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A NICKEL HYDROXIDE-VERMICULITE COMPLEX: PREPARATION AND CHARACTERIZATION

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Abstract—A nickel hydroxide-vermiculite complex (NHVC) with $c\sin\beta$ = 1.41 nm and particle sizes from 0.075 to 0.15 mm was obtained hydrothermally by adding nickel nitrate solution to vermiculite from Transvaal, South Africa. The quantity of nickel hydroxide included in NHVC was controlled by adjusting the concentration of the nickel nitrate solution. The thermal behavior of NHVC at 450°C or above was independent of the Ni content. However, small differences exist in the dehydration behavior of NHVC below 450°C. One-dimensional Fourier electron density analysis of the NHVC structure containing 2.43 mol of Ni per half unit cell showed that Ni cations occupy the interlayer of NHVC, and 10% of the total Ni cations is in the ditrigonal cavity of the basal-oxygen plane of the tetrahedral sheet.

Key Words—Clay-Inorganic Complex, One-Dimensional Fourier Electron Density Map, Nickel Hydroxide, Vermiculite.

INTRODUCTION

Reactions involving the insertion of chemical species in the interlayer of layered materials have been widely researched to design new materials with varying and unique properties. One type of intercalating reaction involves the hydrolysis of metal ions to form a mono-molecular metal hydroxide in the interlayer. This reaction produces a structure similar to chlorite. The transition metals of Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} show similar intercalating behavior as more typical non-transition metals, such as Mg^{2+} or Al^{3+} (Brindley and Kao, 1980; Ohtsuka *et al.*, 1990; Yamanaka and Brindley, 1978). Transition elements generate interesting physical properties, including two-dimensional magnetic effects (*e.g.*, Takahashi *et al.*, 1986, 1988).

Most studies have examined intercalations involving smectites and artificial mica-like materials for interlayering complexes. The mica-like material, $NaMg_{2.5}Si_4O_{10}F_2$, used by Ohtsuka *et al.* (1990) and Takahashi *et al.* (1986, 1988) is similar to vermiculite owing to its high layer charge. However, its properties are similar to smectite in both small particle size and high-swelling behavior. Vermiculite is similar to smectite in having a large ion-exchange capacity, although it differs in its higher layer charge. Vermiculite crystals may also be large, on the cm scale. Therefore, vermiculite-inorganic complexes are expected to have different physical properties than smectite. No Ni hydroxide-vermiculite complexes have been reported, although Ni-vermiculite was reported by Alcover *et al.* (1973).

Synthesis of the Ni hydroxide-clay complex is often based on the technique reported by Yamanaka and Brindley (1978). In this technique, the clay samples are dispersed in $Ni(NO_3)_2$ solution. Then, NaOH is titrated into the suspension to intercalate Ni hydroxide. Because the swelling of vermiculite is limited, a Ni hydroxide-vermiculite complex (NHVC) could not be synthesized. In contrast, a technique that has produced a lead hydroxide-vermiculite complex (Uehara *et al.*, 1995) was adopted. Uehara *et al.* (1995) prepared a lead hydroxide-vermiculite complex by hydrothermal processing of vermiculite in $Pb(NO_3)_2$ solution. Since Ni often forms $[Ni(OH_2)_6]^{2+}$ in solution with a six coordinate octahedral structure (Heslop and Robinson, 1967), we used an analogous method to synthesize NHVC.

This paper describes (a) the preparation of NHVC; (b) the characterization of NHVC using powder X-ray diffraction (XRD) methods, thermogravimetry-differential thermal analysis (TG-DTA), and high-temperature X-ray diffraction (HTXRD); and (c) one-dimensional Fourier analysis of the structure.

