Intercalation Behavior of *n*-Alkylamines into a Protonated Form of a Layered Perovskite Derived from Aurivillius Phase Bi$_2$SrTa$_2$O$_9$

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Intercalation behavior of *n*-alkylamines into a protonated form of a layered perovskite, H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$], derived from an Aurivillius phase, Bi$_2$SrTa$_2$O$_9$, has been investigated. H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] can accommodate *n*-alkylamines (C$_m$H$_{m+1}$NH$_2$; m = 4, 8, 12, 18) to form intercalation compounds via an acid−base mechanism. The interlayer distance increases to 2.071(2) (m = 4), 2.840(9) (m = 8), 3.83(1) (m = 12), and 5.17(2) (m = 18) nm. In contrast, H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] does not form any intercalation compound with pyridine, which is a weaker base, indicating that the protons in H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] are weakly acidic. The IR spectra of the intercalation compounds with *n*-alkylamines (m = 12 and 18) clearly show that *n*-alkyl chains possess an all-trans conformation. A linear relationship is observed between the interlayer distance and the number of carbon atoms in *n*-alkyl chains, and this corresponds to a bilayer arrangement of the *n*-alkyl chains with a tilt angle of 60°. Despite the relatively high proton content (1.8 H$^+$ per [Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$]), only 0.9−1.0 mol of *n*-alkylamines per [Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] is intercalated. This observation can be reasonably interpreted based on the surface geometry of the perovskite-like slab and the size of *n*-alkylamines.

Introduction

It is well-known that various layered compounds accommodate organic ions and molecules to form intercalation compounds.[1−3] The reaction mechanisms include ion exchange, ion−dipole interaction, hydrogen bonding, redox reactions, and acid−base reactions. The acid−base reactions are involved in intercalation chemistry for protonated forms of various layered transition metal oxides,[4] such as layered titanates,[5] titanoniobate,[6,7] and niobates.[8]

Ion-exchangeable layered perovskites consist of perovskite-like slabs terminated along the (100) plane of 3D perovskites and interlayer cations. These are classified into two groups, Dion−Jacobson phases (M[A$_{n−1}$B$_n$O$_{3n+1}$]) and Ruddlesden−Popper phases (M$_2$[A$_{n−1}$B$_n$O$_{3n+1}$]).[9−12] Both of these phases can be converted into their protonated forms (H[A$_{n−1}$B$_n$O$_{3n+1}$]

and H$_2$[A$_{n−1}$B$_n$O$_{3n+1}$]) by acid treatment.[10,13−18] The protonated forms of the Dion−Jacobson phases can accommodate *n*-alkylamine in their interlayer spaces via the acid−base mechanism.[10,14,15,19−24] In contrast, a protonated form of a Ruddlesden−Popper phase, H$_2$La$_2$Ti$_3$O$_{10}$, did not accommodate *n*-alkylamines.[22] This difference was ascribed to the displacement in layer stacking by (a + b)/2 in H$_2$La$_2$Ti$_3$O$_{10}$. Schaak et al.[25] recently reported the partial intercalation of *n*-dodecylamine into H$_2$CaNaTa$_3$O$_{10}$ in heptane, and to the

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best of our knowledge this is the only report on the intercalation behavior of the protonated forms derived from the Ruddlesden−Popper phases via the acid−base mechanism.

Aurivillius phases (Bi$_2$A$_{n-1}$B$_n$O$_{3n+3}$), another series of layered perovskites, consist of perovskite-like slabs and bismuth−oxide sheets.[26−29] We have reported that acid treatment of the Aurivillius phases resulted in the formation of the protonated forms of layered perovskites; so far, two conversions, from Bi$_2$ANaNb$_3$O$_{12}$ into H$_{1.8}$[A$_{0.8}$Bi$_{0.2}$NaNb$_3$O$_{10}$] (A = Sr, Ca)[30−32] and from Bi$_2$SrTa$_2$O$_9$ into H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] (HST),[33] have been reported. The compositions of these protonated forms are close to those of the Ruddlesden−Popper phases, but the layer charge decreases slightly from −2 per [A$_{n-1}$B$_n$O$_{3n+1}$] to −1.8 per [A$_{n-1}$B$_n$O$_{3n+1}$] because of a cation disorder (Sr, Ca ↔ Bi). We have shown that H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$NaNb$_3$O$_{10}$] can accommodate *n*-butylamine and *n*-octylamine in the interlayer space via the acid−base mechanism.[30,32] The amounts of intercalated *n*-alkylamines, however, were about 1.0 per [Sr$_{0.8}$Bi$_{0.2}$NaNb$_3$O$_{10}$]; only approximately half of the protons reacted with *n*-alkylamines.

