



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Version of record first published: 27 Oct 2006

To cite this article: Wenfeng Shangguan & Akira Yoshida (2000): Modification of the Interlayer in HTiNbO₅ and its Physicochemical Characterization, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 219-224

To link to this article: <http://dx.doi.org/10.1080/10587250008026143>

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Modification of the Interlayer in HTiNbO₅ and its Physicochemical Characterization

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(In final form July 5, 1999)

A layered titanoniobate, in which the interlayer of the metal oxide based on octahedral framework is pillared with silica, has been prepared from HTiNbO₅ by employing alkylamines (C_nH_{2n+1}NH₂, n = 4, 6, 8, 10) and tetraethylorthosilicate as interlayer exchange guests and a pillar precursor, respectively. The incorporated amine had bilayer arrangements in the interlayer space and their ammonium head groups pointed to the host (TiNbO₅) layers. While the basal spacing of the compounds increased with the chain length of alkylamine, the inclination angle also increased. The intercalated structure facilitated the incorporation of tetraethylorthosilicate into the interlayers, and silica-pillared layered titanoniobate was obtained after calcination. The physicochemical properties of the resultant pillared compounds were characterized on the interlayer microstructure, nitrogen adsorption and UV-VIS absorption spectra.

Keywords: layered compound; titanoniobate; intercalation; pillaring

INTRODUCTION

There has been intense research activity in the synthesis and characterization of layered metal oxides due to the properties of ion exchange and intercalation^[1-6]. A novel class of porous materials can be prepared from proton-exchanged layered compounds by pillaring method, such as alumina-pillared layered H₂Ti₃O₇^[4], silica-pillared H₂Ti₄O₉^[5] and HLaNb₂O₇^[6]. This kind of layered porous materials is expected to be applied as photocatalysts^[7-9]. Since Wadsley^[10] first prepared potassium titanoniobate KTiNbO₅ and found that it

was layered structure, its ion-exchange properties and intercalation reactions had been widely studied^[11-15]. We have reported in communication^[16] the preparation of silica-pillared layered titanoniobate. We describe here the intercalation and pillaring processes of HTiNbO₅ using various alkylamines (C_nH_{2n+1}NH₂) with different number of carbon (NC = 4, 6, 8, 10) and tetraethylorthosilicate (TEOS), and some physicochemical characterizations are presented for the amine-intercalated and silica-pillared titanoniobate.

EXPERIMENTAL

The starting material of KTiNbO₅, which was prepared by heating a mixture of K₂CO₃, TiO₂, and Nb₂O₅ at 1060 °C in air, was converted to HTiNbO₅ in 6 N HNO₃ solution at room temperature. Intercalations were carried out by adding HTiNbO₅ into alkylamines - ethanol solution and stirring at room temperature for one week. Obtained amine-intercalated titanoniobate was then added to TEOS solution, and stirred for 7 days at *ca.* 85 °C. After reaction, the product was separated, washed, dried, and then finally calcined at 500 °C.

X-ray powder diffraction pattern was taken by using a diffractometer with Cu-K α radiation (Rigaku Geigerflex). The thermogravimetric and differential thermal analysis (TG-DTA) were performed using a thermal analysis system (Rigaku TAS-200). Nitrogen adsorption (Autosorb-1, Yuasa Aionikusu), transmission electron microscopy (TEM, JEOL JEM-200CX microscope) and UV-VIS diffuse reflectance (Jasco V-550) were also employed in the study.

