

Synthesis of micas using metakaolin as an aluminosilicate source

We tried to synthesize micas containing K in the interlayers and Mg or Zn in the octahedral sheets with

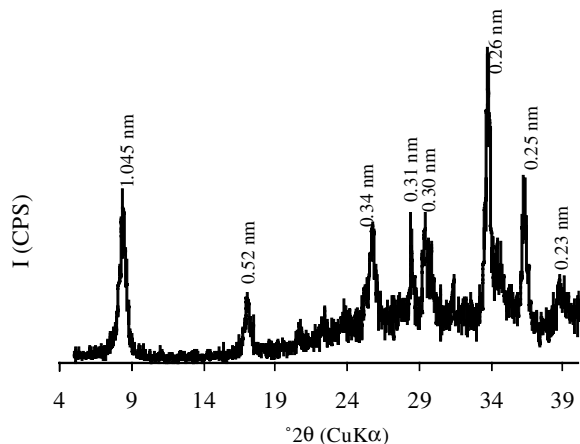


Figure 5. XRD pattern for Zn mica prepared in the presence of RbOH under microwave-hydrothermal conditions at 200°C for 4 h.

metakaolin as the source for Si and Al. These results are presented in Table 3. In a few cases, metakaolin recrystallized to form kaolinite and in most cases broad Zn mica resulted. Little or no crystallization occurred when a Mg source and metakaolin were used to crystallize Mg mica. These results are consistent with the results obtained above using silicic acid and Al nitrate where Mg mica did not form either. Zn mica (sample #6 in Table 3) of theoretical composition, $\text{K}_2\text{Si}_2\text{Al}_2\text{Zn}_3\text{O}_{10}(\text{OH})_2$ was further characterized by solid-state NMR, SEM and FTIR. The Zn mica synthesized under M-H conditions showed three main ^{29}Si resonances at -89 , -85.2 and -81.2 ppm from TMS (not illustrated) and these can be assigned to Q3(1Al), another Q3(1Al) and Q3(2Al) environments, respectively. The relative areas of the above resonances are 58:100:54, respectively. The ^{29}Si MAS-NMR also showed a low proportion ($\sim 8\%$) of Q3(3Al) environment at -77.4 ppm from TMS which suggests that an Al-deficient mica compared to that of the theoretical composition, $\text{K}_2\text{Si}_2\text{Al}_2\text{Zn}_3\text{O}_{10}(\text{OH})_2$ resulted. This is because the above composition with 1:1 Si:Al ideally should give only one resonance at ~ -78 ppm (Komarneni *et al.*, 1998). This is further supported qualitatively by the fact that a significant amount of Al

Table 5. Powder XRD analyses of Zn, Co and Ni mica synthesis under M-H conditions.

Sample no.	Gel composition	Sources used	Temp. (°C)	Time (h)	Phase analysis (XRD)
1	$1.92\text{K}_2\text{O}:0.08\text{Al}_2\text{O}_3:$ $0.31\text{ZnO}:0.42\text{SiO}_2:84\text{H}_2\text{O}$	Al nitrate, Zn sulfate, H_2SiO_3 , KOH	200	4	Well crystallized mica phase
2	$1.92\text{K}_2\text{O}:0.08\text{Al}_2\text{O}_3:$ $0.31\text{CoO}:0.42\text{SiO}_2:84\text{H}_2\text{O}$	Al nitrate, Co chloride, H_2SiO_3 , KOH	200	4	Very poorly crystallized 1.16 nm phase
3	$1.92\text{K}_2\text{O}:0.08\text{Al}_2\text{O}_3:$ $0.31\text{NiO}:0.42\text{SiO}_2:84\text{H}_2\text{O}$	Al nitrate, Ni chloride, H_2SiO_3 , KOH	200	4	No phase formation

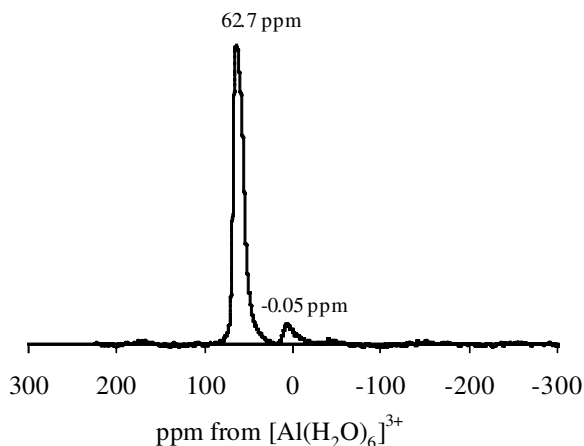


Figure 6. ^{27}Al MAS-NMR spectrum for Zn mica prepared in the presence of RbOH under microwave-hydrothermal conditions at 200°C for 4 h.

went into octahedral sites (peak area ratio of tetrahedral to octahedral Al is 6.87) and hence less Al is available to form the ideal composition given above. Further studies would be needed to synthesize this highly charged Zn mica.