We report here the intercalation behavior of *n*-alkylamines into H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] (HST). We propose the structural model of the resulting intercalation compounds based on the amounts of intercalated *n*-alkylamines and discuss the reason for the intercalation of limited amounts of *n*-alkylamines. To the best of our knowledge, this is the first systematic study of intercalation behavior of protonated forms of layered perovskites H$_x$[A$_{n-1}$B$_n$O$_{3n+1}$] with $x > 1$.

Experimental Section

Intercalation of *n*-Alkylamines. The preparation procedures for HST were described elsewhere.[33] As reactant *n*-alkylamines, *n*-butylamine (C4A), *n*-octylamine (C8A), *n*-dodecylamine (C12A), *n*-octadecylamine (C18A), and pyridine (Py) were utilized. About 0.5 g of HST was dispersed in 30 mL of an *n*-alkylamine (or pyridine)−tetrahydrofuran (THF) mixture (1:1 as volume) and refluxed for 7 days. After centrifugation, the crude product was washed with THF and air-dried.

Analyses. The X-ray diffraction (XRD) patterns of the products were obtained with MacScience M03XHF[22] with Mn-filtered Fe Kα radiation. The interlayer distances of intercalation compounds were determined from 00*l* reflections. Any reflection at $2\theta \leq 2.5°$ was excluded for interlayer distance calculation. Elemental analysis was performed as an internal service at the Waseda University Material Characterization Center. The infrared (IR) spectra of the products were recorded on a Perkin-Elmer Spectrum One spectrometer with the KBr-disk technique.

Results and Discussion

Figure 1 shows the XRD patterns of HST and its reaction products with *n*-alkylamines (hereinafter ex-
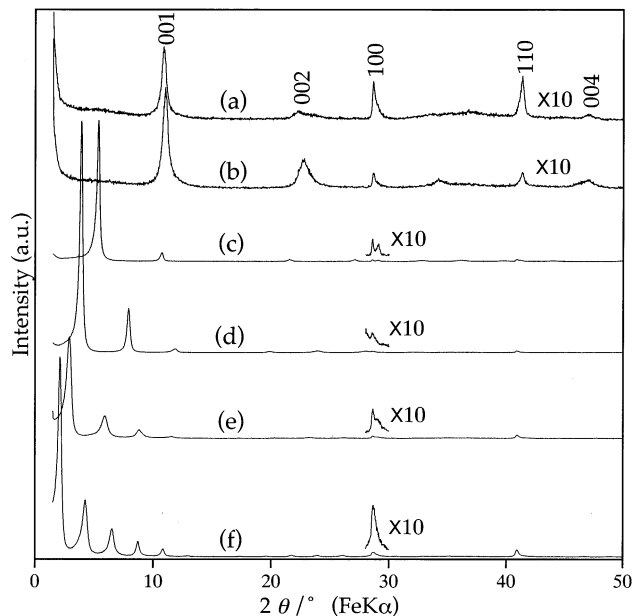

Figure 1. XRD patterns of (a) H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] (HST), (b) Py−HST, (c) C4A−HST, (d) C8A−HST, (e) C12A−HST, and (f) C18A−HST.

pressed as C*m*A−HST, where *m* represents the number of carbon atoms in *n*-alkylamines). After the reactions, the (00*l*) reflections of HST disappear, and new sets of (00*l*) reflections appear. The interlayer distance of the reaction products with *n*-alkylamines increases with an increase in the number of carbon atoms in the *n*-alkyl chain: 2.071(2) (C4A−HST), 2.840(9) (C8A−HST), 3.83(1) (C12A−HST), and 5.17(2) (C18A−HST) nm. In contrast, the reflections, which are assigned as (100) and (110) in the XRD pattern of HST, are observed at the same position in the reaction products. Thus, *n*-alkylamines are successfully intercalated into HST without any structural change in the perovskite-like slabs.

