Chem. Mater. **1990**, *2*, 511–517

Table VI. X-ray Powder Diffraction Data for $BaIn_2S_4$ Platelets[a]

h	*k*	*l*	d_{obs}, Å	d_{calc}, Å	I/I_0
0	2	2	5.608	5.6063	7
4	0	0	5.457	5.4520	29
2	2	2	4.989	4.9859	9
1	1	3	4.205	4.2023	5
1	5	1	4.041	4.0409	5
4	2	2	3.910	3.9086	100
4	4	0	3.843	3.8414	39
0	0	4	3.277	3.2766	12
0	6	2	3.162	3.1613	77
1	5	3	3.042	3.0456	13
1	7	1	2.985	2.9824	5
3	5	3	2.833	2.8326	4
8	0	0	2.726	2.7260	55
0	8	0	2.693	2.7067	4
4	4	4	2.493	2.4929	94
4	8	0	2.424	2.4244	14
6	4	4	2.220	2.2197	7
8	0	4	2.0960	2.0956	21
8	6	2	2.0646	2.0645	41
1	7	5	1.9927	1.9915	21
1	11	1	1.9390	1.9390	5
4	10	2	1.9236	1.9238	18
0	6	6	1.8683	1.8688	6
2	6	6	1.8426	1.8419	13
12	0	0	1.8172	1.87173	11
6	10	2	1.7898	1.7896	8
12	4	0	1.7232	1.7228	16
8	8	4	1.6565	1.6570	9
0	0	8	1.6376	1.6383	6
0	12	4	1.5803	1.5806	7
8	6	6	1.5407	1.5414	6
12	4	4	1.5242	1.5249	8

[a] *Fddd*; *a* = 21.808 (3), *b* = 21.654 (4), *c* = 13.107 (2) Å.

covalently bonded two-dimensional net with the formula $In_2S_4^{2-}$.

Crystals of $BaIn_2S_4$ formed as light yellow platelets up to 1 mm per side. The X-ray powder diffraction pattern of crushed platelets agreed well with that calculated by using the reported single-crystal structure data,[7] as shown in Figure 5. The X-ray powder diffraction data, given in Table VI, were indexed by using an orthorhombic unit cell consistent with space group *Fddd* (*a* = 21.808 (3), *b* = 21.654 (4), and *c* = 13.107 (2) Å), in good agreement with the literature report.[7] The stability of $BaIn_2S_4$ toward water, as required by the isolation of the crystals from the flux, is in contrast to an earlier report[7] of its decomposition in moist air. Orthorhombic $SrIn_2S_4$ is reportedly[6] isostructural with $BaIn_2S_4$, although, curiously, $SrIn_2S_4$ was obtained as whiskers while $BaIn_2S_4$ was obtained with the platelet morphology.

Conclusions

Yellow $Ca_{3.3}In_{6.5}S_{13}$ crystals obtained in the present study appear to be isostructural with $Ca_{3.1}In_{6.6}S_{13}$,[5] $Pb_3In_{6.67}S_{13}$,[11] and $Sn_{2.5}In_7S_{13}$[12] by detailed comparison of the observed and calculated X-ray powder diffraction patterns.

Bronze crystals of a new phase, $Ca_{1.2}In_{1.9}S_4$ ("$Ca_{3.9}In_{6.2}S_{13}$") were obtained. On the basis of the X-ray powder diffraction data, the structure of this phase is considerably different from that of the $Ca_{3.3}In_{6.5}S_{13}$-type series. A new monoclinic phase, $Sr_{0.9}In_{2.1}S_4$, was obtained as yellow whiskers. The X-ray powder diffraction data indicated that the structure of this compound is substantially different from that of known, orthorhombic $SrIn_2S_4$, which was also obtained in the form of golden-yellow whiskers.

Orthorhombic $BaIn_2S_4$ was obtained as light yellow platelets. This compound is isostructural with orthorhombic $SrIn_2S_4$, and the indexed X-ray powder diffraction data of both compounds are reported.

Further studies to assess the potential of these compounds as optical windows are in progress and will include quantitative transmission measurements on single crystals using an IR microscope.

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Registry No. $Ca_{1.2}In_{1.9}S_4$, 125390-58-1; $Cr_{0.9}In_{2.1}S_4$, 128302-16-9; $Ca_{3.3}In_{6.5}S_{13}$, 128302-17-0; $SrIn_2S_4$, 51404-22-9; $BaIn_2S_4$, 51403-86-2.

Synthesis of Metal Hydroxide–Layer Silicate Intercalation Compounds (Metal = Mg(II), Ca(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II))

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Layer silicate intercalation compounds with metal(II) hydroxide (metal(II) = Mg, Ca, Mn, Fe, Co, Ni, Zn, and Cd) are prepared by adding a base into the metal salt solutions containing layer silicates with cation-exchange properties. The preparation procedures for the intercalates with manganese(II), iron(II), and cobalt(II) hydroxides are conducted under oxygen-free conditions. The hydroxides of these metal cations can crystallize with the cadmium iodide layer structure; the basic unit layer of these metal hydroxides is intercalated into the two-dimensional silicate interlayer region.