EXPERIMENTAL

The starting material was vermiculite, Transvaal, South Africa, with a particle size of 0.075–0.15 mm as determined by using sieves. First, 500 mg of vermiculite were placed in a 100-mL Teflon bottle, and then 60 mL of 1 M, 2 M, or a saturated $Ni(NO_3)_2$ solution of ~4.3 M were added. The bottle was sealed in a Morey-type stainless-steel bomb and maintained for 84 h at 250°C. After cooling, the NHVC was washed with distilled water and dried at room temperature.

The chemical composition of NHVC and the Transvaal vermiculite, except for CO_2, NO_2, and H_2O, was determined by electron microprobe (JEOL JXA733)

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Table 1. Chemical composition and formulae of (1) Transvaal vermiculite, (2) NHVC-1M, (3) NHVC-2M (4) NHVC-SAT.

	(1)	(2)	(3)	(4)
SiO_2	40.17	33.34	32.70	30.23
Al_2O_3	10.78	8.66	8.64	7.99
MgO	23.99	18.43	17.50	15.65
Fe_2O_3	6.02	4.40	4.50	4.86
TiO_2	0.81	0.76	0.58	0.50
K_2O	4.89	1.58	0.37	0.11
NiO	—	19.49	22.44	29.58
CO_2	Trace	Trace	Trace	Trace
NO_2	Trace	Trace	Trace	Trace
H_2O	13.34	13.33	13.26	11.08
Total	100.00	99.99	99.99	100.00
Composition per formula unit containing $O_{10}(OH)_2$				
Si	3.02	3.05	3.07	3.07
Al	0.96	0.93	0.96	0.93
Mg	2.50	2.52	2.45	2.37
Fe^{3+}	0.34	0.30	0.32	0.37
Ti	0.05	0.05	0.04	0.04
Interlayer per formula unit containing $O_{10}(OH)_2$				
K	0.47	0.18	0.04	0.01
Ni	—	1.44	1.69	2.42
Mg	0.19	—	—	—
OH	—	2.22	2.58	4.01
H_2O	2.00	0.90	0.72	—
Adsorption composition				
H_2O	0.35	1.07	1.14	0.75

with an energy-dispersive analysis system (Noran Instruments Voyager III). CO_2, NO_2, and H_2O were determined with a CHN analyzer (Yanaco MT-5). The intercalation compounds were assumed to have the formula $Ni_x(OH)_{2x-0.84}yH_2O$ ($2x + 2y - 0.84$ was fixed, $0.4 < x < 2.8$).

Samples of NHVC were dispersed in distilled water by using an ultra-sonic vibrator and air-dried on a glass slide. These samples were analyzed by XRD with a Rigaku Rint-2000, equipped with a graphite monochromator (CuKα) to obtain basal-reflection intensities for determining a one-dimensional electron density distribution. The intensities of the basal reflections were computed from the formula: $I_{00l} = |F_{00l}|^2$ Lp and $F_{(00l)} = \sum f_{n(00l)} \exp(2\pi(lz_n))$ where $|F_{00l}|$ is the structure factor, Lp is the Lorentz-polarization factor, $f_{n(00l)}$ is the atomic scattering factor, and z_n is the coordinate of atom n based on the unit cell. Scattering factors for atoms were obtained from Maslen *et al.* (1992). The random-powder form was applied to the Lorentz-polarization factor, $Lp = (1 + \cos^2 2\theta' \cos^2 2\theta)/(1 + \cos^2 2\theta')/(\sin^2 2\theta \cos \theta)$, where θ = Bragg angle for the sample and θ' = Bragg angle for monochromator crystal. This equation is more appropriate than the single-crystal form for calculating the intensities of 00*l* reflections (Reynolds, 1980). HTXRD patterns were obtained using a Rigaku Rint-2000 diffractmeter with a high temperature attachment (Rigaku 2311B1), using Ni-filtered CuKα radiation.

The samples for TG-DTA were maintained with silica gel in a desiccator for 48 h. They were then analyzed with a Rigaku Thermo-flex TAS200 at a heating rate of 10 K min^{-1} in air.

