

Pressure-Induced Intercalation of Alcohol Molecules into a Layered Titanate

S. Nakano,* T. Sasaki, K. Takemura, and M. Watanabe

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received April 10, 1998

Revised Manuscript Received June 22, 1998

High-pressure (HP) will effectively insert small molecules into cavities in microporous crystals. Hazen et al.,¹ on compressing a 4A-type zeolite in various pressure-transmitting media, demonstrated the insertion of water, ethanol, and methanol molecules into the cavities of the zeolite. Perottoni and Jornada² have reported that a defect pyrochlore NH_4NbWO_6 showed a 5% expansion of the unit cell volume at 2.5 GPa in methanol–ethanol–water medium, which was ascribed to the pressure-induced insertion of water molecules. Assink et al.³ found that various gases such as H_2 , He, O_2 , and N_2 were loaded into octahedral interstitial sites of the fcc lattice of C_{60} and C_{70} fullerenes (between “soccer balls”) at HP.

Although most of layered compounds are active in intercalation reactions, few pressure-induced reactions have been reported except those on graphite and clay minerals. Guérard and Hérolde⁴ and Sonnenschein et al.⁵ have reported that some graphite intercalation compounds (GICs) were synthesized on compression of graphite with alkali or lanthanide metals. Wada et al.⁶ have claimed that HP promoted the intercalation of water molecules into clay minerals such as kaolinite and Na-vermiculite. However, these GICs and clay complexes had been prepared even without HP.^{7–9} That is to say, no intercalation reaction which was driven exclusively by HP conditions has been reported for layered compounds.¹⁰

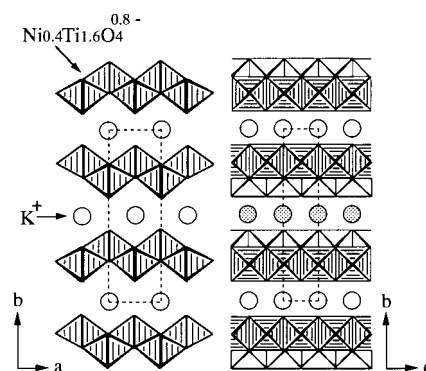


Figure 1. Crystal structure of a layered titanate $\text{K}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4$ (K-titanate) with the lepidocrocite-type structure. The unit cell is shown by broken lines.

Several types of layered titanates have been synthesized and their intercalation behaviors at ambient pressure have been examined extensively.¹¹ In the present study, we have compressed a layered titanate with the lepidocrocite (γ - FeOOH)-type structure¹² with methanol or ethanol to see if a pressure-induced reaction takes place. In situ XRD measurements indicated an abrupt interlayer swelling of pentylamine–titanate complex in the alcohol media under HP. We report here the first and distinct observation of pressure-induced intercalation of alcohol molecules into the layered titanate.

The lepidocrocite-type layered titanates accommodating three kinds of guest were prepared to study the effect of different spacings and chemical environments of the interlayer space. The titanate $\text{K}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4$ (referred to as K-titanate) was synthesized by a solid-state reaction procedure akin to the previous report.¹³ The K-titanate accommodates potassium ions between $[\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4]^{0.8-}$ layers, as depicted in Figure 1. A protonated form of $\text{H}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4 \cdot \text{H}_2\text{O}$ was prepared by leaching the K-titanate in a 1000 mol m^{-3} HCl aqueous solution according to the procedure described previously.¹¹ A pentylamine complex was derived by treating the protonic form with a pentylamine aqueous solution. The chemical composition of the complex was determined to be $(\text{C}_5\text{H}_{11}\text{NH}_3)_{0.5}\text{H}_{0.3}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4 \cdot n\text{H}_2\text{O}$ ($n \approx 1.5$) by chemical analysis.

The crystallographic data of these products are listed in Table 1. The a and c lattice parameters were very

(1) (a) Hazen, R. M. *Science* **1983**, *219*, 1065. (b) Hazen, R. M.; Finger, L. W. *J. Appl. Phys.* **1984**, *56*, 1838.

(2) Perottoni, C. A.; da Jornada, J. A. H. *Phys. Rev. Lett.* **1997**, *78*, 2991.