Introduction

We previously reported preparation of metal(II) hydroxide (metal = Fe, Co, Ni)–layer silicate (2:1 layer silicate) intercalation compounds in which a basic unit layer of the metal hydroxide alternates with a silicate layer, the intercalated 3d transition elements forming a bidimensional lattice.[1-3]

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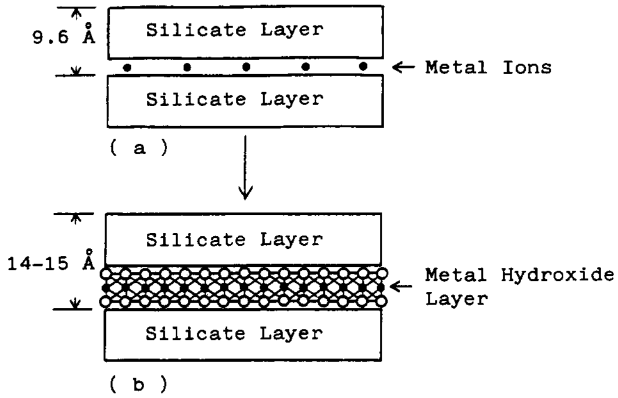

Figure 1. Intercalation of metal hydroxide into layer silicate: (a) an expandable 2:1 layered silicate where interlayer water is omitted to be simplified and (b) a metal hydroxide–layer silicate intercalation compound.

These intercalates exhibit characteristics that differ from the metal hydroxides. The magnetic properties of these complexes have been investigated and show behavior of low-dimensional magnets such as the graphite intercalation compounds.[4-6]

If the composition of the metal hydroxide interlayer is systematically regulated, one will not only gain a better understanding of a novel low-dimensional material but also potentially obtain functional materials with various physicochemical properties.

In nature, layer silicates (2:1 layer silicate) with metal hydroxide interlayers are known and are referred to as chlorite or chlorite-like minerals. These minerals have a wide range of composition with a number of ions being considered to be the constituents of the natural hydroxide interlayers.[7] The nature and the occurrences of these materials have been the subject of continued interest; much work has been done on the syntheses of the materials with aluminum(III) hydroxide[8-12] and magnesium(II) hydroxide,[8,12,13-15] both of which are principal components of the natural hydroxide interlayer. The nickel(II) hydroxide–layer silicate intercalation compound has also been evaluated.[3,16,17]

It would be of interest to determine what kind of cations can lead to the formation of metal hydroxide interlayers in the layer silicates besides Mg(II), Fe(II), Co(II), Ni(II), and Al(III) ions. We think that the crystal structure of the metal hydroxide plays an important role in the metal hydroxide interlayering process. The hydroxides of the divalent metal ions (Mg^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}) cited above crystallize with the cadmium iodide layer structure. Aluminum(III) hydroxide also has a layer structure that is closely related to that of CdI_2. Furthermore, it is known that the divalent Mn^{2+}, Ca^{2+}, Zn^{2+}, and Cd^{2+} ions can also produce hydroxides with the CdI_2 structure.[18]

In this context, it is expected that these latter ions (Mn^{2+}, Ca^{2+}, Zn^{2+}, and Cd^{2+}) would also provide hydroxide sheets between the silicate layers. The present work was undertaken with the objective of examining this supposition. The concept of this study is schematically represented in Figure 1.

Experimental Section

Materials. A 10 wt % sol of sodium fluoride tetrasilicic mica ($NaMg_{2.5}Si_4O_{10}F_2$) from Topy Industries Ltd., Japan, was used. This synthetic mica has a high crystallinity, a large cation-exchange capacity (a high-layer charge), and a high thermal stability. Impurities of α-cristobalite and magnesium fluoride richterite, $Na_2Mg_6F_2(Si_4O_{11})_2$, were removed by centrifugation after the completely dispersed and diluted mica sol had been obtained by adding deionized distilled water. The purified sol was then condensed with an evaporator and air-dried at 100 °C. The characteristics of the mice were described in our previous work.[1] Sodium fluoride tetrasilicic mica has a 2:1 layer structure, Na^+ ions being located between the silicate layers to compensate the negative layer charge that arises from magnesium vacancies in the central octahedral sheet. These Na^+ ions are exchangeable in water, and the theoretical cation exchange capacity is 254 mequiv/100 g of the clay. This layer silicate has swelling properties in water and belongs to the so-called "expandable layer silicate" class of minerals.

Methods. Layer silicate intercalation complexes with metal(II) hydroxide were prepared as follows: 2.0 g of silicate powder was added to 200 mL of 0.1 M metal(II) salt solution to give 1 mol of metal/100 g of clay. The solution was stirred continuously for 2 days to enable ion-exchange between the metal ions and the sodium ions located in the silicate. For the metal salts, we used the nitrates of magnesium(II), calcium(II), manganese(II), cobalt(II), nickel(II), zinc(II), and cadmium(II) and the chloride of iron(II). These divalent metal cations form hydroxides with the CdI_2 structure.

The solutions were then titrated with 200 mL of 0.1 M sodium hydroxide solutions at a rate of 10 mL/h to yield a OH/metal mole ratio of 1.0, while stirring vigorously. In the case of Mn(II) salt solutions, the titration was carried out with the OH/metal mole ratios of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 in order to study the titration process in detail. The amount of metal hydroxide formed was controlled by adjusting the OH/metal ratio. Moreover, in the case of calcium(II) salt solutions, a titration to a OH/Ca ratio of 2.0 in addition to a OH/Ca ratio of 1.0 was performed with 200 mL of 0.2 M sodium hydroxide solution, since calcium(II) hydroxide is moderately soluble in water. After these titrations, the solutions were continuously stirred for 2 days. The resulting products were collected by centrifugation, repeatedly washed with deionized distilled water, and then dried at 100 °C.

The hydroxides of manganese(II), iron(II), and cobalt(II) are thermodynamically unstable with respect to oxidation by O_2 and are easily oxidized by air, while calcium(II) hydroxide is easily carbonated by air. Hence, these metal hydroxides–clay complexes were prepared under a N_2 gas atmosphere. Deionized distilled water free from dissolved O_2 and CO_2 was obtained by bubbling N_2 gas through the boiling water. The resulting products were then dried at 50 °C in vacuum.