RESULTS AND DISCUSSION

Chemical composition and structural formulae

Table 1 shows the chemical data for the starting material and NHVC. Hereafter, NHVC is expressed as NHVC-SAT, NHVC-2M, or NHVC-1M according to the concentration of the $Ni(NO_3)_2$ solution used in the synthesis procedure. Based on the layer charge of 0.84 for the Transvaal vermiculite by ion-exchange with Na (Uehara *et al.*, 1995) and the chemical data, structural formulae were calculated (Table 1).

The exchangeable cations of the starting material are primarily K and Mg. In NHVC, the amount of interlayer Ni increases as the concentration of $Ni(NO_3)_2$ solution rises. However, K remained in NHVC-1M, even after synthesis durations as long as 144 h. However, when higher concentrations were used, nearly all the K was removed. The 2:1 layer structure is retained in NHVC, although it is unclear if a slight decrease in Mg in the octahedral sheet occurs with increasing Ni.

Powder X-ray diffraction

Figure 1 shows XRD patterns of the Transvaal vermiculite and NHVC. The starting material has diffraction characteristics with the following $c\sin\beta$ values: 1.01 nm, which corresponds to no interlayer water; 1.26 nm, of one layer of H_2O and the 2:1 layer; 1.43-nm spacing indicating two layers of H_2O, and a reflection at 2.6 nm which represents interstratification. NHVC shows a basal reflection at 1.41 nm and does not show interstratification. Note that the patterns for NHVC clearly show a strong 002 reflection. The XRD data and the chemical analysis (Table 1) show that NHVC is intercalated with Ni hydroxide.

High-temperature X-ray diffraction

Figure 2 shows the relationship between the *d*-values of NHVC and temperature. Figure 3 and Figure 4 show the HTXRD patterns of NHVC-SAT and NHVC-1M. As clearly shown in Figure 2, differences of the *d*(001) and *d*(004)-values indicate that these basal reflections are not related by an integer number of wavelengths and that the structure becomes more disordered as temperature increases. The *d*(001) and *d*(004)-values of NHVC-SAT are not apparently different to 400°C. The *d*(001)-value decreases between 400–600°C, presumably because of dehydroxylation of the interlayer. In the HTXRD patterns (Figure 3), the reflections increase in width at 300°C, and the rel-

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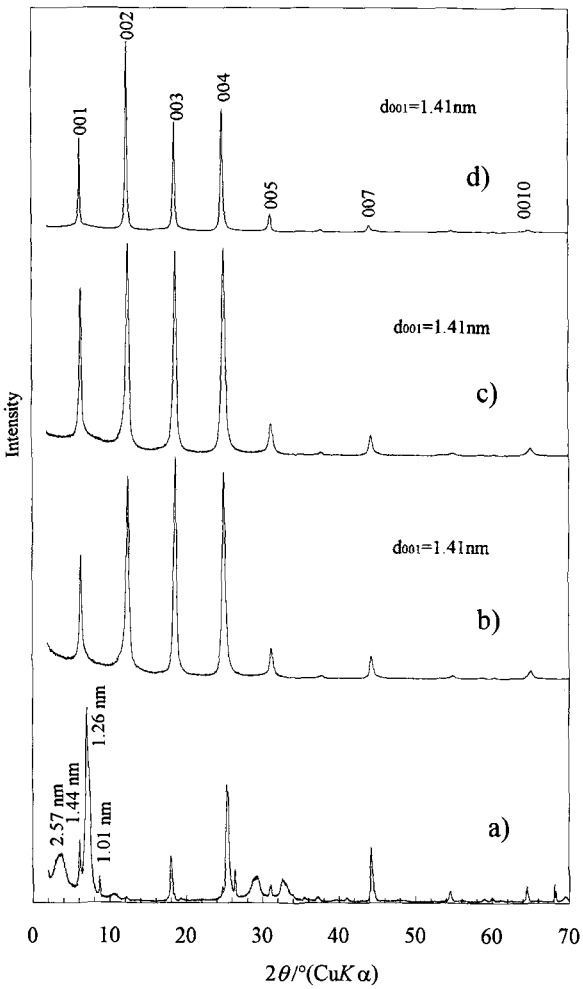


