

Intercalation of substituted alkylammonium ions into layered potassium niobate $K_4Nb_6O_{17}$

S. YAKABE

PRESTO, Japan Science and Technology Corporation, 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan

T. NAKATO*[†]

PRESTO, Japan Science and Technology Corporation, 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan; Laboratory of Environmentally Benign Materials Chemistry, Faculty of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8 Saiwaicho, Fuchu-shi, Tokyo 183-8509, Japan
E-mail: tnakat@cc.tuat.ac.jp

Substituted alkylammonium ions (protonated hydroxy amine and diamine) were intercalated into layered niobate $K_4Nb_6O_{17}$ in order to introduce functional substituents into the interlayer spaces of the niobate. In the case of reaction with 3-hydroxypropylammonium ion, the intercalation compound incorporated the ammonium ions in a bilayer arrangement, by which the hydroxyl substituents were located in the middle of the interlayer spaces to form intermolecular hydrogen bonding. For the intercalation compounds with alkyldiammonium ions, the intercalated alkyldiammonium ions were present in monolayer and oriented transversally with respect to the niobate layers. © 2003 Kluwer Academic Publishers

1. Introduction

$K_4Nb_6O_{17}$ is a layered material possessing photoactivity, exemplified by efficient photocatalysis for water splitting [1, 2], and intercalating capability [3]. Its structure is made up of the $[Nb_6O_{17}]^{4-}$ layers constructed by corner- and edge-shared NbO_6 octahedra and the interlayer K^+ ions. The layered structure is characterized by two structurally distinguishable interlayer spaces, referred as interlayers I and II, which are alternately located between the $[Nb_6O_{17}]^{4-}$ layers [4]. Because of its peculiar layered structure and photoactivity, intercalation reaction of $K_4Nb_6O_{17}$ has attracted attention as a potential method for constructing novel nanomaterials exhibiting advanced photofunctions. Since the two interlayer spaces exhibit different intercalating reactivity [5, 6], nanostructure of the intercalated materials may be controlled more precisely than the samples obtained from other usual layered niobates.

$K_4Nb_6O_{17}$ forms intercalation compounds with various inorganic and organic cationic species through exchange of the interlayer K^+ ions [3, 5–12]. Among various cationic species, intercalation of alkylammonium ions has been investigated well from both the fundamental and applicative points of view [3, 6]; for example the alkylammonium-intercalated niobates have often been utilized for preparing intercalation compounds of $K_4Nb_6O_{17}$ with photofunctional species through dis-

placement of the pre-intercalated alkylammonium ions [6–8]. Studies using spectroscopic probe molecules co-intercalated with alkylammonium ions have shown that incorporation of alkylammonium species change the interlayer microenvironment of the layered niobate [8]. Intercalation of organic species with various functional moieties into $K_4Nb_6O_{17}$ is of interest because they may alter the interlayer microenvironments to those not achievable with alkylammonium ions.

In this study, we carried out intercalation of substituted alkylammonium ions into $K_4Nb_6O_{17}$. We used organoammonium species substituted by hydroxyl and additional ammonium groups as the reactants, and the products were characterized by powder X-ray diffraction (XRD), infrared spectroscopy (IR), and elemental analyses. The intercalation reactions are recognized as the first step of modifying the interlayer microenvironment of $K_4Nb_6O_{17}$ with the substituents, which may interact with extra molecules through, for example, hydrogen bonding to entrain them.

2. Experimental

$K_4Nb_6O_{17} \cdot 3H_2O$ was prepared by mixing K_2CO_3 and Nb_2O_5 (obtained from Wako Pure Chemical Ltd.) in a molar ratio of 2.1:3.0 and subsequent heating at 1100°C for 10 h in air, according to the method of Nassau *et al.*

*Author to whom all correspondence should be addressed.