Chemical analyses of the complexes were performed by the atomic absorption method using a Seiko Instruments Model SAS 760. X-ray diffractograms were obtained from specimens basally oriented on glass slides with a Rigaku diffractometer, RU-200, using Cu Kα radiation. Differential thermal and thermogravimetric analyses (DTA-TGA) were carried out with a Rigaku

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Table I. Elemental Analysis of Metal(II) Hydroxide–Layer Silicate[a] Intercalation Compounds[b]

fixed metal(II)	element, wt % SiO_2	 Na_2O	 $Me^{II}O$	mole ratio (1)[c], (SiO_2 = 4 mol) Na	 Metal(II)	ion-exchange ratio,[d] %	mole ratio (2)[e] metal(II)
Mica[a]	57.34	5.88		0.80			
Mg	43.86	1.26	17.95[f]	0.22	2.44	78	3.1
Ca	48.23	1.41	5.58	0.23	0.50	77	0.65
Mn	38.61	1.16	27.18	0.23	2.31	77	3.0
Fe	37.07	1.04	26.86	0.22	2.42	78	3.1
Co	37.35	0.63	30.16	0.13	2.59	87	3.0
Ni	38.71	1.24	26.98	0.25	2.24	75	3.0
Zn	37.03	1.03	29.72	0.22	2.37	78	3.0
Cd	31.49	0.89	38.15	0.22	2.27	78	2.9

[a] Sodium fluoride tetrasilicic mica ($NaMg_{2.5}Si_4O_{10}F_2$). Interlayer charge is +1 per formula unit. Initial interlayer cations are Na^+; 0.2 Na^+ ions are displaced by 0.2 H^+ ions when the silicate sol is diluted in distilled water to eliminate impurities. [b] Prepared with a OH/metal mole ratio of 1.0. [c] Amount of fixed metal (mole) per formula unit of the clay (SiO_2 = 4 mol). [d] Calculated by means of {(1 − Na mole ratio (1)) × 100}. Sodium fluoride tetrasilicic mica has a higher layer charge density than do smectites. Hence, in this clay some of the interlayer sodium cations remain unexchanged, whereas in smectites the ion exchange of the interlayer cations usually goes to completion. [e] Amount of fixed metal (mole) per formula unit of the clay on the basis of the hypothetical 100% ion-exchanged clay. Calculated by means of {(metal(II) mole ratio (1)) × 100/(ion-exchange ratio)}. [f] From subtracting the amount of MgO in the initial mice from the total MgO in the resulting product.

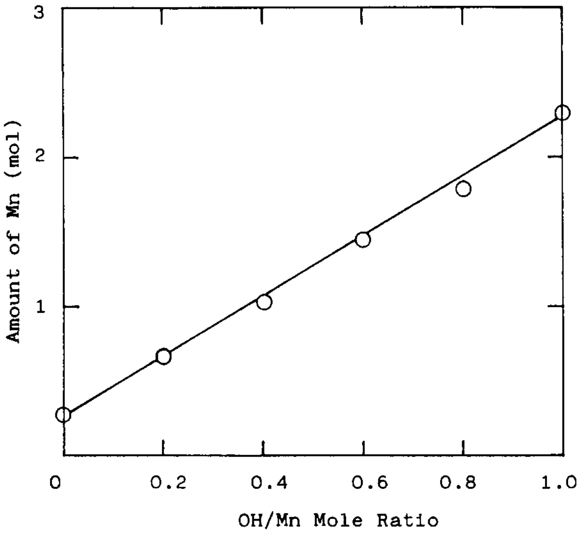

Figure 2. Amount of Mn in manganese(II) hydroxide–layer silicate intercalation compounds as a function of the OH/Mn mole ratio in titration. Amount of Mn (mol): Mn (mole) per formula unit of layer silicate. Layer silicate: sodium fluoride tetrasilicic mica.

thermoanalyzer M8076 at a heating rate of 10 °C/min.

Results and Discussion

Chemical Analyses. We controlled the amount of metal hydroxide formed by adjusting the OH/metal ratio: the amount of metal ion in the resulting products increased with the addition of alkali, that is, with an increase in the OH/metal mole ratio (Figure 2). Except for Ca^{2+} ion, the values of the fixed metal ions at the OH/metal mole ratio of 1.0 were approximately 2.3 mol/formula unit of the clay (Table I). Since the ion-exchange ratio of the clay was approximately 78%, the value of 2.3 mol of the fixed metal(II) corresponds to approximately 3.0 mol of metal(II) on the basis of the hypothetical 100% ion-exchanged mica (Table I), that is, in accord with the upper limit of the chemical composition of the metal(II) hydroxide–layer silicate intercalation compounds, which is expressed by $[Me^{II}_x(OH)_{2x-1}(H_2O)]^+(Mg_{2.5}Si_4O_{10}F_2)$ ($^1/_2 \le x \le 3$).[1]

In the case of calcium(II) ions (OH/Ca = 1.0), the content of Ca^{2+} was much smaller than that of the other divalent metal ions. This is due to the high solubility of calcium(II) hydroxide: the amount of intercalated calcium(II) hydroxide was small, and the calcium(II) hydroxide tended to leach out with washing.