RESULTS AND DISCUSSION

KTiNbO₅ has a layer structure and orthorhombic symmetry, in which MO₆ (M = Ti, Nb) octahedra are linked in the *b*-direction to form the layers with the potassium ions in the interlayer spaces^[10]. After treatment with HNO₃, it was changed into HTiNbO₅, which was with no interlayer water and did not swell in water. The expansion in *c*-direction due to intercalation reaction with alkylamine facilitated TEOS to incorporate into the interlayers as pillars. Fig. 1 shows the influence of the chain length of an alkylamine intercalated into the interlayers on the lattice parameter (*c* value) of the intercalated, together with the *c* value of silica-pillared compounds without and with calcination at 500 °C. It can be found that the *c*-lattice parameters of the amine-intercalated compounds are remarkably depended on the sort of alkylamine, increasing with NC. After TEOS incorporates into the interlayers, the *c* values decrease by 7~14% compared to those of the originals, which indicates that the pillars

propping up the TiNbO₅ layers are not TEOS, but still alkylamine chains (also see below). The *c* value of silica-pillared compounds remains almost constant (*ca.* 26 Å) expect for that from NC = 4 (*ca.* 20 Å) after calcination in 500 °C, being larger than that of HTiNbO₅ (16.75 Å). Meanwhile, the results of TG-DTA measurement showed that the decomposition and exhaustion of the interlayer organic matter finished around 500 °C. Thus, it is demonstrated that TEOS has incorporated into the interlayers, and silica clusters were formed to act as pillars propping up the Ti(Nb) - O layers after calcination. TEM observation revealed that the silica-pillared layered structure was clearly visible.

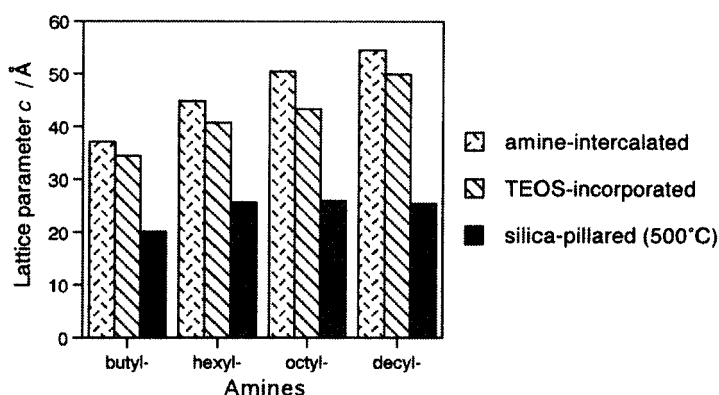


FIGURE 1 Influence of various amine-intercalations on the interlayer distances of the amine-intercalated and silica-pillared HTiNbO₅ compounds.

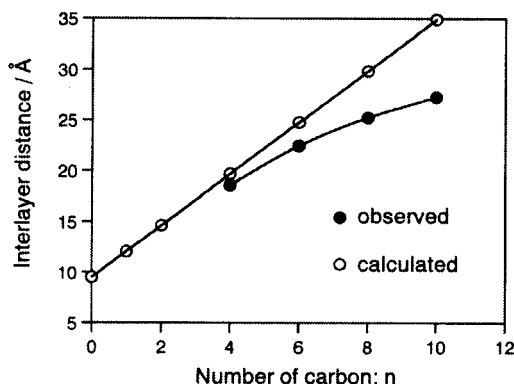


FIGURE 2 Evolution of the interlayer distance of the amine-intercalated compounds as a function of the meanlength of the NC_n chain.

As already known, the half of the *c*-lattice parameter of HTiNbO₅ corresponds to the basic interlayer distance. Kikkawa *et al.*^[15] had reported the interlayer distance of HTiNbO₅ intercalated with methyl-, ethyl-, propyl- and butylamine (C_nH_{2n+1}NH₂, *n* = 1 ~ 4), indicating that the distance almost linearly increases with the numbers of carbon. It is proposed that the intercalated amines form a double layer with the ammonium head groups pointing to the host (TiNbO₅⁻) layers. Thus, the interlayer distance (*d*) of the compounds intercalated with the alkylamines can be estimated by