Figure 1. XRD patterns for a) Transvaal vermiculite, b) NHVC-1M, c) NHVC-2M, d) NHVC-SAT.

ative intensities of 002, 003, and 004 are changed. Above 600°C, where there are no reflections of higher-order, the interlayer structure probably has decomposed. In addition, the *d*-value at 1.15 nm at 600°C gradually decreases with increasing temperatures, and is ~1.0 nm at 900°C. HTXRD did not detect NiO in this temperature range. Moreover, the 001 peak of these heat-treated samples broadened with increasing Ni content in the interlayer. Therefore, although the Ni hydroxide is dehydroxylated, NiO probably exists in the interlayer as monomolecules. This result was consistent with the results reported by Ohtsuka *et al.* (1987), Fuda *et al.* (1987), and Yamanaka and Senda (1993).

The *d*(001) and *d*(004)-values of NHVC-1M were significantly different at >100°C, perhaps because the interlayer water in NHVC-1M is removed at low temperatures and the interlayer structure is disordered at these temperatures (Figure 2). This is clear from the significant broadening of the reflections at 100°C in

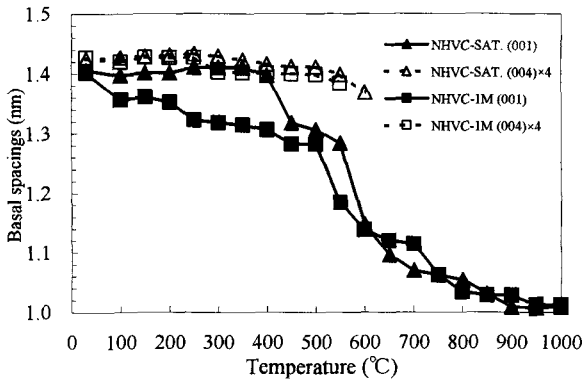


Figure 2. The *d*-values of 001 and 004 reflections of NHVC-SAT and NHVC-1M as a function of temperature.

the HTXRD patterns shown in Figure 4. However, the behavior of NHVC-1M at 450°C or above was similar to that of NHVC-SAT.

Thermal analysis

Figure 5 shows TG-DTA curves of the starting material and NHVC. In the TG-DTA curve of the starting