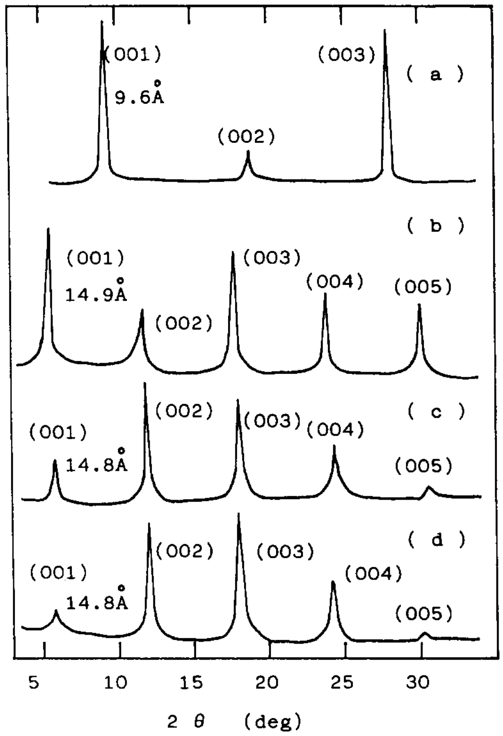

Figure 3. X-ray powder diffraction patterns of (a) a starting layer silicate (anhydrous form), (b) magnesium(II) hydroxide–, (c) zinc(II) hydroxide–, and (d) cadmium(II) hydroxide–layer silicate intercalation compounds prepared with a OH/metal mole ratio of 1.0. Layer silicate: sodium fluoride tetrasilicic mica.

XRD Analyses. No free metal hydroxide could be detected in the XRD spectra for the reaction products (metal(II) = Mg, Mn, Fe, Co, Ni, Zn, and Cd; Figure 3). Moreover, the d_{001} basal spacings of these products were in the range 14.6–15.1 Å, which is expanded from the 9.6-Å basal spacing of the initial mica (Table II). These facts indicate that the metal hydroxide forming reaction occurred in the interlayer space of the silicate.

Furthermore, the basal spacings of the products were constant, independent of the amount of metal incorporated into the silicate (Figure 4), suggesting that the metal hydroxide sheet developed between the silicate layers.

We estimated the change in X-ray intensities of the basal 00*l* reflections with the interlayering of metal hydroxide for the metal hydroxide–layer silicate intercalation

Table II. Basal Spacings of Metal(II) Hydroxide–Layer Silicate Intercalation Compounds[a]

fixed metal(II)	basal spacing, Å 100 °C[b]	 200 °C[c]	 500 °C[c]
initial mica[d]	9.6	9.6	9.6
Mg	14.9	14.9	9.6
Ca			
OH/Ca = 1.0	15.5[e]	9.6	9.6
OH/Ca = 2.0[f]	15.1[e]	15.1	9.6
Mn	14.7[e]	14.6	9.6
Fe	14.7[e]	14.7[g]	9.6[g]
Co	14.6[e]	14.5	9.6
Ni	14.7	14.7	9.6
Zn	14.8	14.8	9.6
Cd	14.8	14.6	9.6

[a] Prepared with a OH/metal mole ratio of 1.0. Layer silicate: sodium fluoride tetrasilicic mica. [b] Drying in air for 24 h. [c] Heat treatment in air for 2 h. [d] Anhydrous form. [e] Drying in vacuum at 50 °C for 24 h. [f] Before washing with water. [g] Heat treatment in Ar for 2 h.

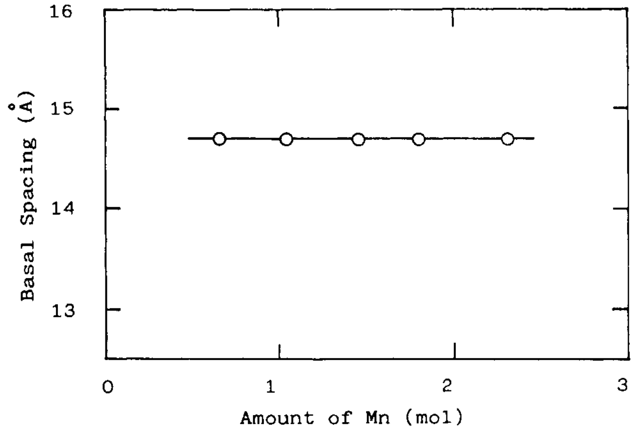

Figure 4. Basal spacings of manganese(II) hydroxide–layer silicate intercalation compounds as a function of the amount of Mn. Amount of Mn (mol): Mn (mole) per formula unit of layer silicate. Layer silicate: sodium fluoride tetrasilicic mica.

compound. The calculations on the intercalation compounds were performed assuming the formula $[\mathrm{Me^{II}}_x(\mathrm{OH})_{2x-1}(\mathrm{H_2O})]^+(\mathrm{Mg_{2.5}Si_4O_{10}F_2})$ ($^1/_2 \le x \le 3$; Me = divalent metal; Table III), and the intensities of the basal reflections (I_{00l}) were computed from the formula

$$I_{00l} = |F_{00l}|^2\Xi$$

where $|F_{00l}|$ is the structure factor, and Ξ is the Lorentz–polarization factor. Scattering factors for atoms, except for O^{2-}, were obtained from ref 20 and the scattering factor for O^{2-} from Tokonami.[21] The random powder form was applied to the Lorentz–polarization factor

$$\Xi = (1 + \cos^2 2\theta)/(\sin 2\theta \sin \theta)$$

because this form is more appropriate than the single-crystal form for most purposes even when basally oriented clay powder layers are employed.[22]

As can be seen in Figure 5, the development of the metal hydroxide sheet causes the 001 intensity to decrease and the 002–004 intensities to increase. In fact, the observed X-ray intensities for the reaction products (metal = Mn) changed in a similar manner with the addition of alkali (Figure 6).

