New Conversion Reaction of an Aurivillius Phase into the Protonated Form of the Layered Perovskite by the Selective Leaching of the Bismuth Oxide Sheet

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Oxides with the general formula $M[A_{n-1}B_nO_{3n+1}]$ and $M_2[A_{n-1}B_nO_{3n+1}]$ (M = Rb, K, etc., A = Na, Ca, La, etc., B=Ti, Nb and Ta) represent a class of perovskite-related oxides with layered structures, where $[A_{n-1}B_nO_{3n+1}]$ denotes a negatively charged perovskite-like slab with thickness of n, and M is an ion-exchangeable monovalent-interlayer cation.[1,2] The monovalent-interlayer cation is readily exchanged with protons ($M^+ \rightarrow H^+$) by ion-exchange reactions with acidic solutions, resulting in their corresponding protonated forms, $H[A_{n-1}B_nO_{3n+1}]$ and $H_2[A_{n-1}B_nO_{3n+1}]$.[3−6] These protonated forms have attracted increased attention, as they exhibit various properties and can be utilized as hosts for various functional materials.[7] Because the synthesis of $M[A_{n-1}B_nO_{3n+1}]$ and $M_2[A_{n-1}B_nO_{3n+1}]$ has been limited to those with B = Ti, Nb, and Ta, the B-site cations of the corresponding protonated forms have been restricted to these elements.

The Aurivillius phases, $Bi_2O_2[A_{n-1}B_nO_{3n+1}]$, are a series of perovskite-related oxides possessing layered structures, where $[A_{n-1}B_nO_{3n+1}]$ denotes the perovskite-like slab.[8] The perovskite-like slab in $Bi_2O_2[A_{n-1}B_nO_{3n+1}]$ is structurally analogous to that in the layered perovskites with ion-exchange capability (Figure 1). The perovskite-like slab in the layered perovskites with ion-exchange capability is relatively stable in acidic solutions, since the protonated forms were obtained by acid treatment.[2−5] By analogy, the perovskite-like slab in $Bi_2O_2[A_{n-1}B_nO_{3n+1}]$ is also presumed to be stable in acidic solutions. On the other hand, bismuth oxosalts (which possesses a structure similar to the bismuth oxide sheet in $Bi_2O_2[A_{n-1}B_nO_{3n+1}]$[8c]) and bismuth oxide are soluble in acidic solutions.[9] Such a large difference in acid resistance between the perovskite-like slab and the bismuth
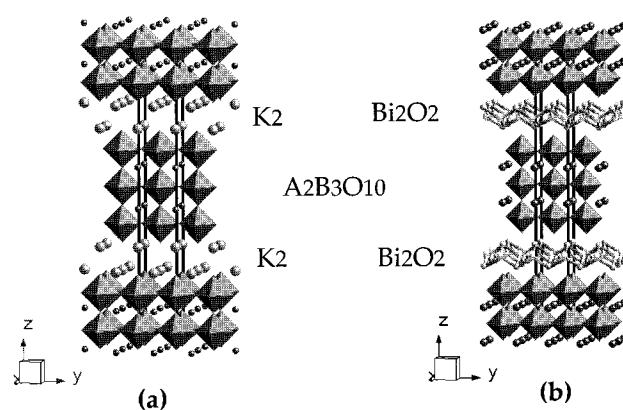

Figure 1. The schematic structures of $n = 3$ layered perovskites (a) $K_2[A_2B_3O_{10}]$ and (b) $Bi_2O_2[A_2B_3O_{10}]$.

oxide sheet may lead to a selective leaching of the bismuth oxide sheet by acid treatment.

We report in this communication a new conversion reaction for preparing a protonated form of a layered perovskite by hydrochloric acid treatment of an Aurivillius phase Bi_2O_2-$[SrNaNb_3O_{10}]$. The present reaction involves not only the selective leaching of the bismuth oxide sheet, but also the introduction of protons for charge compensation to maintain the layered perovskite-like structure. As numerous Aurivillius phase compounds have been reported with combinations of various elements and n values (A = Na, Ca, Bi, etc.; B = W, Nb, Ti, etc.; $1 \leq n \leq 8$),[10] the present conversion reaction opens the possibility to achieve protonated forms of layered perovskites with an extensive range of compositions.