[†] Current address: Graduate School of Bio-Applications and Systems Engineering (BASE), Tokyo University of Agriculture and Technology, 2-24-16, Naka-cho, Koganei-shi, Tokyo 184-8588, Japan.

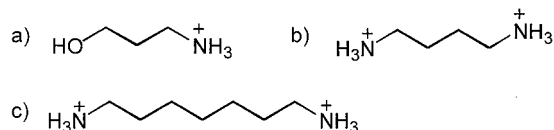


Figure 1 Substituted ammonium ions used in the present study: (a) 3-hydroxypropylammonium ion, (b) butyldiammonium ion, and (c) hexyldiammonium ion.

[13], and was confirmed by XRD. Hydrochloride salts of 3-amino-1-propanol (PAOH), butyldiamine (BDA), and hexyldiamine (HDA) (purchased from Tokyo Kasei Co.) were used as received. Structural formulae of the substituted alkylammonium ions are shown in Fig. 1.

Reactions of $K_4Nb_6O_{17} \cdot 3H_2O$ with the substituted alkylammonium ions were carried out by the procedure similar to that utilized for preparing intercalation compounds of the niobate with alkylammonium ions [3, 6]. $K_4Nb_6O_{17} \cdot 3H_2O$ was allowed to react with an aqueous solution of the organoammonium chloride at room temperature or $120^\circ C$ for 1 day or 2 weeks. Reactions at $120^\circ C$ were conducted by using a Teflon-lined autoclave (Taiatsu Techno Co.) under an autogenous pressure. Amount of the organoammonium ions added was 10 times (in mole) that of K^+ ions included in $K_4Nb_6O_{17}$. The solid product was separated by centrifugation, washed with water, and then dried under ambient conditions.

XRD patterns of the samples were measured by a MAC Science MX Labo diffractometer (monochromated Cu K_α radiation). IR spectra were recorded on a Jasco Valor-III spectrometer (KBr disk technique). Compositions of the samples were estimated from the data of X-ray fluorescence spectroscopy (XRF, Rigaku RIX-3000), thermogravimetry (TG, Seiko Instruments TG/DTA 6300 analyzer) and CHN analysis.

3. Results and discussion

Owing to the peculiar layered structure of $K_4Nb_6O_{17}$, two types of intercalation compounds can form through cation exchange of the niobate. One is the sample where the guest molecules are located in every other interlayer spaces, and the other contains the guest in all the interlayers. We designate the former and latter types of intercalation compounds as A- and B-type, respectively, as described in our previous paper [6]. We can judge the type of intercalation compounds mainly from the XRD data. The expansion of the basal spacing on intercalation (Δd -value) is estimated by subtracting the basal spacing of anhydrous $K_4Nb_6O_{17}$ from that of the intercalation compound, and the d_{020} -value (1.66 nm) and d_{040} -value (0.83 nm) [14] are used as the basal spacings of pristine $K_4Nb_6O_{17}$ for A- and B-type of intercalation compounds, respectively. Fig. 2 schematically indicates the two types of intercalation compounds and estimation of their Δd -values.

The reaction of $K_4Nb_6O_{17} \cdot 3H_2O$ with PAOH under moderate conditions (room temperature, 1 day) yielded an intercalation compound, which was evidenced by the XRD and IR measurements. Fig. 3a and b compares the XRD patterns of $K_4Nb_6O_{17} \cdot 3H_2O$ before and after the reaction with PAOH. The reaction prod-

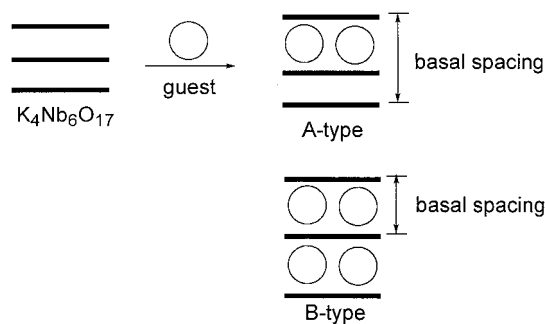


Figure 2 Schematic representation of the two possible types of intercalation compound given by $K_4Nb_6O_{17}$.