The reaction of HST with pyridine does not result in any change in the XRD pattern, indicating no intercalation reaction (Figure 1b). Since pyridine is a much weaker base (pK$_b$ = 8.82) than *n*-alkylamines used (pK$_b$ = 3.35−3.40), the basicity of pyridine is not large enough for intercalation; the protons in HST are thus weakly acidic.

Figure 2 demonstrates the IR spectra of C12A−HST and C18A−HST. Both of the spectra exhibit four major bands in the CH stretching region. It is well-known that the positions of the antisymmetric stretching band (~2920 cm^{-1}) and the symmetric stretching band (~2850 cm^{-1}) of CH$_2$ groups (abbreviated $\nu_{as(CH_2)}$ and $\nu_{s(CH_2)}$, respectively) are sensitive to chain conformation; these two bands shift to lower wavenumbers as disorder (kink- and gauche-blocks)[34] is introduced into the *n*-alkyl chains.[35,36] Actually, these band positions have been utilized in the conformational analysis of the *n*-alkyl chains of alkylammonium ions in the interlayer space

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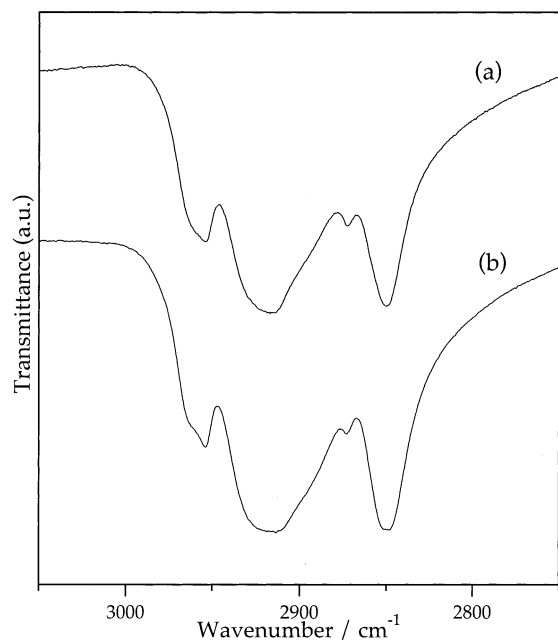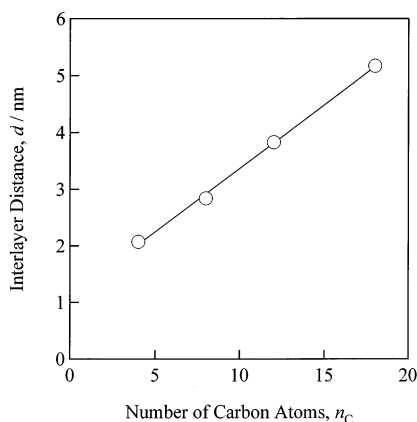
Figure 2. IR spectra of (a) C12A−HST and (b) C18A−HST.

Figure 3. Plot of interlayer distance, d versus the number of carbon atoms in the alkyl chain, n_C for the n-alkylamine−HST intercalation compounds.

of montmorillonite.[37] In the IR spectrum of C12A−HST, the $\nu_{as(CH_2)}$ band and the $\nu_{s(CH_2)}$ band are observed at 2918 and 2849 cm^{-1}, respectively, and these band positions correspond to an all-trans conformation.[37] The IR spectrum of C18A−HST also exhibits these two bands at the same wavenumbers, indicating that the n-alkyl chains possess the all-trans conformation in C18A−HST.