(3) (a) Assink, R. A.; Schirber, J. E.; Loy, D. A.; Morosin, B.; Carlson, G. A. *J. Mater. Res.* **1992**, *7*, 2136. (b) Samara, G. A.; Hansen, L. V.; Assink, R. A.; Morosin, B.; Schirber, J. E.; Loy, D. *Phys. Rev. B* **1993**, *47*, 4756. (c) Schirber, J. E.; Samara, G. A.; Morosin, B.; Assink, R.; Loy, D.; Wang, H.; Williams, J.; Zhu, Q.; Kniaz, K.; Fischer, J. E. In *High-Pressure Science and Technology-1993*; Schmidt, S. C., Shaner, J. W., Samara, G. A., Ross, M., Eds.; American Institute of Physics: New York, 1994; p 639.

(4) (a) Guérard, D.; Hérolde, A. *Carbon* **1975**, *13*, 337. (b) Makrini, M. E.; Guérard, D.; Lagrange, P.; Hérolde, A. *Carbon* **1980**, *18*, 203. (c) Guérard, D.; Chaabouni, M.; Lagrange, P.; Makrini, M. E.; Hérolde, A. *Carbon* **1980**, *18*, 257.

(5) Sonnenschein, R.; Hanfland, M.; Syassen, K. *Phys. Rev. B* **1988**, *38*, 3152.

(6) (a) Wada, N.; Raythatha, R.; Minomura, S. *Solid State Commun.* **1987**, *63*, 783. (b) Wada, N.; Omura, Y. In *Proceedings of the International Conference - AIRAPT-16 and HPCJ-38 - on High Pressure Science and Technology*; Nakahara, M., Ed.; Japan Society of High Pressure Science and Technology: Kyoto, Japan, 1998; p 727.

(7) Hérolde, A. *Bull. Soc. Chim. Fr.* **1955**, *187*, 999.

(8) Raythatha, R.; Lipsicas, M. *Clays Clay Miner.* **1985**, *33*, 333.

(9) Wada, N.; Okui, H.; Omura, Y.; Fujiwara, A.; Suematsu, H.; Murakami, Y. In *Material Research Society Symposium Proceedings*; Materials Research Society: Pennsylvania, 1997; Vol. 453, p 95.

(10) Jayaraman et al. have suggested a possibility of pressure-induced intercalation of water as medium into a layered oxide CuGeO_3 on the basis of Raman spectroscopy, but later they attributed it to a phase transformation depending on hydrostaticity: (a) Jayaraman, A.; Wang, S. Y.; Ming, L. C.; Cheong, S.-W. *Phys. Rev. Lett.* **1995**, *75*, 2356. (b) Haines, J.; Adams, D. M. *Phys. Rev. Lett.* **1996**, *77*, 204. (c) Jayaraman, A.; Wang, S. Y.; Ming, L. C.; Cheong, S.-W. *Phys. Rev. Lett.* **1996**, *77*, 205. (d) Jayaraman, A.; Sharma, S. K.; Wang, S. Y.; Cheong, S.-W. *Current Sci.* **1996**, *71*, 306.

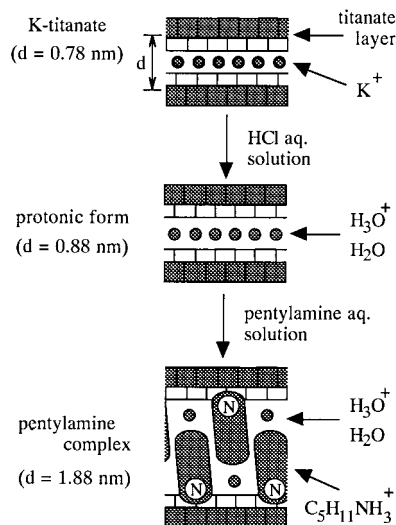
(11) (a) Izawa, H.; Kikkawa, S.; Koizumi, M. *J. Phys. Chem.* **1982**, *86*, 5023. (b) Clément P.; Marchand, R. *C. R. Acad. Sc. Paris Série II* **1983**, *296*, 1161. (c) Sasaki, T.; Watanabe, M.; Komatsu, Y.; Fujiki, Y. *Inorg. Chem.* **1985**, *24*, 2265. (d) Sasaki, T.; Komatsu, Y.; Fujiki, Y. *Chem. Mater.* **1992**, *4*, 894. (e) Sasaki, T.; Watanabe, M.; Michiue, Y.; Komatsu, Y.; Izumi, F.; Takenouchi, S. *Chem. Mater.* **1995**, *7*, 1001. (f) Sasaki, T.; Izumi, F.; Watanabe, M. *Chem. Mater.* **1996**, *8*, 777.