Table III. Structural Model and Parameters for the Synthesized Metal(II) Hydroxide–Layer Silicate[a] **Intercalation Compound with a Chemical Composition of** $[\mathrm{Me^{II}}_x(\mathrm{OH})_{2x-1}(\mathrm{H_2O})]^+(\mathrm{Mg_{2.5}Si_4O_{10}F_2})$ **($^1/_2 \le x \le 3$)**

	composition	Z, Å
silicate layer[b]	6O	
	4Si	
	4O	
	2F	
	5Mg	0.000
	2F	1.023
	4O	1.128
	4Si	2.730
	6O	3.335
metal hydroxide interlayer	OH, H_2O	(d[c] − 2.20)/2
	$\mathrm{Me^{II}}$	d/2
	OH, H_2O	

[a] Layer silicate: sodium fluoride tetrasilicic mica. [b] Derived from parameters for potassium fluoride tetrasilicic mica.[19] [c] d: observed basal spacing (Å).

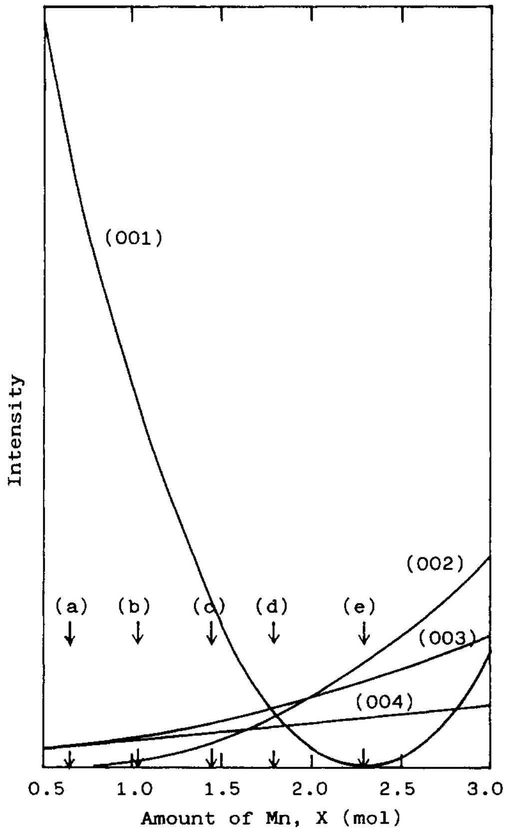

Figure 5. Change in X-ray intensities of the basal (00l) reflections with the interlayering of manganese(II) hydroxide for manganese(II) hydroxide–layer silicate intercalation compounds $[\mathrm{Mn}_x(\mathrm{OH})_{2x-1}(\mathrm{H_2O})]^+(\mathrm{Mg_{2.5}Si_4O_{10}F_2})$ ($^1/_2 \le x \le 3$). Amount of Mn (mol): Mn (mole) per formula unit of layer silicate. Layer silicate: sodium fluoride tetrasilicic mica. Calculations based on the model shown in Table III. Parts a–e correspond to the amount of Mn intercalated in titration at the OH/Mn mole ratios of 0.2, 0.4, 0.6, 0.8, and 1.0, respectively.

The intercalates (metal(II) = Mg, Mn, Fe, Co, Ni, Zn, and Cd) maintained their structures after calcining at 200 °C, but upon heating at 500 °C they collapsed to a basal spacing of 9.6 Å owing to the dehydration of the metal hydroxide sheet (Table II).

As described previously, calcium(II) hydroxide, being moderately water soluble, was not fixed in the silicate under the conditions of a OH/Ca mole ratio of 1.0. The basal spacing of the product prepared with the OH/Ca

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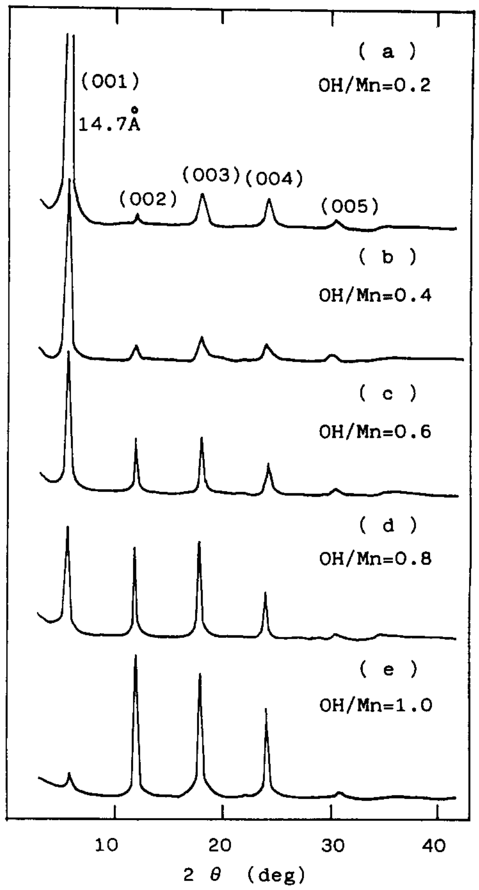

Figure 6. X-ray powder diffraction patterns of manganese(II) hydroxide–layer silicate intercalation compounds prepared with OH/Mn mole ratios of (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8 and (e) 1.0. Layer silicate: sodium fluoride tetrasilicic mica.

