Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$: New Variant of a Hexagonal Tungsten Oxide (HTO)-Like Layered Framework Containing Both a Main-Group Cation, In^{3+}, and a Lone-Pair Cation, Te^{4+}

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Ⓢ Supporting Information

ABSTRACT: A novel hexagonal tungsten oxide (HTO)-like layered framework containing a main-group cation, In^{3+}, and a lone-pair cation, Te^{4+}, is reported. Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$ exhibits a layered structure consisting of InO$_6$, TeO$_3$, and TeO$_4$ polyhedra. The synthesis, crystal structure determination, characterization, and reactivity of the material will be presented.

The hexagonal tungsten oxide (HTO) materials have drawn enormous attention because of their applicable characteristics such as photocatalytic, electrocatalytic, optical, and adsorption properties.[1] Especially, noncentrosymmetric HTOs have suggested a variety of technologically important functional properties such as second-harmonic generation, piezoelectricity, and pyroelectricity.[2] Until now, most of the reported HTO frameworks were composed of octahedrally coordinated d^0 transition metals (V^{5+}, Mo^{6+}, and W^{6+}) or the d^{10} cation (Sb^{5+}). The HTO structure exhibits layers with an array of three- and six-membered rings formed from linkages of corner-shared MO$_6$ octahedra. One or both sides of the layers in HTOs are often capped by other cations such as Sb^{3+}, Se^{4+}, Te^{4+}, and P^{5+}.[3] Herein we discovered a novel variant of the layered HTO-like framework material, Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$. Although a layered HTO-like framework containing a lone-pair cation, I^{5+}, has been reported,[4] to the best of our knowledge, Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$ is the first example of an HTO-like framework that contains *both a main-group cation from the p block and a lone-pair cation*. In this Communication, we report the phase-pure synthesis, crystal structure, characterization, and reactivity of Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$.

Crystals of Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$ were grown hydrothermally by combining Na$_2$CO$_3$, In(NO$_3$)$_3$·xH$_2$O, TeO$_2$, and water in a Teflon-lined autoclave at 230 °C for 5 days.[5] Colorless block-shaped crystals have been isolated in phase pure form in 75% yield based on TeO$_2$.[6] The powder X-ray diffraction (XRD) pattern for the ground sample is in good agreement with the calculated data from the single-crystal model (see the Supporting Information).

Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$ exhibits a layered crystal structure that is composed of InO$_6$ octahedra, TeO$_3$, and TeO$_4$ polyhedra (see Figure 1). A unique In^{3+} cation is bonded to six oxygen atoms in a slightly distorted octahedral environment, with bond distances ranging from 2.077(7) to 2.173(6) Å. Two kinds of Te^{4+} cations connected to three and four oxygen atoms exhibit asymmetric TeO$_3$ and TeO$_4$ polyhedra attributable to their lone pairs. The three-coordinate Te^{4+} cations reveal Te—O
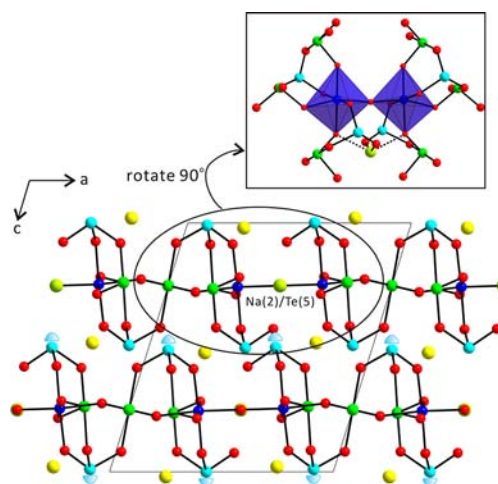

Figure 1. Ball-and-stick diagram of Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$ in the *ac* plane. The three-coordinate TeO$_3$ groups serve as intralayer linkers, by capping the layer from above and below. The lone pairs on two rows of Te^{4+} cations are shown schematically and are not the result of electron-localized function calculations (cyan, three-coordinate Te; green, four-coordinate Te; blue, In; yellow, Na; light green, Na/Te; red, O).