(12) Reid, A. F.; Mumme, W. G.; Wadsley, A. D. *Acta Crystallogr.* **1968**, *B24*, 1228.

Table 1. Crystallographic Data of Three Kinds of Lepidocrocite-Type Layered Titanate

titanate	lattice type	<i>a</i> (nm)	<i>b</i> (nm) ^a	<i>c</i> (nm)
K-titanate	<i>C</i>	0.3856(5)	1.560(2)	0.2975(5)
protonic form	<i>I</i>	0.3797(1)	1.758(1)	0.2994(1)
pentylamine complex	<i>C</i>	0.3825(1)	3.760(3)	0.2979(2)

^a Twice the basal spacing.

**Figure 2.** Synthesis process from K-titanate to protonic form and then pentylamine complex.

similar for the three titanate phases, indicating that host layers of $[\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4]^{0.8-}$ were kept unchanged during the guest exchange process ($\text{K}^+ \rightarrow \text{H}_3\text{O}^+ \rightarrow \text{C}_5\text{H}_{11}\text{NH}_3^+$), as illustrated in Figure 2. The pentylammonium ions, $\text{C}_5\text{H}_{11}\text{NH}_3^+$, are oriented nearly perpendicular to the host layer in the interlayer space to form an intermeshed (interdigitated) layer.¹⁴ This is suggested from a plot of interlayer spacings for a series of *n*-alkylamine complexes versus their chain length.¹⁵

The titanate was loaded into a gasketed diamond-anvil cell (DAC)¹⁶ with methanol, ethanol, or their mixture (methanol:ethanol = 4:1 vol) and compressed up to about 10 GPa. The alcohols behave as hydrostatic pressure-transmitting media, their hydrostatic limits being about 8.6, 2.0, and 10.4 GPa, respectively.¹⁷ It should be noted that these titanates do not take up the alcohol molecules at ambient pressure and temperature.¹⁸ Structural changes on compression were followed by in situ XRD measurements with graphite-monochromatized Mo K α radiation ($\lambda = 0.071069$ nm)

(13) Groult, D.; Mercey, C.; Raveau, B. *J. Solid State Chem.* **1980**, *32*, 289.

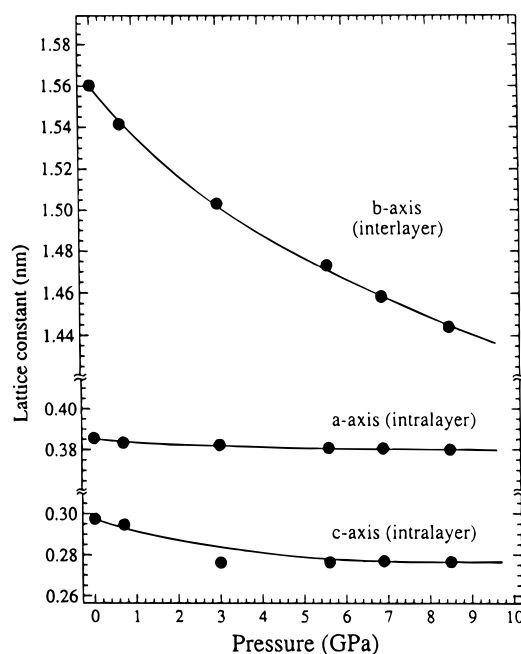
(14) The intermeshed layer model has already been mentioned about alkylamine dichalcogenide complex: Whittingham, M. S. in *Intercalation Chemistry*; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: London, 1982; p 2.

(15) The interlayer spacing as a function of the chain length of intercalated alkylamine displayed a linear relationship as described for a number of hosts (see ref 11b). The basal spacing increment per additional carbon atom suggested that the alkyl chains constituted the intermeshed layer which is oriented nearly perpendicular to the host layer.

(16) Takemura, K.; Shimomura, O.; Tsuji, K.; Minorura, S. *High Temperatures-High Pressures* **1979**, *11*, 311.