The relationship between the interlayer distance, d and the number of carbon atoms in the n-alkyl chain, n_C, is demonstrated in Figure 3. A linear relationship is clearly observed, as expressed with $d = 0.22n_C + 1.13$. Since IR analysis of C12A−HST and C18A−HST indicates that the n-alkyl chains in these intercalation compounds essentially exhibit the all-trans conformation, the linear relationship observed in Figure 3 strongly suggests similar conformations for the n-alkyl chains in C4A−HST and C8A−HST. The mean increment of the interlayer distance ($\Delta d/\Delta n_C$) is 0.22 nm. This value corresponds to a tilted bilayer arrangement

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Table 1. n-Alkylamine Contents of the CmA−HST Intercalation Compounds

amine	C (mass %)	n-alkylamine content (mol per [Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$])
C4A	6.62	0.9
C8A	11.8	0.9
C12A	17.6	0.9
C18A	24.7	1.0

of the n-alkyl chains in the interlayer space of HST. The tilt angle of the n-alkyl chains with respect to the surface of the perovskite-like slabs (ab plane) is calculated to be 60°.

The amounts of intercalated n-alkylamines are calculated from carbon contents and are listed in Table 1. The amounts estimated from nitrogen contents deviate from the values listed in Table 1 slightly, and the margin of error in the amounts of n-alkylamines is within 5%. Though 1.8 H$^+$ per [Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] are available for the acid−base reaction, only 0.9−1.0 mol of n-alkylamines per [Sr$_{0.8}$Bi$_{0.2}$Ta$_2$O$_7$] is intercalated. It should be noted that a similar observation was reported for another protonated form derived from an Aurivillius phase, H$_{1.8}$[Sr$_{0.8}$Bi$_{0.2}$NaNb$_3$O$_{10}$].[30,32]

The present results can be further compared with the intercalation behavior of n-alkylamines into the Dion−Jacobson phases, H[A$_{n-1}$B$_n$O$_{3n+1}$]; the surface geometry of the Dion−Jacobson phases is essentially identical to that of HST, but the proton concentration on the surface is lower, ideally 1.0 mol per [A$_{n-1}$B$_n$O$_{3n+1}$]. In the studies of triple-layered compounds, H[Ca$_2$Nb$_3$O$_{10}$][19] and H[CaLaNb$_2$TiO$_{10}$],[21] a few bilayer arrangements of the n-alkyl chains with different tilt angles were observed for each layered perovskite, and some intercalation compounds exhibited two interlayer distances corresponding to different arrangements. In the present study, in contrast, only one arrangement was detected. Among these reported arrangements, a similar tilt angle was observed for H[Ca$_2$Nb$_3$O$_{10}$] (expressed as $d = 0.2249n_C + 1.7129$ nm for C12A−C18A).[19] As a double-layered compound, an intercalation compound of H[LaNb$_2$O$_7$] with C8A was reported with an interlayer distance of 3.038(5) nm,[15] which is slightly larger than that of C8A−HST (2.840(9) nm). It should be noted that the reported amounts of n-alkylamines in fully intercalated compounds were essentially 1 mol per [A$_{n-1}$B$_n$O$_{3n+1}$]; all the protons were involved in the acid−base reactions.[19,21]

These analytical results and the aforementioned comparison indicate that the intercalation behavior of HST and that of the Dion−Jacobson phases are similar. To discuss this similarity, a structural model for the interlayer space of CmA−HST should be proposed. For the ion-exchangeable layered perovskites (Dion−Jacobson phases and Ruddlesden−Popper phases), however, the structures of intercalation compounds with n-alkylamines have not been sufficiently discussed. Another series of (100)−terminated layered perovskites, the so-called organic−inorganic perovskites, (RNH$_3$)$_2$-[(CH$_3$NH$_3$)$_{n-1}$M$_n$X$_{3n+1}$] (where M is a divalent metal and X is a halogen; note that CH$_3$NH$_3^+$ acts as A-site ions and RNH$_3^+$ is present in the interlayer space), have been structurally characterized; the n-RNH$_3^+$ ions fit into cavities on the (100) surface of the perovskite-like slabs to form hydrogen bonds with halogen atoms.[38]
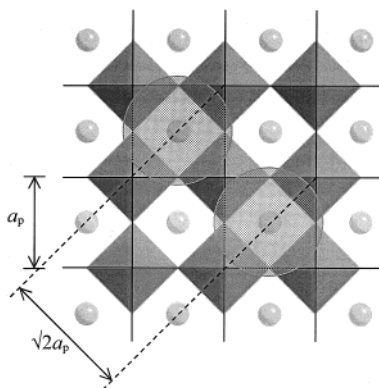
Figure 4. Idealized structural model along the *ab* plane. Large circle indicates cross section of *n*-alkylamine.