bond lengths ranging from 1.832(6) to 1.970(6) Å. The four-coordinate Te^{4+} cations, however, show Te—O bond distances ranging from 1.832(6) to 2.260(5) Å. These bond distances are consistent with those of previously reported tellurites.[7] The InO$_6$ and TeO$_4$ polyhedra share their corners to form a layered structure. The asymmetric TeO$_3$ groups cap the InO$_6$ and TeO$_4$ polyhedra from above and below and serve as intralayer linkers. The lone pairs associated with the three-coordinate TeO$_3$ group also point approximately along the [001] and [00—1] directions (see Figure 1). Two unique alkali-metal cations, Na(1)$^+$ and Na(2)$^+$, reside between the layers. Na$^+$ cations are surrounded by six oxygen atoms, with Na—O contact distances ranging from 2.253(6) to 2.721(8) Å. Upon examination of the thermal ellipsoid for Na(2) in Na$_{1.4}$InTe$_{3.6}$O$_{9.4}$, the Na(2) atom was found to be disordered. On the basis of the bond distances and coordination environments, Na$^+$ cations are mixed with a very small amount of Te^{4+} at the position. A mixed-occupancy model was successfully refined to 0.88(3) and 0.119(8) for Na(2) and Te(5), respectively. We also determined that a

fractional occupancy occurred in O(4). In doing so, a fractional occupancy of 0.904(9) was refined for O(4).

One very interesting structural feature of $Na_{1.4}InTe_{3.6}O_{9.4}$ is that the framework of the layer is related to that of HTOs (see Figure 2). The layer of HTO consists of corner-shared MO_6
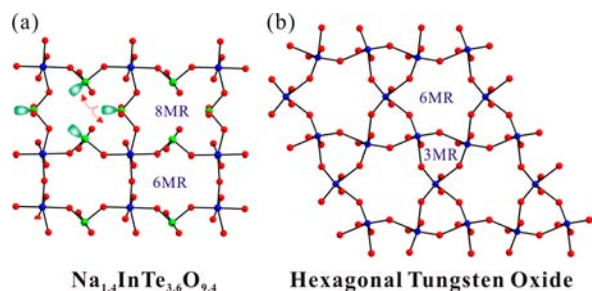

Figure 2. Ball-and-stick representations of one layer for (a) $Na_{1.4}InTe_{3.6}O_{9.4}$ and (b) HTO. The layer of HTO consists of corner-shared MO_6 octahedra that are linked to form a network of three- and six-membered rings, whereas the layer of $Na_{1.4}InTe_{3.6}O_{9.4}$ exhibits six- and eight-membered rings obtained from corner-shared InO_6 octahedra and TeO_4 polyhedra.

octahedra that are connected to form a network of three- and six-membered rings. However, the connectivity in the layer of $Na_{1.4}InTe_{3.6}O_{9.4}$ exhibits six- and eight-membered rings obtained from corner-shared InO_6 octahedra and TeO_4 polyhedra. Because Te^{4+} cations are connected to only four oxygen atoms in $Na_{1.4}InTe_{3.6}O_{9.4}$, it is difficult to form three-membered rings with one InO_6 octahedron and two TeO_4 polyhedra. Instead, lone pairs on Te^{4+} cations open up the rings and form six- and eight-membered rings.

As seen in Figure 3, while the lone pairs on the TeO_4 groups in the six-membered rings (6-MRs) are pointing outward, those in the eight-membered rings (8-MRs) are pointing inward. The location and direction of lone pairs on the TeO_4 groups have an important structural consequence. The Na^+ cations residing in the 6-MRs are coplanar with the ring, in which plenty of space for the Na^+ cation is available, whereas the Na^+ cations near the 8-MRs sit above and below the rings attributable to the occupancy of lone pairs.