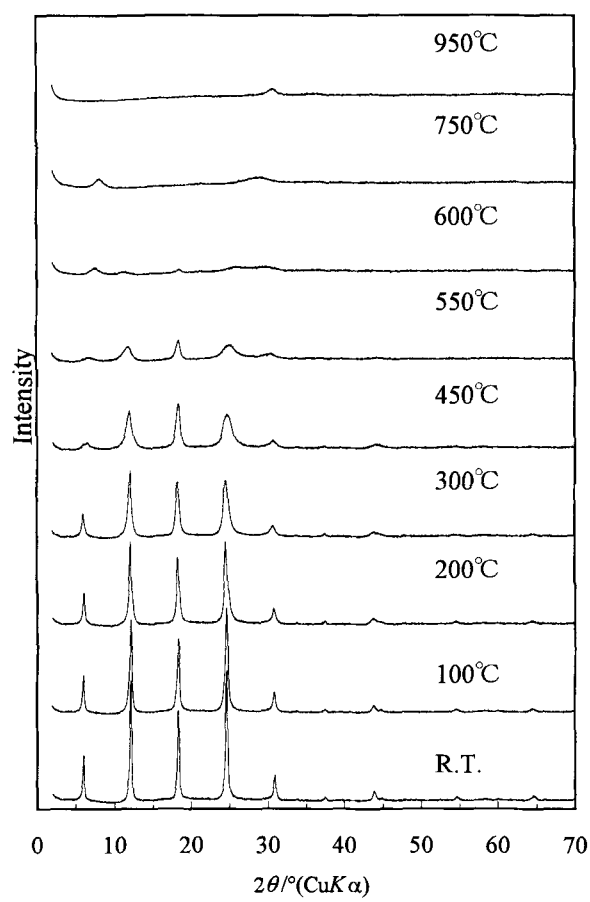


Figure 3. XRD patterns of the NHVC-SAT at various temperatures.

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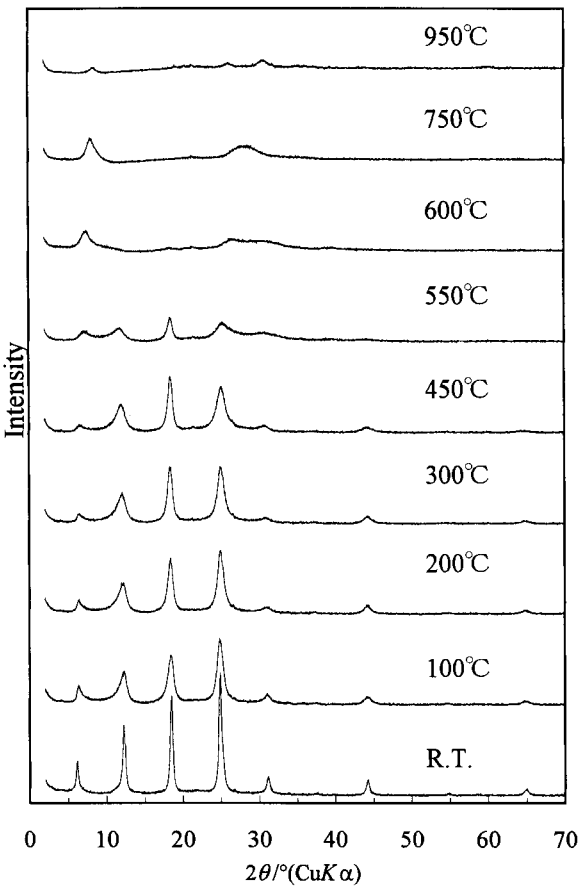


Figure 4. XRD patterns of NHVC-1M at various temperatures.

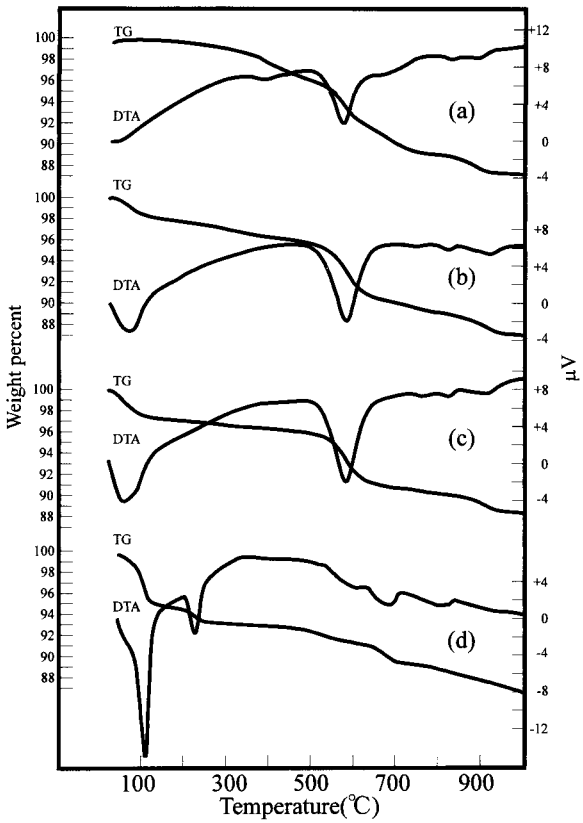


Figure 5. TG-DTA curves. (a) NHVC-SAT, (b) NHVC-2M, (c) NHVC-1M, (d) Transvaal vermiculite.