The synthesis[11] of polycrystalline $Bi_2O_2[SrNaNb_3O_{10}]$ (BSNN) was conducted by a procedure similar to those of $Bi_2O_2[Bi_{0.5}$-$Na_{1.5}Nb_3O_{10}]$[12] and $Bi_2O_2[CaNaNb_3O_{10}]$.[13] The acid-treated product (HSNN) was prepared by stirring 1 g of BSNN in 200 mL of 6 M HCl at room temperature for 72 h. After the reaction, the centrifuged and washed HSNN was dried under ambient conditions.

The lattice parameters of BSNN (tetragonal; S.G. *I4/mmm*, $Z = 2$; $a = 0.39007(1)$ nm, $c = 3.2926(1)$ nm) refined by Rietveld analysis[14] of the XRD pattern (Figure 2a) were comparable to those of structurally related compounds, i.e. $Bi_2O_2[Bi_{0.5}Na_{1.5}$-$Nb_3O_{10}]$[12] and $Bi_2O_2[CaNaNb_3O_{10}]$.[13] The XRD pattern for HSNN (Figure 2b) was successfully indexed based on a tetragonal cell with $a = 0.390 \pm 0.001$ nm and $c = 1.43 \pm 0.02$ nm.[15] The (00*l*) diffraction peaks of BSNN disappeared after the acid treatment, and new (00*l*) diffraction peaks appeared at higher 2θ angles. On the other hand, the diffraction peaks characteristic of the perovskite sublattice (110) and (200) were observed at the same 2θ angles. The (*hk*0) peaks revealed the retention of the structure along the *ab* plane, while the presence of the (00*l*) peaks at higher 2θ angles indicated the contraction of the basal spacing. The broadness of the (*hkl*) ($l \neq 0$) peaks compared to the (*hk*0)

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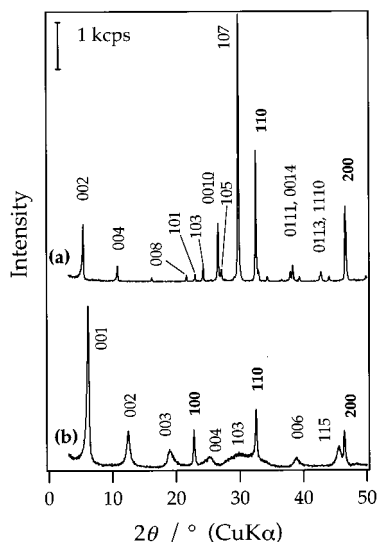
Figure 2. The XRD patterns (a) before and (b) after the acid treatment of $Bi_2O_2[SrNaNb_3O_{10}]$.

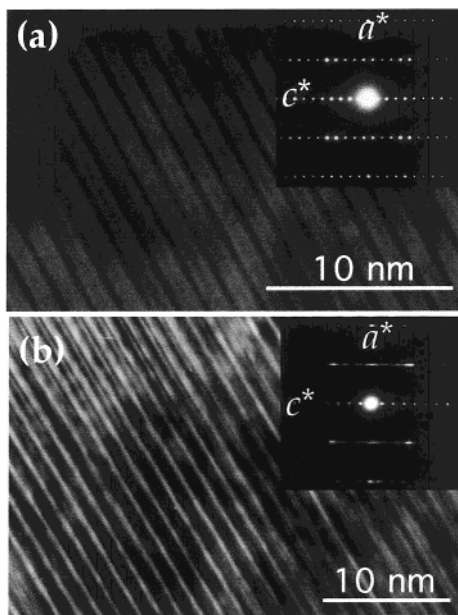**Figure 3.** TEM lattice images along the [010] zone (a) before and (b) after the acid treatment of $Bi_2O_2[SrNaNb_3O_{10}]$. The corresponding ED patterns are shown in the insets.

peaks indicated stacking disorder. The appearance of the (100) diffraction peak showed that the doubling of the c axis observed in BSNN does not occur in HSNN.[16] The lattice parameter of HSNN was comparable to the values of protonated forms of layered perovskite with $n = 3$ obtained by conventional ion-exchange reactions, i.e. $HCa_2Nb_3O_{10}$ ($a = 0.3849$ nm and $c = 1.437$ nm)[3] and $H_2La_2Ti_3O_{10}$ ($a = 0.382$ nm and $c = 2.766$ nm (the c axis is doubled due to the displacement of the perovskite-like slabs)).[5]