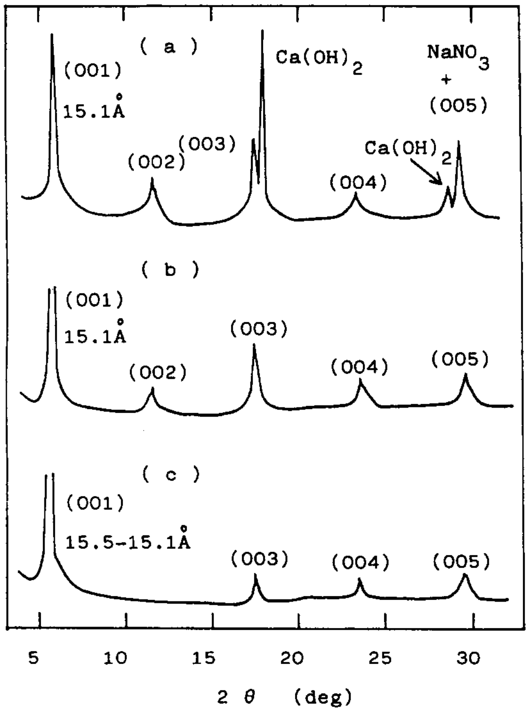

Figure 7. X-ray powder diffraction patterns of calcium(II) hydroxide–layer silicate intercalation compounds (a) before washing and after (b) 5 and (c) 15 washings with water, for samples prepared with a OH/Ca ratio of 2.0. Layer silicate: sodium fluoride tetrasilicic mica.

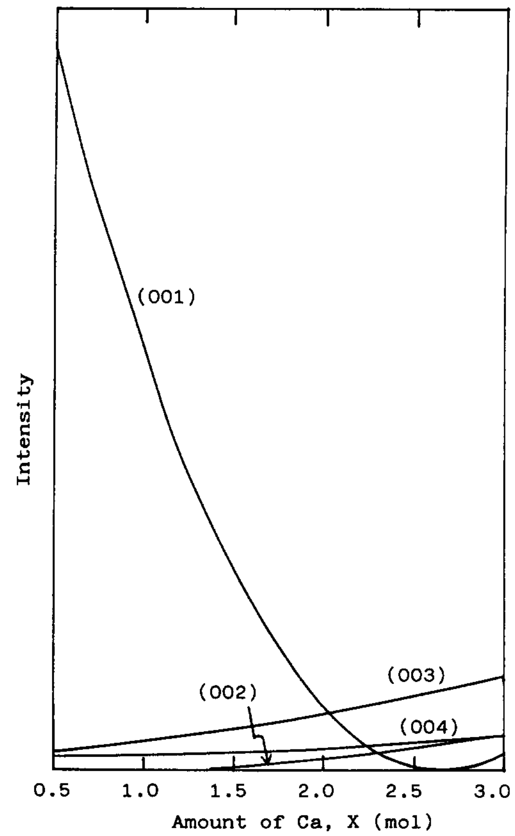

Figure 8. Change in X-ray intensities of the basal (00*l*) reflections with the interlayering of calcium(II) hydroxide for calcium(II) hydroxide–layer silicate intercalation compounds [(Ca$_x$(OH)$_{2x-1}$(H$_2$O)]$^+$(Mg$_{2.5}$Si$_4$O$_{10}$F$_2$) ($^1/_2 \le x \le 3$). Amount of Ca (mol): Ca (mole) per formula unit of layer silicate. Layer silicate: sodium fluoride tetrasilicic mica. Calculations based on the model shown in Table III.

mole ratio of 1.0 was 15.5 Å. Calcium(II) ions, hydrated with its six water molecules, were located between the silicate layers. Upon heating at 200 °C the basal spacing reduced to 9.6 Å due to the dehydration of the coordinated water of the calcium(II) ions (Table II).

On the other hand, Figure 7 shows the XRD patterns of the silicates with calcium(II) hydroxide before and after washing with water, for samples prepared with a OH/Ca mole ratio of 2.0. Figure 8 shows the calculated X-ray intensities of the basal reflections as interlayering progresses for the calcium(II) hydroxide–layer silicate intercalation compound. It is apparent from both Figures 7 and 8, especially from the changes in the intensities of the 001 and 002 reflections, that calcium(II) hydroxide interlayers developed and that these interlayers dissolved with washing.[23] This layer silicate complex with calcium(II) hydroxide had a basal spacing of 15.1 Å and held its structure after heating at 200 °C.

Thermal Analyses. Differential thermal analysis revealed two or three endothermic peaks below 500 °C for the reaction products containing the metal hydroxide (metal(II) = Mg, Mn, Fe, Co, Ni, Zn, and Cd). Figure 9 illustrates the DTA-TGA curves for the silicate with magnesium(II) hydroxide, manganese(II) hydroxide, zinc(II) hydroxide, and cadmium(II) hydroxide. These endothermic peaks below 500 °C were attributed to the dehydration of absorbed water and of the metal hydroxide interlayer [Me$^{II}_x$(OH)$_{2x-1}$(H$_2$O)]$^+$: the first peak presumably corresponds to the loss of absorbed water, the second

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[23] The calcium(II) hydroxide interlayer, [Ca$_x$(OH)$_{2x-1}$(OH$_2$)]$^+$ to be exact, leaches out with washing, and then the dissolved Ca^{2+} ions are incorporated into the clay.