material, endotherm and weight loss due to the dehydration of the interlayer are observed at <300°C. Moreover, a small endotherm and weight loss are observed near 550°C, probably caused by interlayer dehydroxylation in the vermiculite. Weight loss and an endothermic peak observed at ~700°C and a gradual weight loss observed at higher temperatures may be caused by the loss of hydroxyl groups of the 2:1 layer. The weight loss and endothermic peak observed at <200°C in NHVC-1M and NHVC-2M come from the dehydration of the interlayer. This endothermic peak and weight loss become smaller as Ni density in the interlayer increases, indicating that interlayer water is lacking in NHVC-SAT. A weight loss caused by dehydroxylation of the interlayer is at ~600°C, and it becomes greater as the amount of Ni increases. Moreover, the gradual weight loss in NHVC-SAT may be caused by dehydroxylation of the interlayer at ~300°C. This corresponds to the broadening of the reflection widths at >300°C in the HTXRD patterns (Figure 3). These results show that dehydroxylation of the interlayer may begin gradually at this temperature as shown in Yamanaka and Senda (1993). The significant dehydration of the interlayer at ~200°C or below in NHVC-1M may be the reason dehydroxylation at 300°C was not discernible.

Structural formula and structural model

The above properties of the NHVC suggest that the material can be regarded as being composed of vermiculite intercalated with nickel hydroxide. Based on these results and the fact that the basal spacing of NHVC is ~1.4 nm, Ni may be located in the center of the interlayer (z = 0.5), similar to the Ni hydroxide-smectite complex reported by Yamanaka and Brindley (1978). Figure 6 shows the change in calculated intensities of 001 and 004 reflections with increasing Ni, assuming that all the Ni is at the center of the interlayer (z = 0.5). The measured intensity of the 001 reflection is lower than the calculated intensity for NHVC-1M. This may be attributed to the residual K in the interlayer of NHVC-1M. NHVC-2M showed a better correlation between the measured and calculated intensities. The intensity of the 002 reflection increased as the Ni density increased, showing good correlation with experimental results. However, the observed 001 diffraction intensity of NHVC-SAT is higher than the calculated value. To resolve this in-

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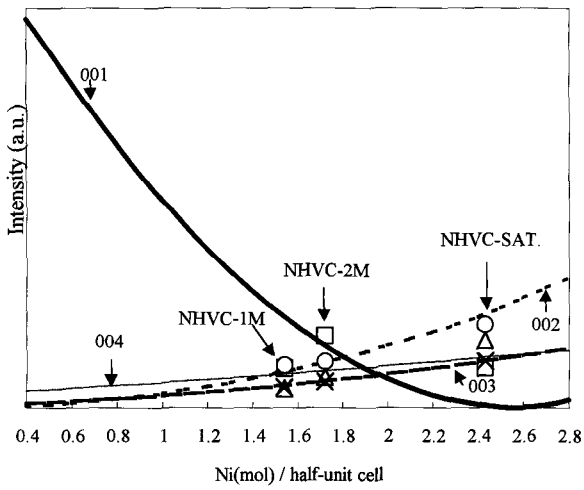


Figure 6. Calculated and observed XRD intensities of 00*l* reflections for NHVC as a function of nickel content. □ = observed intensity of 001 reflections; ○ = observed intensity of 002 reflections; × = observed intensity of 003 reflections; △ = observed intensity of 004 reflections. Note: observed intensities were obtained by applying a slit correction.

Table 2. Observed and calculated structure factors of 00*l* reflections for NHVC-SAT.

