Intercalation of α,ω-Diaminoalkanes in the Interlayer Space of the Protonated Form of the Layered Perovskite $H_{1.8}Bi_{0.2}Sr_{0.8}Ta_2O_7$

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(Received August 24, 2006; CL-060969; E-mail: ys6546@waseda.jp)

α,ω-Diaminoalkanes ($NH_2(CH_2)_nNH_2$; $n = 2$, 4, 8, and 12) are intercalated in the interlayer space of the protonated form of a layered perovskite, $H_{1.8}Bi_{0.2}Sr_{0.8}Ta_2O_7$ (HSrTa). The amounts of α,ω-diaminoalkanes, which possess a monolayer arrangement in the interlayer space, are calculated as ca. 0.5 per $[Bi_{0.2}Sr_{0.8}Ta_2O_7]$. A model for α,ω-diaminoalkane–HSrTa intercalation compounds is proposed, and the model is consistent with that proposed for *n*-alkylamine–HSrTa intercalation compounds.

Among inorganic–organic hybrids, intercalation compounds in which inorganic sheets and organic ions or molecules are stacked alternatively are interesting materials because they exhibit various properties,[1,2] and it is known that ion-exchangeable layered perovskites exhibit intercalation behavior.[2] These compounds consist of perovskite-like slabs $[A_{m-1}B_mO_{3m+1}]$ (where the thickness of a perovskite-like slab is expressed as *m*) and interlayer cations, M. Ion-exchangeable layered perovskites can be classified into two phases: $MA_{m-1}B_mO_{3m+1}$ (Dion–Jacobson phases) and $M_2A_{m-1}B_mO_{3m+1}$ (Ruddlesden–Popper phases).[2] Acid treatment of the ion-exchangeable layered perovskites leads to the formation of the protonated forms, $H_xA_{m-1}B_mO_{3m+1}$ (Dion–Jacobson phases, $x = 1$, and Ruddlesden–Popper phases, $x = 2$).

Reaction of the protonated forms of the Dion–Jacobson phases, $HA_{m-1}B_mO_{3m+1}$ ($x = 1$), with organic bases (*n*-alkylamines, α,ω-diaminoalkane, etc.) leads to the formation of intercalation compounds via the acid–base mechanism.[3,4] The protonated forms of the Ruddlesden–Popper phases, $H_2A_{m-1}B_mO_{3m+1}$ ($x = 2$), on the contrary, have not formerly been considered to form intercalation compounds with *n*-alkylamines,[5] but three research groups have recently reported the intercalation of *n*-alkylamine into Ruddlesden–Popper phases.[6–8]

We previously reported the preparation of the protonated forms of ion-exchangeable layered perovskites, $H_x[(Bi,A)_{m-1}B_mO_{3m+1}]$, by acid treatment of $Bi_2A_mB_mO_{3m+3}$ via selective leaching.[9,10] The structure of $H_x[(Bi,A)_{m-1}B_mO_{3m+1}]$ (x is typically 1.8) is very similar to that of the Ruddlesden–Popper phases. Among these, $H_{1.8}Bi_{0.2}Sr_{0.8}Ta_2O_7$ (HSrTa) can accommodate *n*-alkylamines to form intercalation compounds. Surprisingly, only 1.0 of 1.8 interlayer protons in HSrTa could react with *n*-alkylamines; the amounts of *n*-alkylamines per $[Bi_{0.2}Sr_{0.8}Ta_2O_7]$ were around 1.0.[11] These observations can be interpreted by the fact that *n*-alkylamines in the intercalation compounds formed a bilayer arrangement and that the maximum amounts of *n*-alkylamines in the interlayer space were governed by both the surface geometry of the perovskite-like slabs and the cross-sectional area of the *n*-alkylchain.

Here, we report the intercalation of α,ω-diaminoalkane ($NH_2(CH_2)_nNH_2$; $n = 2$, 4, 8, and 12; hereafter expressed as C*n*D) into HSrTa. We focus on the limitation of the amount of organic amines in the interlayer space as well as on the interlayer arrangement of α,ω-diaminoalkanes.