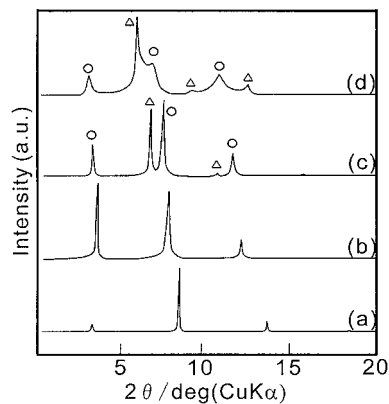


Figure 3 XRD patterns of (a) $K_4Nb_6O_{17} \cdot 3H_2O$, (b) PAOH- $K_xNb_6O_{17}$ intercalation compound, (c) BDA- $K_xNb_6O_{17}$ intercalation compound, and (d) HDA- $K_xNb_6O_{17}$ intercalation compound. Circles represent the X_{BDA} - (in trace (c)) and X_{HDA} - (in trace (d)) phases. Triangles indicate the Y_{BDA} - (in trace (c)) and Y_{HDA} - (in trace (d)) phases.

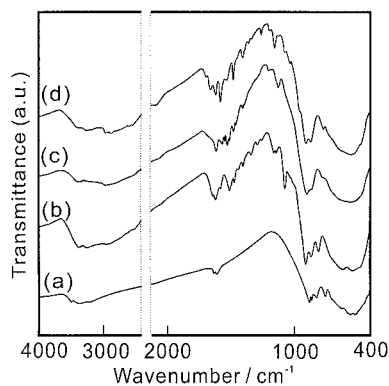


Figure 4 IR spectra of (a) $K_4Nb_6O_{17} \cdot 3H_2O$, (b) PAOH- $K_xNb_6O_{17}$ intercalation compound, (c) BDA- $K_xNb_6O_{17}$ intercalation compound, and (d) HDA- $K_xNb_6O_{17}$ intercalation compound.

uct gives the most intense diffraction peak accompanied by higher-order peaks at $d = 2.16$ nm ($2\theta = 4.13^\circ$), and this d -value is larger than the d_{020} -value (1.85 nm), corresponding to the sum of the spacings of interlayers I and II, of $K_4Nb_6O_{17} \cdot 3H_2O$. IR spectrum of the product shown in Fig. 4b exhibits adsorption bands due to both the alcohol (3395 cm^{-1} , $\nu_s(O-H)$; 1394 cm^{-1} , $\delta_s(O-H)$; 1068 cm^{-1} , $\nu_s(C-H)$) and ammonium (1611 cm^{-1} , $\delta_{as}(N-H)$; 1506 cm^{-1} , $\delta_s(N-H)$) moieties, and the adsorption bands appear at the same positions as those due to the hydrochloride salt of PAOH with the same profiles. This result confirms the formation of PAOH- $K_xNb_6O_{17}$ intercalation compound.

The XRD profile of the reaction product is similar to those observed for the A-type intercalation compounds of $K_4Nb_6O_{17}$ with organic cations such as methylviologen [7] and tris(2,2'-bipyridine)metal complexes [6]. The Δd -value is estimated as 0.50 nm by assuming that the guest species is accommodated in every other interlayer spaces to form the A-type sample. Since the Δd -value of the A-type butylammonium- $K_xNb_6O_{17}$ intercalation compound has been reported to be 0.74 nm [6], the present Δd -value rationalizes the formation of A-type intercalation compound. PAOH molecules would be arranged in an inclined bilayer within the interlayer space, as assumed for the intercalated butylammonium ions. The composition of the PAOH- $K_xNb_6O_{17}$ intercalation compound was determined by using XRF, CHN and TG analyses. Molar ratio of $K:C_3H_6(OH)NH_3:Nb$ was 1.8:1.5:6.0. The result supports the assumption that PAOH- $K_xNb_6O_{17}$ is an A-type intercalation compound because the $C_3H_6(OH)NH_3^+/Nb$ atomic ratio was smaller than 2.0/6.0.