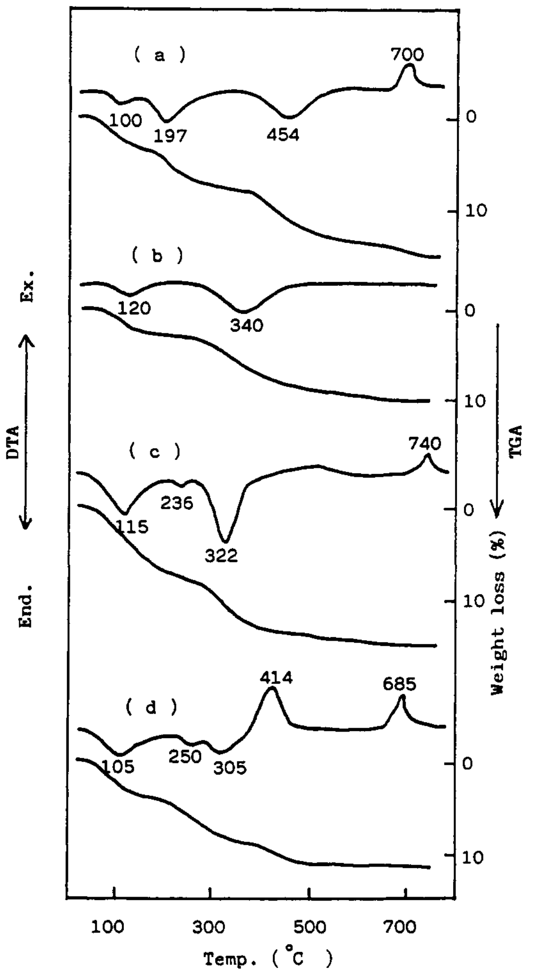

Figure 9. DTA-TGA curves for metal(II) hydroxide–layer silicate intercalation compounds (metal(II) = (a) Mg, (b) Mn, (c) Zn, and (d) Cd) prepared with a OH/metal mole ratio of 1.0. Layer silicate: sodium fluoride tetrasilicic mica. All samples are measured in an air atmosphere.

to the loss of coordinated water, and the third to the loss of hydroxyl groups. The first and second peaks appear close together, and so sometimes it is difficult to distinguish between them.

At above 500 °C, additional endothermic and exothermic peaks are also found in some complexes (Mg, Co, Zn, and Cd). These peaks possibly occur due to the decomposition or sublimation of the interlayer ($CdO \rightarrow Cd$, $CdO \rightarrow$ vapor), and also from a reaction between the metal oxide (MgO, CoO, ZnO, and CdO) and the silicate layers.

Layer Silicate Intercalation Compound with Metal Hydroxide. In general, the coordinated water of the cations in interlayers of the layer silicates having cation-exchange properties is more dissociated than free water,[24,25,26] e.g.

$$[Me^{II}(OH_2)_6]^{2+} \rightarrow [Me^{II}(OH)(OH_2)_5]^+ + H^+ \quad (1)$$

because the hydrated water is polarized by the combined effect of the metal cation and the negative layer charge. This situation applies to the hydrated cations in the clay interlayers in polyvalent metal salt solutions. This is because the clays swell only a little in these salt solutions as well as in the air.[27]

Table IV. Solubility Products and Solubilities for the Metal(II) Hydroxides with the CdI_2 Structure

solid phase	solubility product[a] K_{sp} (I = 0; 25 °C)	solubility[b] (25 °C)
$Mg(OH)_2$ (inactive)	1.3×10^{-11}	9×10^{-4}
$Ca(OH)_2$	4.0×10^{-6}	0.07
$Mn(OH)_2$	1.6×10^{-13}	3×10^{-4}
$Fe(OH)_2$ (inactive)	7.9×10^{-16}	5×10^{-5}
β-$Co(OH)_2$ (inactive)	2.0×10^{-16}	3×10^{-5}
$Ni(OH)_2$ (inactive)	6.3×10^{-18}	1×10^{-5}
$Zn(OH)_2$	$(0.34\text{-}3.2) \times 10^{-16}$	$(2\text{-}4) \times 10^{-5}$
β-$Cd(OH)_2$ (inactive)	4.0×10^{-15}	1×10^{-4}

[a] From Feitknecht and Schindler.[31] I: ionic strength. [b] Solubility: g/100 mL of solution.

The degree of this dissociation increases with decreasing water content of the interlayer and with increasing polarizing power of the cation. The polarizing power of a cation is dependent not only on its charge and radius but also on its electron configuration.[28] The calcium ion is the least polarizing among all the cations forming the CdI_2 structure.

Yamanaka and Brindley[17] suggested that the mechanism of the metal hydroxide interlayering process is dependent on the acidic character (protic acidity) of the layer silicates (eq 1), in their study of the nickel(II) hydroxide–montmorillonite intercalation compound.

In the system of polyvalent metal salt solutions containing the layer silicates, the dissociated protons (in solid) will further ion exchange with the metal ions (in solution; Suzuki et al.,[29] Whittingham[30]):

$$\underset{\text{in solid}}{H^+} + \underset{\text{in solution}}{[Me^{II}(OH_2)_6]^{2+}} \rightarrow \underset{\text{in solution}}{H^+} + \underset{\text{in solid}}{[Me^{II}(OH_2)_6]^{2+}} \quad (2)$$

Then, upon addition of alkali metal to the suspension, the protons (in solution) are neutralized, further hydrolysis of the metal ions ($[Me^{II}(OH_2)_6]^{2+}$ in solid) proceeds (i.e., new protons are generated), and polynuclear complexes develop by the olation of the hydrolyzed metal cations. The metal hydroxide interlayers grow by a repetition of this procedure.

Thus the overall hydrolysis reaction is shown as follows:

$$x[Me^{II}(OH_2)_6]^{2+} \rightarrow \underset{\text{interlayer}}{[Me^{II}{}_x(OH)_{2x-1}(OH_2)]^+} + yH^+ + zH_2O \quad (3)$$

so that the metal hydroxide interlayer has a charge of +1 to compensate the negative layer charge of −1 of sodium fluoride tetrasilicic mica.

As stated above, the divalent metal cations that can form hydroxides with the CdI_2 structure lead to the formation of metal hydroxide sheets between the silicate layers. In the case of calcium(II) ion, the polarizing power is small: calcium ion shows less tendency to hydrolyze, and this hydroxide is moderately soluble in water (Table IV). Thus the fixation of calcium(II) hydroxide in the clay is somewhat more difficult compared with the other metal hydroxides that form the CdI_2 structure.