Thus, though the sizes of the cavities in these $[(CH_3NH_3)_{n-1}M_nX_{3n+1}]$ slabs are larger than those in the $[A_{n-1}B_nO_{3n+1}]$ slabs in the ion-exchangeable layered perovskites, we assume similar configurations of reacted *n*-alkylamines in the following discussion.

Figure 4 demonstrates a proposed structural model along the *ab* plane for the C*m*A–HST intercalation compounds. In the Ruddlesden–Popper phases, the amount of protons is equal to the number of cavities, and a comparable amount of protons is present in HST (corresponds to ~90% of the number of cavities). On the other hand, the amount of protons corresponds to only half the number of cavities in the Dion–Jacobson phases. (It should be noted that these relationships do not depend on the thickness of the perovskite-like slabs, as indicated by the general formula $H_x[A_{n-1}B_nO_{3n+1}]$.) The diameter of *n*-alkylamines with the all-trans *n*-alkyl chain is estimated from the cross section (0.186 nm^2)[39] to be 0.486 nm, and the distance between the nearest neighboring cavities (center to center) corresponds approximately to a_p (*a* parameter of cubic perovskite oxide, about 0.39 nm) for all the ion-exchangeable layered perovskites. Thus, as shown in Figure 4, if one cavity is occupied, the nearest neighboring cavities are not available for another guest species. The second-nearest cavities are separated by ~0.52 nm ($\sqrt{2} \times a_p$), and this distance is sufficient to accommodate two *n*-alkyl chains. In the protonated forms derived from the Dion–Jacobson phases, in contrast, reacted *n*-alkylamines are expected to occupy every other cavity. Thus, the distance between the nearest occupied cavities is ~0.52 nm.

These structural considerations provide a reasonable interpretation for HST behavior, which is similar to that of the Dion–Jacobson phases. The above discussion is also consistent with the presence of 2 mol of RNH_3^+ ions per $[A_{n-1}B_nX_{3n+1}]$ in the organic–inorganic perovskites since the nearest neighboring cavities are separated by ~0.5 nm, which is sufficient to accommodate two *n*-alkyl chains.[38] Since the interlayer surface geometry of HST is essentially identical with that of $H_{1.8}[Sr_{0.8}Bi_{0.2}NaNb_3O_{10}]$, the intercalation of limited amounts of C4A and C8A (0.9–1.0 mol per $[Sr_{0.8}Bi_{0.2}NaNb_3O_{10}]$) can be interpreted in a similar fashion.

Conclusions

We have demonstrated that $H_{1.8}[Sr_{0.8}Bi_{0.2}Ta_2O_7]$ (HST) can accommodate *n*-alkylamines ($C_mH_{m+1}NH_2$; $m = 4$, 8, 12, 18) to form intercalation compounds via the acid–base mechanism. Pyridine, which is a weaker base, cannot be intercalated into HST, indicating that the protons attached to TaO_6 octahedra in HST are weakly acidic. The four *n*-alkylamines examined exhibit only one type of orientation in the interlayer space of HST: a bilayer arrangement of the *n*-alkyl chains with a tilt angle of 60°. The amounts of intercalated *n*-alkylamines are 0.9–1.0 mol per $[Sr_{0.8}Bi_{0.2}Ta_2O_7]$, though 1.8 mol can be maximally intercalated on the basis of the proton content. The interlayer surface geometry of the $[Sr_{0.8}Bi_{0.2}Ta_2O_7]$ slabs clearly explains the limited intercalation behavior by assuming the presence of reacted *n*-alkylamines in the cavities on the surface of the perovskite-like slabs; the *n*-alkylamines are too bulky to fit every cavity, and the presence of the *n*-alkylamines is spatially possible only in every other cavity. The present study provides fundamental information for the "*Chimie Douce*" approach to functional materials for the Aurivillius-phases derived protonated forms, which could extend the narrow composition range of perovskite-like slabs in the ion-exchangeable layered perovskites.

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