(17) Piermarini, G. J.; Block, S.; Barnett, J. D. *J. Appl. Phys.* **1973**, *44*, 5377.

(18) When these titanates were soaked in a methanol-ethanol mixture for 5 days, no change in the XRD patterns was observed.

**Figure 3.** Pressure dependence of the lattice parameters of K-titanate in a methanol medium.

in combination with an imaging plate detector. The pressure was determined from the fluorescence shift of small ruby crystals within the pressure chamber.¹⁹

The pressure dependence of the lattice parameters of the K-titanate in methanol medium is depicted in Figure 3. The *b*-axis noticeably decreased as compared with the *a*- and *c*-axes, which is compatible with the fact that the interlayer bonding is much weaker than the intralayer one. The protonic form gave a similar pressure dependence of the lattice parameters.

In contrast, the pentylamine complex in methanol revealed an abrupt change in the XRD patterns, as depicted in Figure 4. The $0k0$ basal reflections drastically shifted in a discontinuous fashion to lower angles at about 1 GPa, while only ordinary shrinkage was observed for the *a*- and *c*-axes. Figure 5 shows the pressure dependence of the interlayer spacing, which is half the *b*-axis. The pentylamine complex, as can be seen from the figure, underwent an interlayer expansion by about 0.27 nm (16%) at 1 GPa. In the pressure releasing process, the interlayer separation as well as the other lattice parameters reversed to the original values without a significant hysteresis.

The interlayer expansion of 0.27 nm is comparable to that in the case of intercalation of methanol into clay minerals.²¹ The present uniaxial expansion is most likely to be due to the intercalation of methanol molecules into interlayer spaces. To confirm this hypothesis, a similar experiment was carried out using ethanol

(19) Mao, H. K.; Bell, P. M.; Shaner, J. W.; Steinberg, D. J. *J. Appl. Phys.* **1978**, *49*, 3276.

(20) Two changes of the lattice type, *C*-lattice to *P*-lattice and *P*-lattice to *A*-lattice (*A*-base-centered lattice), were observed at about 1 and 2 GPa, respectively, besides the uniaxial expansion. These changes may be explained by the sliding of neighboring titanate layers by $a/2$ and then by $d/2$.

(21) It has been reported that single-layer intercalation of methanol or ethanol into clay minerals led to interlayer expansion by about 0.24–0.35 nm at atmospheric pressure. See, for example: (a) Brindley, G. W.; Ray, S. *Am. Miner.* **1964**, *49*, 106. (b) Carr, R. M.; Chih, H. *Clay Minerals* **1971**, *9*, 153. (c) Bauer, J. F.; Sclar, C. B. *Am. Miner.* **1985**, *70*, 362. (d) Ref. (6).

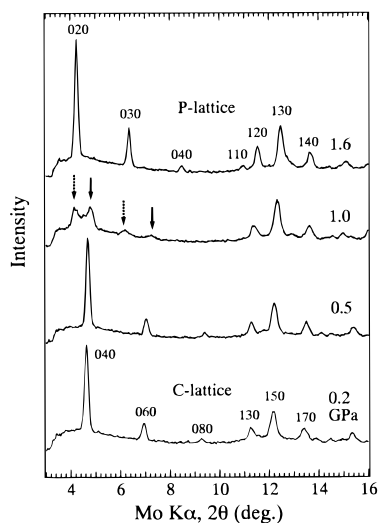


Figure 4. XRD patterns of pentylamine-titanate complex in a methanol medium in the course of compression. Each pattern was indexed as orthorhombic structure. *C*-lattice and *P*-lattice mean *C*-base-centered lattice and primitive one, respectively.²⁰ Two phases with a different degree of swelling coexisted at 1.0 GPa as designated by solid and dashed arrows.