IR spectrum of the PAOH- $K_xNb_6O_{17}$ intercalation compound gives further information about this sample. Profile and position of the broad alcoholic O-H band (3395 cm^{-1}) of PAOH- $K_xNb_6O_{17}$ intercalation compound are the same as those of 3-amino-1-propanol hydrochloride, as mentioned above. This fact indicates the presence of intermolecular interactions among the hydroxy groups of intercalated PAOH molecules as in the case of crystalline hydrochloride salt of PAOH. Taking into account the bilayer arrangement of the intercalated PAOH molecules, we suppose that the terminal ammonium groups interact to niobate layers similarly to alkylammonium-intercalated $K_4Nb_6O_{17}$ [3]. Thus the hydroxyl groups would be located in the middle of interlayer spaces to interact adjacent PAOH molecules which are electrostatically bound to the niobate layers present at both sides of the interlayer region. The intercalated PAOH molecules may be utilized to entrain extra molecules through hydrogen bonding of the alcoholic -OH groups.

We note that reactions of $K_4Nb_6O_{17}$ with PAOH under more severe conditions, e.g., at 120°C for 2 weeks gave the same A-type intercalation compound, whereas previous studies of direct reactions of $K_4Nb_6O_{17}$ with monovalent cations have been reported [5] to produce B-type intercalation compounds finally. The present study shows that K^+ ions in interlayer II, whose reactivity is lower than that of interlayer I, are not exchanged for PAOH. Since steric effect of PAOH molecule should not be large, we assume that alcoholic -OH groups would affect the relatively low reactivity of cation exchange; partial dissociation of the -OH groups would give the ionic strength of the PAOH cations weaker than that of alkylammonium cations to prevent the exchange for K^+ ions in interlayer II.

Reactions of $K_4Nb_6O_{17}$ with alkyldiammonium ions, i.e., BDA and HDA, at 120°C for 2 weeks yielded double-phase mixtures as the products, but analytical data strongly suggested intercalation of these organic species. XRD patterns of the reaction products with BDA and HDA, shown in Fig. 3c and d, indicate coexis-

tence of two phases in the samples. For the product with BDA, one phase is represented by the diffraction peak at $d = 2.22\text{ nm}$ ($2\theta = 3.97^\circ$) accompanied by intense higher order peaks, and the other phase is indicated by a small peak at $d = 1.24\text{ nm}$ ($2\theta = 7.16^\circ$). We designate the former and latter phases as X_{BDA} - and Y_{BDA} -phases, respectively. For the sample obtained with HDA, two series of the diffraction peaks are observed; one is given by the first-order peak at $d = 2.36\text{ nm}$ ($2\theta = 3.69^\circ$) and the other is shown by the intense first-order peak at $d = 1.39\text{ nm}$ ($2\theta = 6.36^\circ$); the former and latter phases will be named X_{HDA} - and Y_{HDA} -phases, respectively. Basal spacings larger than 2.1 nm (for A-type intercalate) and 1.2 nm (for B-type sample) are possible for intercalation of the alkyldiammonium ions, because previous studies [15–20] concerning intercalation of alkyldiammonium ions into inorganic layered compounds have indicated Δd -values of 0.38–0.63 nm and 0.60–0.74 nm for BDA and HDA ions, respectively. The IR spectra of both the products clearly exhibited adsorption bands due to the corresponding alkyldiammonium ions (e.g., 1600 cm^{-1} , $\delta_{as}(N-H)$; 1500 cm^{-1} , $\delta_s(N-H)$). Thus, our products should contain intercalation compounds of $K_4Nb_6O_{17}$ with the alkyldiammonium ions.