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(26) Fripiat, J. J. *ACS Symp. Ser.* **1976**, *34*, 261–274.

(27) In polyvalent metal salt solutions, the clay interlayers have two or three water layers depending on the type of the cations, concentration of the salts, and layer charge of the silicate. See: Norrish, K. *Discuss. Faraday Soc.* **1954**, *18*, 120–134.

(28) Generally, small cations are more polarizing than large cations of the same charge; the transition-metal ions have a large polarizing power because they have one or more d electrons that shield the nucleus poorly. See: Huheey, J. E. *Inorganic Chemistry*, 3rd. ed.; Harper & Row: New York, 1983; pp 129–131.

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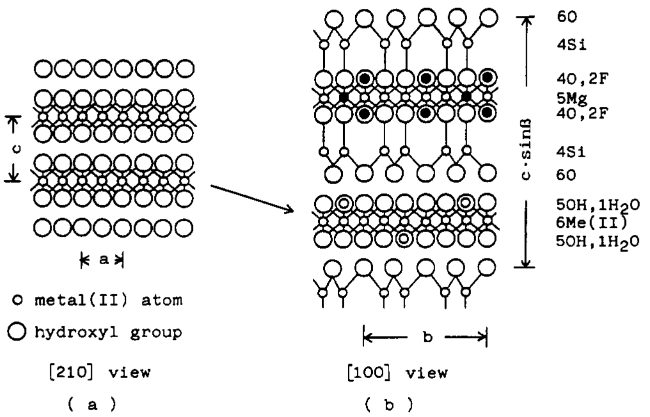

Figure 10. Relationship between (a) the CdI_2 structure and (b) a metal(II) hydroxide–layer silicate intercalation compound, a schematic representation. Layer silicate: sodium fluoride tetrasilicic mica.

Aluminum(III) hydroxides have a layer structure analogous to the CdI_2 structure and can be intercalated into the layer silicate in a similar manner. The structure of the metal hydroxides with the CdI_2 structure is based on a double layer of close-packed hydroxyl groups in which metal ions occupy all of the octahedral holes between the two OH layers. This basic structural unit layer packs together in the sequence of hexagonal close packing. On the other hand, aluminum(III) hydroxides (gibbsite (γ-$Al(OH)_3$), bayerite (α-$Al(OH)_3$), and nordstrandite) are composed of a similar unit layer of hydroxyl groups with two-thirds of the octahedral holes filled with aluminum(III) ions. The structure of the aluminum(III) hydroxides differs mainly from the CdI_2 structure in the way in which the unit layers are superposed.[18]

In the metal hydroxide–layer silicate intercalation compound, the basic structural unit layers (CdI_2 type or aluminum(III) hydroxide type) are intercalated in the two-dimensional silicate interlayer region (Figure 10). We do not think that all of the di- or trivalent cations can form metal hydroxide sheets between the silicate layers[32] because the Ba^{2+}, Sr^{2+}, and Pb^{2+} divalent ions are too large for the CdI_2 structure.[18] Similarly, the aluminum(III) hydroxide structure is not suitable for larger trivalent ions such as La^{3+} and Y^{3+}.[18]

It is known that cadmium(II) hydroxide has the polytypes α-$Cd(OH)_2$, β-$Cd(OH)_2$, γ-$Cd(OH)_2$;[31,33,34] the stable form at 25 °C is β-$Cd(OH)_2$ with the CdI_2 structure. On the other hand, there are various crystalline forms for zinc(II) hydroxide: α-, β_1-, β_2-, γ-, δ-, and ϵ-$Zn(OH)_2$.[35,36] However, ϵ-$Zn(OH)_2$, which is the only phase that is stable in water below 39 °C, does not adopt the CdI_2 layer structure; it has an orthorhombic form consisting of $Zn(OH)_4$ tetrahedra linked three-dimensionally through OH groups. In contrast, the α form of $Zn(OH)_2$ has the CdI_2 type layer structure, and the β_1 and β_2 forms possess layer structures analogous to the CdI_2 structure. It is therefore suggested that the unstable form of $Zn(OH)_2$ with the CdI_2 structure is selectively formed in the two-dimensional, spatially restricted, silicate interlayer region.

Conclusions

Intercalation of metal hydroxide into expandable 2:1 layer silicates has been investigated. We have found that the divalent metal cations (Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}) which can form hydroxides with the CdI_2 structure lead to the formation of metal hydroxide sheets in the interlamellar space. In the intercalation compounds, the basic unit layer of the metal hydroxides is sandwiched between the silicate layers, and the intercalated metal cations form a bidimensional lattice. Our results suggest that the crystal structure of the metal hydroxides plays an important role in the metal hydroxide interlayering process.

Registry No. Magnesium nitrate, 10377-60-3; calcium nitrate, 10124-37-5; manganese dinitrate, 10377-66-9; cobalt dinitrate, 10141-05-6; nickel dinitrate, 13138-45-9; zinc nitrate, 7779-88-6; cadmium nitrate, 10325-94-7; ferrous chloride, 7758-94-3; sodium hydroxide, 1310-73-2.

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(32) So far there is nothing in the literature that demonstrates that the metal cations forming hydroxides with structures other than the CdI_2 structure lead to the formation of metal hydroxide interlayers in the layer silicates. The metal cations forming hydroxides with structures other than the CdI_2 structure will constitute part of the metal hydroxide interlayers by coprecipitating with the metal cations forming the CdI_2-type hydroxides.

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