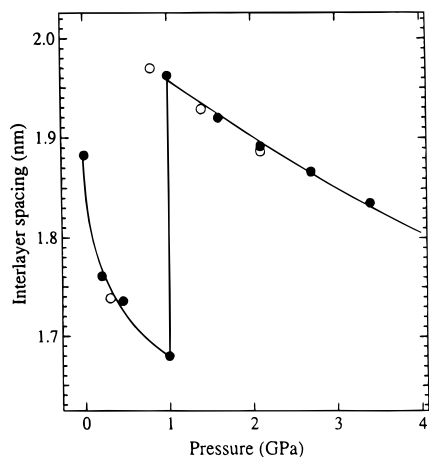


Figure 5. Pressure dependence of the interlayer spacing of pentylamine-titanate complex in a methanol medium. The closed and open circles denote the data in pressure-increasing and decreasing process, respectively.

instead of methanol. Again reversible swelling by 0.23 nm (14%) was observed at 2 GPa. The different expansion pressures between the two alcohol media strongly suggest that the swelling is not attributed to transformation of the complex or rearrangement of the interlayer pentylamine but to pressure-induced intercalation of alcohol molecules into the pentylamine complex.

Moreover, in the additional experiment using a methanol-ethanol mixture (4:1 by volume), the swelling occurred at 1 GPa, which coincides with the pressure observed when only methanol was used. The lattice parameters of the expanded titanate changed in a

manner very similar to the methanol case. This phenomenon can be reasonably understood by selective uptake of methanol molecules at 1 GPa and no incorporation of ethanol molecules into a resulting methanol-intercalated phase even at higher pressures.

The larger molecular size of ethanol may be responsible for the higher intercalation pressure than methanol. Similar basal spacings of the intercalated products suggest parallel orientation of the intercalated alcohols to the host layer.

In another experiment, Nujol was used as a pressure medium instead of the alcohols. In this case no swelling of the pentylamine complex was observed up to 3.4 GPa. This fact also supports that the expansion is not due to a transformation of the complex but to the intercalation which is affected by guest size.²²

Furthermore, the medium dependence excludes the possibility for the insertion of water molecules as a possible impurity in the media, which has actually been observed for defected pyrochlore.²

As the alcohol-intercalated complex is unquenchable, the molar amount of the intercalated alcohol molecules cannot be determined by chemical analysis. However, it can be estimated from the increase in interlayer volume of the complex. The unit cell volume expands by about 0.0615 nm³ in methanol at 1 GPa and 0.0524 nm³ in ethanol at 2 GPa. Assuming that the densities of the alcohols in the interlayer are close to those of liquid alcohols²³ at a given pressure, the volume expansion corresponds to 0.6 mol of methanol and 0.4 mol of ethanol, respectively, per formula weight of the pentylamine complex, (C₅H₁₁NH₃)_{0.5}H_{0.3}Ni_{0.4}Ti_{1.6}O₄·*n*H₂O. These uptakes are comparable to the molar amount of the interlayer pentylammonium ion C₅H₁₁NH₃⁺ in the complex (0.5 mol). The incorporation of alcohol molecules can be expected to depend on the content and spatial arrangement of the pentylammonium ions. Some particular interactions may exist between alcohol molecules and pentylammonium ions.

In summary, lepidocrocite-type titanates containing different kinds of guests were compressed in a pressure-transmitting medium of methanol and ethanol up to about 10 GPa by means of a DAC. In situ X-ray diffraction measurements indicated an abrupt and reversible interlayer expansion of pentylamine-titanate complex, suggesting a novel pressure-induced intercalation of alcohol molecules into the interlayer gallery. The uniaxial expansion which occurred in methanol at 1 GPa reached to 16% (0.27 nm) and that in ethanol at 2 GPa to 14% (0.23 nm). In both cases, the molar amounts of the intercalated alcohol molecules were estimated to be comparable to those of pentylammonium ions in the complex on the basis of the volume expansion. This suggests the existence of an interaction between alcohol molecules and pentylammonium ions.

Acknowledgment. The authors are very grateful to Dr. H. Yusa for technical support with the DAC, and Dr. H. Fujihisa for offering the analysis program for XRD patterns.

CM980273H

(22) Nujol consists of fluid hydrocarbons C_{*n*}H_{2*n*+2} (5 ≤ *n* ≤ 15), whose alkyl chain lengths are larger than methanol and ethanol.

(23) (a) Brown, J. M.; Slutsky, L. J.; Nelson, K. A.; Cheng, L.-T. *Science* **1988**, *241*, 65. (b) Bridgman, P. W. In *International Critical Tables*; McGraw-Hill: New York, 1928; Vol. 3, p 41.