00*l*	$\|F_{obs}\|$	F_{calc}[1]
1	27.95	22.24
2	81.24	77.29
3	91.06	−92.77
4	146.50	139.72
5	48.24	45.88
6	26.62	28.67
7	86.20	−80.05
8	13.93	8.95
9	17.92	−11.77
10	80.72	84.77
11	1.87	−0.97
12	73.46	93.70
13	15.41	−20.60
14	59.01	68.37

R = 0.10.
[1] Obtained from the final z-parameters.

consistency, the structure of NHVC-SAT was examined in more detail with a one-dimensional Fourier electron-density analysis.

Two adsorption sites of nickel were considered in the one-dimensional Fourier electron-density analysis. One site is located at the center of the interlayer, and the other is in the center of the ditrigonal cavity of the basal oxygens of the tetrahedral sheet. The Ni occurring at two adsorption sites is consistent with the study of the interstratification process of nickel hydroxide in smectite (Fuda *et al.*, 1990). Figure 7 shows a structural model and the corresponding electron density. Table 2 shows the structure factors calculated from the structural model shown in Figure 7. The model which corresponds best to the observed intensities is based on 10% of the total Ni in the ditrigonal cavity of basal oxygens (z = 0.206). The structural formula for NHVC-SAT is then represented as: $Ni_{2.19}Ni^*_{0.23}K_{0.01}OH_{4.01}(Si_{3.07}Al_{0.96})(Mg_{2.37}Fe_{0.37}Ti_{0.04})O_{10}(OH)_2 \cdot 0.75H_2O$, where Ni* is defined as the cation located at z = 0.206. The reliability factor, $R = (\sum\|F_{o(00l)}|-|F_{c(00l)}\|)/\sum|F_{o(00l)}|$, for this model is 0.10, which is considered reasonable.

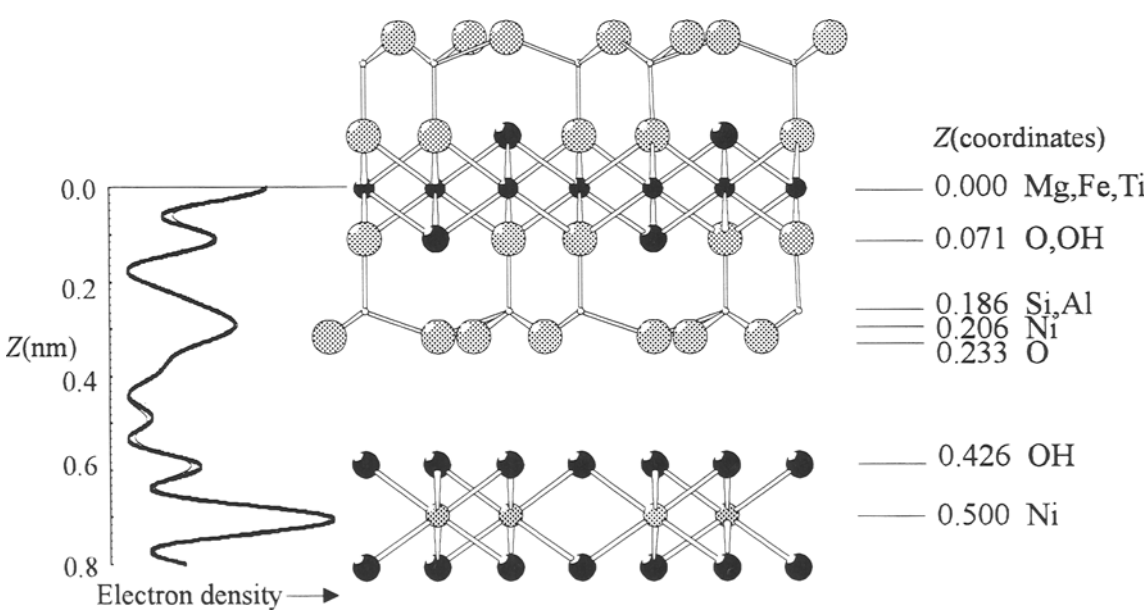


Figure 7. One-dimensional curves of electron density normal to *ab* plane and structural model for NHVC-SAT. Boldface line: calculated, lightface line: observed.