Transmission electron micrographs (TEM) and the corresponding electron diffraction (ED) patterns along the [010] zone of BSNN and HSNN are shown in Figure 3. Alternating rows of dark and light contrast were observed for both BSNN and HSNN, in accordance with the retention of the layered structure observed by XRD. The periodicities between the alternating rows were 1.6 and 1.4 nm before and after the acid treatment, in agreement with

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(16) The lack of c axis doubling implies that no displacement of the perovskite-like slabs is involved, unlike BSNN where the perovskite-like slabs are displaced by 1/2 along the diagonal direction of the two a axes.

the c axis (half the c axis in the case of BSNN) obtained from XRD.

Scanning electron microscopic observations showed no distinct difference in the size (~5 μm) or morphology of the particles before and after the acid treatment. Furthermore, ED studies of numerous HSNN particles showed no ring pattern, indicating that all the particles were crystalline solids. Consequently, the simultaneous dissolution of both the bismuth oxide sheet and the perovskite-like slab and the possibility of amorphization as a result of the acid treatment can be disregarded.

Inductively coupled plasma emission spectroscopy (ICP) revealed the composition ratios of metals were Bi:Sr:Na:Nb = 2.00:1.00:1.02:3 for BSNN and Bi:Sr:Na:Nb = 0.21:0.80:0.95:3 for HSNN, indicating the selective leaching of Bi and the partial loss of Sr from BSNN. As the composition analysis results were the same even after acid treatment for a month, partially undissolved Bi cannot be due to incomplete reaction. These results, combined with the fact that (Bi+Sr):Nb = 1.01:3, suggest that partial disordering of cations (Bi $\leftrightarrow$ Sr) is present in the parent compound BSNN, similar to that reported for $Bi_2O_2[ANb_2O_7]$ (A = Ca, Sr, Ba, and Pb).[17]

Thermogravimetric analysis of HSNN dried at 120 °C revealed 2.7 mass % loss which started from 160 °C, agreeing with the proton content according to the overall reaction

$$Bi_{1.8}Sr_{0.2}O_2[Bi_{0.2}Sr_{0.8}NaNb_3O_{10}] \xrightarrow{HCl}$$
$$H_{1.8}[Bi_{0.21}Sr_{0.80}Na_{0.95}Nb_3O_{10}]$$
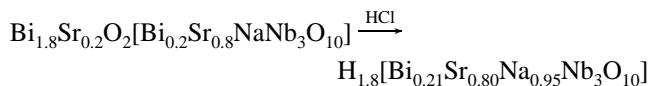
Notice that the proton content is equivalent to the formal charge of the perovskite-like slab. The overall reaction can thus be regarded as the replacement of the positively charged bismuth-oxide sheet (containing Sr) with protons so as to compensate for the negatively charged perovskite-like slab ($\{[Bi_{1.8}Sr_{0.2}O_2]^{1.8+}\}_x \rightarrow 1.8xH^+$).

The intercalation of butylamine (C4A) and octylamine (C8A) was performed as alkylamines are known to be intercalated into the interlayer space of protonated forms of layered niobates.[1,18] The c axis increased when HSNN was reacted with C4A (1.41 $\rightarrow$ 2.46 nm) and C8A (1.41 $\rightarrow$ 3.33 nm), while the a axis was the same as that of HSNN ($a = 0.390$ nm). These values are comparable to those of related intercalation compounds, C4A–$H[Ca_2Nb_3O_{10}]$ and C8A–$H[Ca_2Nb_3O_{10}]$.[3,7a] Chemical analysis revealed 0.9 mol of C4A and 1.0 mol of C8A per unit of $[Bi_{0.21}Sr_{0.80}Na_{0.95}Nb_3O_{10}]$ were intercalated. These results show the formation of C4A- and C8A-HSNN intercalation compounds, which strongly supports the layered structure of HSNN. Although fractional amounts of alkylamine intercalated into layered oxides are not uncommon,[19] unoptimized intercalation conditions may also be a reason for the partial intercalation. The capability of HSNN to accommodate alkylamines, in contrast to $H_2La_2Ti_3O_{10}$,[20] suggests a notable difference in the reactivity of the protons attached to NbO_6 and TiO_6 octahedra.[20]

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