$$d = d_N + 2 n L \quad (1)$$

in which *d_N* is the interlayer distance of NH₄TiNbO₅ (9.51 Å^[15]), *n* is the NC for the intercalated amines C_nH_{2n+1}NH₂, and *L* is the increase in the length of chain per carbon (1.27 Å). Plotting the interlayer distance against NC, thus, a linearly relationship is observed (Fig. 2). However, the relation between NC and the interlayer distance obtained in the present work does not fit with Eq. (1), but shows a curve. It is also noted that the obtained interlayer distance for NC = 4 (18.57 Å) is very close to that reported by Kikkawa *et al.* (18.41 Å). The fact suggests that the intercalated amine chains are may be ranked on a slant in this study (Fig. 3b). The inclination angle of the chains to the perpendicular of the basal layer can be given by the following formula:

$$\theta = \cos^{-1}(d_0/d_c) \quad (2)$$

where *d₀* is the interlayer distance derived from XRD measurement, and *d_c* is that calculated on Eq. (1). The inclination angles increase with the length of amine chains intercalated, being 19°, 25°, 32° and 39° for NC = 4, 6, 8 and 10, respectively.

Based on the model of schematic structure, it is speculated that in the case of TEOS-incorporation, the pillars propping up the TiNbO₅⁻ layer are still the amine chains, and TEOS is merely packed in the interlayer space. The incorporated TEOS gives rise to disordered arrangement of the alkylamine chains in the interlayers, and increase in inclination angle, thereby the interlayer distance decreases (Fig. 3c).

The observation of UV-VIS spectra showed in Fig. 4 indicates that the pillared titanoniobate had an absorption ranging into longer wavelength region compared to those of KTiNbO₅ and HTiNbO₅. Taking into account the spectrum behavior of the SiO₂ powder prepared from TEOS by sol-gel process showed in Fig. 4(e), the effect of free SiO₂ and carbon remainder could be excluded. Thus, the absorption shift might be attributed to (a) formation of a small amount of TiO₂ due to calcination and decomposition, or/and (b) pillared structural effect.

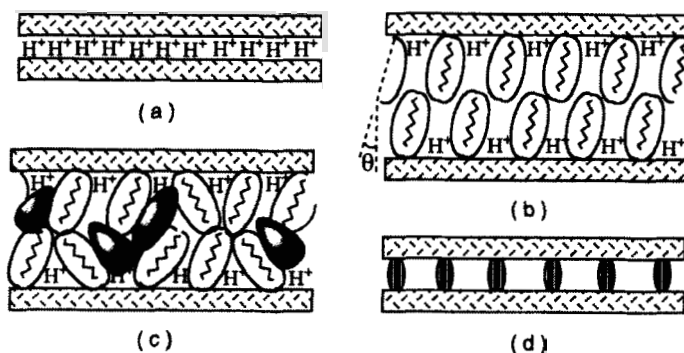


FIGURE 3 Proposed model for the interlayer microstructure of the titanoniobate compound. (a) layer HTiNbO₅; (b) amine-intercalated; (c) TEOS-incorporated; (d) calcined at 500 °C to form a silica-pillared compound.

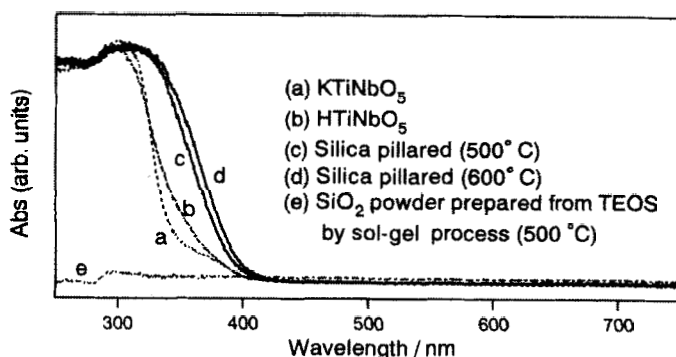


FIGURE 4 UV-VIS reflection spectra of some compounds.