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F_o and F_c are the observed and calculated structure factors, respectively.

We concluded that ~10% of the total Ni is in the exchange sites located in the ditrigonal cavity at the same z-level as the basal-oxygen atoms. This model differs from the common chlorite-like structure. This structure occurs for NHVC containing 2.42 mol of Ni per half unit cell.

REFERENCES

Alcover, J.F., Gatineau, L., and Mering, J. (1973) Exchangeable cation distribution in nickel and magnesium vermiculite. *Clays and Clay Minerals,* **21,** 131–136.

Brindley, G.W. and Kao, C.-C. (1980) Formation, compositions, and properties of hydroxy-Al- and hydroxy-Mg-montmorillonite. *Clays and Clay Minerals,* **28,** 435–443.

Fuda, K., Kimura, M., Miyamoto, N., and Matsunaga, T. (1987) Methanation of low-temperature volatile matter of coal by using Ni-intercalated montmorillonite catalyst. *Journal of the Fuel Society of Japan,* **66,** 427–431.

Fuda, K., Yuri, T., Saito, Y., and Matsunaga, T. (1990) X-ray diffraction intensity change occuring intercalation process of nickel hydroxide into the interlayer space of montmorillonite. *Journal of the Society of Materials Engineering for Resources of Japan,* **3,** 84–91.

Heslop, R.B. and Robinson, P.L. (1967) *Inorganic Chemistry.* Elsevier, Amsterdam, 691–707.

Maslen, E.N., Fox, A.G., and O'Keefe, M.A. (1992) X-ray scattering. In *International Tables for Crystallography, Volume C,* A.J.C. Wilson, ed., The International Union of Crystallography by Kluwer Academic Publishers, Dordrecht, 476–511.

Ohtsuka, K., Suda, M., Ono, M., Takahashi, M., Sato, M., and Ishio, S. (1987) Preparation of nickel(II)-hydroxide-(sodium fluoride tetrasilicic mica) intercalation complexes and formation of ultra fine nickel particles by H_2 reduction. *Bulletin of the Chemical Society of Japan,* **60,** 871–876.

Ohtsuka, K., Suda, M., Tsunoda, M., and Ono, M. (1990) 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)). *Chemistry of Materials,* **2,** 511–517.

Reynolds, R.C. (1980) Theoretical treatment of X-ray diffraction. In *Crystal Structures of Clay Minerals and Their X-ray Identification,* G.W. Brindley and G. Brown, eds., Mineralogical Society, London, 255–266.

Takahashi, M., Sato, M., Ishino, S., Ohtsuka, K., Suda, M., and Ono, M. (1986) Magnetic properties of hydroxy Ni-mica intercalation. *Japanese Journal of Applied Physics,* **25,** 1348–1352.

Takahashi, M., Ishio, S., Onuki, S., Ohutsuka, K., Suda, M., and Ono, M. (1988) Magnetic characterization of 3*d* transition-metal-mica intercalation compounds. *Journal of Applied Physics,* **64,** 5766–5768.

Uehara, M., Yamazaki, A., Suzuta, M. and Tsutsumi, S. (1995) Lead hydroxide vermiculite complex: Preparation and characterization. *Clays and Clay Minerals,* **43,** 744–747.

Yamanaka, S. and Brindley, G.W. (1978) Hydroxide-nickel interlayering in montmorillonite by titration method. *Clays and Clay Minerals,* **26,** 21–24.

Yamanaka, S. and Senda, K. (1993) Thermal evolution of nickel chlorite-like phase derived from montmorillonite. *Clay Science,* **9,** 99–107.

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