Preparation of a protonated form of the layered perovskite $H_{1.8}Bi_{0.2}Sr_{0.8}Ta_2O_7$ (HSrTa) was reported elsewhere.[10] For intercalation of 1,2-diaminoethane (C2D), 0.5 g of HSrTa was refluxed in 40 mL of C2D and 10 mL of water for 3 days.[12] For intercalation of 1,4-diaminobutane (C4D), 1,8-octanediamine (C8D), and 1,12-diaminododecane (C12D), 0.5 g of HSrTa was refluxed in 25 mL of α,ω-diaminoalkane (C4D, C8D, or C12D) and 25 mL of solvent [water (C4D and C8D) or a water–tetrahydrofuran (THF) mixture (volume ratio of THF: water = 4:1) (C12D)]. After refluxing, all the products were centrifuged, washed with distilled water or THF, and dried at room temperature (C*n*D–HSrTa; $n = 2$, 4, 8, and 12).

Figure 1 (left) demonstrates the X-ray (Mn filtered Fe Kα radiation) diffraction (XRD) patterns of HSrTa, C2D–HSrTa, C4D–HSrTa, C8D–HSrTa, and C12D–HSrTa. The XRD patterns of the products show (00*l*) reflections due to a stacking order shift to lower angles and disappearance of the reflections due to HSrTa, indicating the formation of single-phase intercalation compounds. The *c* parameters [estimated from the (00*l*) reflections] of C2D–HSrTa, C4D–HSrTa, C8D–HSrTa, and C12D–HSrTa increase from 0.980(4) nm (HSrTa) to 1.335(2) nm (C2D–HSrTa), 1.570(2) nm (C4D–HSrTa), 2.019(5) nm (C8D–HSrTa), and 2.437(8) nm (C12D–HSrTa). The (100) reflection of HSrTa at 28.7° does not shift in the XRD patterns of any of the products, confirming the preservation of a perovskite-like slab structure.

The infrared (IR, KBr pellet) spectra of C2D–HSrTa, C4D–HSrTa, C8D–HSrTa, and C12D–HSrTa showed new absorption bands at 3350–3150, 3000–2800, 1430–1390, and 1220–

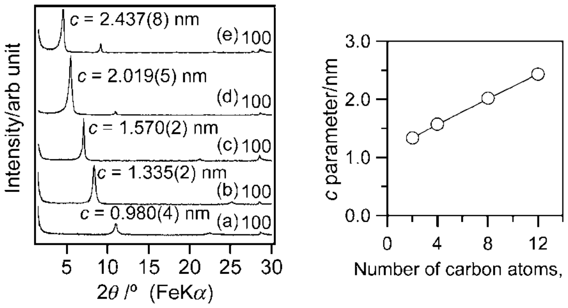

Figure 1. The XRD patterns (left) of (a) HSrTa, (b) C2D–HSrTa, (c) C4D–HSrTa, (d) C8D–HSrTa, and (e) C12–HSrTa. The graph at the right shows the relationship between the number of carbon atoms and the *c* parameter.

1020 cm^{-1} assignable to the $\nu_{(\mathrm{NH})}$, $\nu_{(\mathrm{CH})}$, $\nu_{(\mathrm{C–N})}$, and $\delta_{(\mathrm{C–C–N})}$ modes, respectively.[13] The solid-state ^{13}C nuclear magnetic resonance (NMR) spectra with cross polarization and the magic angle spinning (CP/MAS) techniques also showed signals due to N–*C*H$_2$– and –*C*H$_2$– groups (C2D–HSrTa, 38 ppm; C4D–HSrTa, 41 and 27 ppm; C8–HSrTa, 41 ppm, and a broad signal centered at 30 ppm; C12–HSrTa, 40, 34, 32, 30, 28 ppm), indicating the presence of α,ω-diaminoalkanes in the products. Thus, the XRD, IR, and ^{13}C CP/MAS NMR results clearly demonstrate successful intercalation of α,ω-diaminoalkanes into HSrTa.

Solid-state ^{13}C CP/MAS NMR spectroscopy provided additional information on the states of α,ω-diaminoalkanes in the interlayer space. In the solid-state ^{13}C CP/MAS NMR spectrum of C4D–HSrTa, the signal of an N–CH$_2$–*C*H$_2$– environment in C4D–HSrTa was detected at 27 ppm, while in the liquid-state ^{13}C NMR spectrum (solvent, deuterium oxide) of C4D, a signal due to the N–CH$_2$–*C*H$_2$– environment appeared at 30.3 ppm. This upfield shift of the N–CH$_2$–*C*H$_2$– environment was also observed in the spectrum of C4D in a hydrochloric acid medium (pH $\approx$ 1.2): the ^{13}C NMR spectrum of C4D in an acidic medium (solvent, deuterium oxide) showed a signal due to the N–CH$_2$–*C*H$_2$– environment at 25.0 ppm. The upfield shift observed in this study is, therefore, attributable to the conversion of –NH$_2$ groups into –NH$_3{}^+$ groups.[14] No signal was detected at 30 ppm in the ^{13}C CP/MAS NMR spectra of C4D–HSrTa, indicating that both of the terminal –NH$_2$ groups are converted into NH$_3{}^+$ groups. Although we could not find this upfield shift in the spectra of C8D–HSrTa and C12D–HSrTa because of overlapping with the signals due to –CH$_2$– groups, all α,ω-diaminoalkanes in the interlayer space are expected to be present as diammonium ions.