We suppose that all the phases obtained by the reactions with BDA and HDA should correspond to intercalation compounds of the niobate with the alkyldiammonium ions; the hydrothermal treatment of $K_4Nb_6O_{17}$ at 120°C for 2 weeks without the alkyldiammonium ions yielded the sample whose XRD pattern was identical to that of $K_4Nb_6O_{17}\cdot 3H_2O$. We assign the X_{BDA} - and X_{HDA} -phases to B-type intercalation compounds with the alkyldiammonium ions, and Y_{BDA} - and Y_{HDA} -phases to A-type intercalation compounds. The Δd -values are estimated as 0.56, 0.70, 0.41 and 0.56 nm for the X_{BDA} -, X_{HDA} -, Y_{BDA} -, and Y_{HDA} -phases, respectively, based on this assumption. Difference in the Δd values of X_{BDA} - and X_{HDA} -phases (0.14 nm) is comparable to that between the Y_{BDA} - and Y_{HDA} -phases (0.15 nm). This estimation suggests that addition of a carbon atom to the alkyl chain of alkyldiammonium ions gives the same increment of the basal spacings of the X- and Y-phases, i.e., A- and B-type intercalation compounds, which is in harmony with our assignment of the XRD patterns.

Other analytical techniques give additional information about the interlayer microenvironment of the alkyldiammonium-intercalated niobates. The IR spectra of the intercalation compounds of $K_4Nb_6O_{17}$ with BDA and HDA exhibit absorption bands characteristic not to the $-NH_2$ group but to $-NH_3^+$ group, indicating both terminal nitrogen moieties are present in the cationic form to contribute to compensation of the negative charges given by the $[Nb_6O_{17}]^{4-}$ layers. This fact suggests a transversal monolayer orientation of the intercalated alkyldiammonium ions as observed for the previously reported intercalation compounds of layered niobates with alkyldiammonium ions [15–17]. Composition of the BDA- and HDA-intercalated samples estimated by XRF and TG analyses were $K:(H_3NC_4H_8NH_3):Nb = 0.9:1.1:6.0$ and $K:(H_3NC_6H_{12}NH_3):Nb = 1.4:1.1:6.0$. If the ion

exchange occurred only in interlayer I, the K^+/Nb atomic ratio would be larger than 2.0/6.0 and the diammonium/Nb ratio would be smaller than 1.0/6.0. Our result suggests that the ion exchange reactions occurred in both the interlayers, being in harmony with the deduction from the XRD results. Consequently we conclude that these products with alkyldiammonium ions are mixtures of A-type and B-type intercalation compounds.

The interlayer structure of the alkyldiammonium- $K_xNb_6O_{17}$ intercalation compounds is different from alkylammonium-intercalated $K_4Nb_6O_{17}$; the transversal monolayer of the alkyldiammonium ions can be regarded as "organic pillars" electrostatically bound to the niobate layers. The transversal arrangement of the alkyldiammonium species will provide the interlayer environment which is "more strict" than that of the usual alkylammonium- $K_4Nb_6O_{17}$ intercalation compound. Such interlayer regions would exhibit unusual property of, for example, adsorbing extra molecules.

In conclusion, some substituted alkylammonium ions (protonated hydroxy amine and diamine) were intercalated into $K_4Nb_6O_{17}$ by conventional solid-liquid reactions. The interlayer structure of the intercalation compounds was different from alkylammonium-intercalated $K_4Nb_6O_{17}$. With regard to intercalation of PAOH into $K_4Nb_6O_{17}$, the hydroxyl groups of PAOH molecules were present in the center of the interlayer space, and intermolecular hydrogen bonding formed among the organoammonium ions. When alkyldiammonium ions were used as guest, the products were mixture of A-type and B-type intercalation compounds. The alkyldiammonium ions are arranged in a transversal monolayer with respect to the niobate layers.

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