Syntheses of Mg mica with seeding

Because it was difficult to synthesize Mg mica under the same conditions as those used for Zn mica, seeding with Zn mica was used to facilitate Mg mica synthesis. Results presented in Table 4 show that there is some effect of Zn mica seeds on enhanced crystallization of Mg mica (compare sample 2 with 3). This preliminary result needs to be explored further.

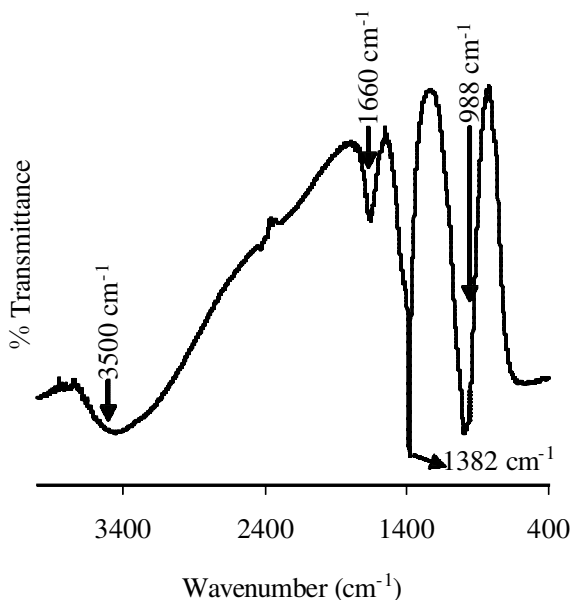


Figure 8. FTIR spectrum for Zn micas prepared in the presence of RbOH under microwave-hydrothermal conditions at 200°C for 4 h.

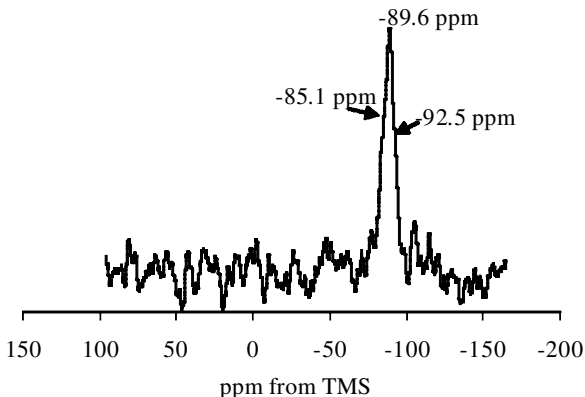


Figure 7. ^{29}Si MAS-NMR spectrum for Zn mica prepared in the presence of RbOH under microwave-hydrothermal conditions at 200°C for 4 h.

Syntheses of Co, Ni and Zn micas

The formation of Co and Ni micas under the same conditions as that of Zn mica was investigated to determine which transition metal is preferred in the octahedral sheet. Results presented in Table 5 clearly show that Zn mica is the easiest to synthesize while Ni was the most difficult. In the case of Co, a poorly crystallized mica-like phase as indicated by a broad peak was obtained (Table 5). Thus, these results are consistent with our earlier results of smectite syntheses (Higashi *et al.*, 2002) where Zn was found to be the best for the formation of 2:1 clays.

CONCLUSIONS

Zinc K-mica with Zn in the octahedral sheets and K in the interlayers and novel Zn Rb-mica with Zn in the octahedral sheets and Rb in the interlayers can be crystallized in a low-temperature range of 150–200°C under conventional- and microwave-hydrothermal conditions. Crystallization of these micas increased under microwave-assisted conditions. It is easier to synthesize Zn K-mica compared to either Mg K-mica, Co K-mica or Ni K-mica under both conventional- and microwave-hydrothermal conditions.

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