Table 1 summarizes the unit cell parameters, BET surface area and the SiO₂ content for the silica-pillared compounds calcined at 500 °C for 2 h, together with KTiNbO₅ and HTiNbO₅. It is clearly found that the incorporation of silica into interlayers produced an interlayer gallery in the *c*-direction and enhanced the surface area. It is also noticeable that the BET surface area is rather lower than that of silica-pillared perovskite Ca - Nb oxide (239 m²·g⁻¹)^[17] prepared through the similar process. It seems that the structural property of the pillared compound is depended not only on the processes for intercalation and pillaring, but also on the nature of original host, such as geometrical construction and electric charge in interlayers.

TABLE 1 Properties of the obtained titanoniobate compounds

Compounds*	Unit cell parameters / Å			Surface area / m ² ·g ⁻¹	SiO ₂ / %
	<i>a</i>	<i>b</i>	<i>c</i>		
KTiNbO ₅	6.41	3.78	18.12	1.8	/
HTiNbO ₅	6.51	3.77	16.75	2.3	/
SiO ₂ (b) -TiNbO ₅	6.46	3.80	20.09	11.4	11.5
SiO ₂ (h) -TiNbO ₅	6.45	3.80	25.62	7.8	14.3
SiO ₂ (o) -TiNbO ₅	6.42	3.81	25.92	9.8	10.7
SiO ₂ (d) -TiNbO ₅	6.40	3.81	25.40	32.0	15.9

* SiO₂ (A) -TiNbO₅: the silica-pillared compound prepared from alkylamine-intercalated layered titanoniobate. The letter of an alphabet in parentheses presents the kind of alkylamine; b: butylamine, h: hexylamine, o: octylamine, d: decylamine. The silica-pillared compounds were calcined at 500 °C for 2 h.

References

- [1] H. Izawa, S. Kikkawa and M. Koizumi, *J. Phys. Chem.*, **86**, 5023 (1982).
- [2] T. Nakato, H. Miyata and K. Kuroda, *Reactivity of Solids*, **6**, 231 (1988).
- [3] S. Takahashi, T. Nakano, S. Hayashi, Y. Sugahara and K. Kuroda, *Inorg. Chem.*, **34**, 5065 (1995).
- [4] M.W. Anderson and J. Klinowski, *Inorg. Chem.*, **29**, 3260 (1990).
- [5] W. Hou, Q. Yan and X. Fu, *Chem. Commun.*, 1371 (1994).
- [6] C. Guo, W. Hou, M. Gou, Q. Yan and Y. Chen, *Chem. Commun.*, 801 (1997).
- [7] T. Sato, Y. Yamamoto, Y. Fujishiro and S. Uchida, *J. Chem. Soc., Faraday Trans.*, **92**, 5089 (1996).
- [8] T. Matsuda, M. Udagawa and I. Kunou, *J. Catal.*, **168**, 26 (1997).
- [9] A. Kudo and H. Kato, *Chem. Lett.*, **867** (1997).
- [10] A.D. Wadsley, *Acta Cryst.*, **17**, 623 (1964).
- [11] H. Rebbah, G. Desgardin and B. Raveau, *Mat. Res. Bull.*, **14**, 1125 (1979).
- [12] H. Rebbah, M. Borel, M. Bernard and B. Raveau, *Rev. Chim. Miner.*, **18**, 109 (1981).
- [13] A. Grandin, M. Borel and B. Raveau, *Rev. Chim. Miner.*, **24**, 351 (1987).
- [14] T. Nakato, H. Miyata, K. Kuroda and C. Kato, *Reactivity of Solids*, **6**, 231 (1988).
- [15] S. Kikkawa and M. Koizumi, *Mat. res. Bull.*, **15**, 533 (1980).
- [16] W. Shangguan, K. Inoue and A. Yoshida, *Chem. Commun.*, 779 (1998).
- [17] W. Shangguan and A. Yoshida, *J. Mat. Sci. Lett.*, **18**, 381 (1999).