In the IR spectra of C8D–HSrTa and C12D–HSrTa, adsorption bands of the CH symmetric stretching mode due to the –CH$_2$– groups [ν_s(CH$_2$)] are observed at 2850 (C8D–HSrTa) and 2849 cm^{-1}(C12D–HSrTa), indicating that *n*-alkylchains in the interlayer space possess an all-trans ordered state.[15] As concerns the number of carbon atoms, n_c, the linear relationship with the *c* parameter (Figure 1, right) suggests that the *n*-alkylchain with $n_c = 4$ also possesses an all-trans ordered state in the interlayer space. The linear relationship is expressed as $c = 0.11n_c + 1.12$.

The ^{13}C CP/MAS NMR result, conversion of both the terminal –NH$_2$ groups of C4D into –NH$_3{}^+$ groups, clearly indicates a monolayer arrangement of guest species. The monolayer arrangement is consistent with the fact that the reported slope (0.22 nm; the relationship is expressed by $c = 0.22n_c + 1.13$ nm[11]) of the *n*-alkylamines–HSrTa intercalation compounds possessing a bilayer arrangement is twice as large as that of the α,ω-diaminoalkane–HSrTa intercalation compounds (0.11 nm). The tilt angle of the *n*-alkylchain is estimated from the slope of the α,ω-diaminoalkane–HSrTa intercalation compounds in Figure 2 to be 60°, which is the same as that of the *n*-alkylamine–HSrTa intercalation compounds. Thus, this model for α,ω-diaminoalkane–HSrTa intercalation compounds possessing a monolayer arrangement of guest species is consistent with that for *n*-alkylamines–HSrTa intercalation compounds.

The ideal maximum amount of α,ω-diaminoalkane is calculated from the surface geometry of the layered perovskite and the cross-sectional area of the *n*-alkylchain to be 0.5 per [Bi$_{0.2}$Sr$_{0.8}$Ta$_2$O$_7$], half the amount of *n*-alkylamines (1.0 per [Bi$_{0.2}$Sr$_{0.8}$Ta$_2$O$_7$]).[11] The actual amounts of α,ω-diaminoalkanes in the interlayer space of all the intercalation compounds were estimated from the carbon content by elemental analysis to be 0.5 per [Bi$_{0.2}$Sr$_{0.8}$Ta$_2$O$_7$], which strongly supports the above estimation. Based on these considerations, a model for the interlayer structure can be proposed as shown in Figure 2.

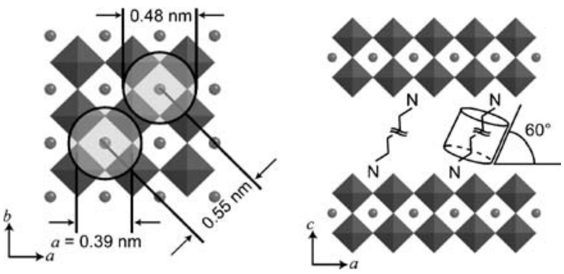

Figure 2. Proposed model for α,ω-diaminoalkane–HSrTa intercalation compounds.

To sum up, we have demonstrated the successful intercalation of α,ω-diaminoalkanes in the interlayer space of HSrTa. The α,ω-diaminoalkane–HSrTa intercalation compounds possess an interlayer *n*-alkylchain arrangement similar to that of *n*-alkylamine–HSrTa intercalation compounds. The amounts of α,ω-diaminoalkanes arranged as a monolayer in the interlayer space are calculated to be $\approx$0.5 per [Bi$_{0.2}$Sr$_{0.8}$Ta$_2$O$_7$], which is consistent with the ideal amount estimated from the surface area of the perovskite-like slab and cross-sectional area of the *n*-alkylchain.

The authors express their gratitude to Prof. Kazuyuki Kuroda, Department of Applied Chemistry, Waseda University, for his valuable discussion. This work was supported by 21COE "Practical Nano-Chemistry" from MEXT, Japan.

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