The thermal behavior of the material was investigated using thermogravimetric analysis (TGA). No weight loss was observed up to 1000 °C. An endothermic peak, however, appeared at 610−640 °C, which indicated that the material melted incongruently above the temperatures. The TGA diagram has been deposited in the Supporting Information. The IR spectrum of the material shows the In−O and Te−O vibrations at around 410 and 550−840 cm^{-1}, respectively. The assignments are consistent with those previously reported.[7i]

The stability of $Na_{1.4}InTe_{3.6}O_{9.4}$ in acidic conditions has been investigated. A total of 30 mg of crystalline $Na_{1.4}InTe_{3.6}O_{9.4}$ was introduced to a vial containing 5 mL of a 0.05 M HCl solution. Colorless block-shaped crystals were grown in 3 days at room temperature and were identified as a new alkali-metal indium tellurite, $NaIn(TeO_3)_2$, by single-crystal XRD analysis.[8] Interestingly, the layered structure of $Na_{1.4}InTe_{3.6}O_{9.4}$ changed to the three-dimensional framework during the reaction (see Figure 4). It seems that crystals of $NaIn(TeO_3)_2$ have been grown in a dilute acidic solution by releasing a small amount of Na^+ and Te^{4+} from $Na_{1.4}InTe_{3.6}O_{9.4}$. Work is underway to confirm the phase purity as well as full characterization of $NaIn(TeO_3)_2$.

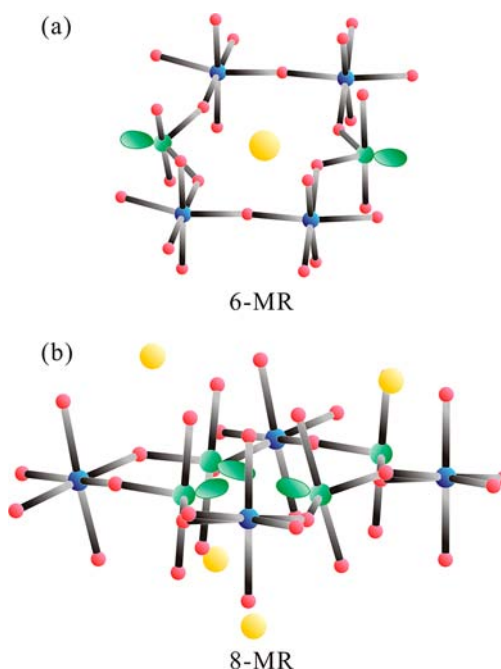**Figure 3.** Ball-and-stick representations of the (a) six- and (b) eight-membered rings in $Na_{1.4}InTe_{3.6}O_{9.4}$. The lone pairs are shown schematically (blue, In; green, Te; yellow, Na; red, O). While the Na^+ cations in the 6-MRs are coplanar with the rings, the Na^+ cations in the 8-MRs reside above and below the rings attributable to the lone pairs.
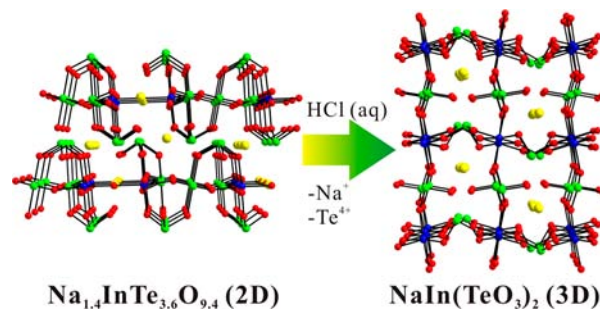

Figure 4. Schematic structural representation for the change of $Na_{1.4}InTe_{3.6}O_{9.4}$ to $NaIn(TeO_3)_2$ in a dilute HCl solution (blue, In; green, Te; yellow, Na; red, O). Note that the layered structure changes to the three-dimensional framework.

In summary, we have reported the phase-pure synthesis, structure, and characterization of a new mixed-metal oxide, $Na_{1.4}InTe_{3.6}O_{9.4}$. The reported material is the first example exhibiting a HTO-like framework composed of both a main-group cation from the p block and a lone-pair cation. A stability test in an acidic solution suggests that the layered structure of $Na_{1.4}InTe_{3.6}O_{9.4}$ changes to the three-dimensional framework of $NaIn(TeO_3)_2$. Extension of this work to other systems with different cations is ongoing and will be reported shortly.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Crystallographic data in CIF format and experimental and calculated powder XRD patterns, TGA diagram, and IR spectrum for $Na_{1.4}InTe_{3.6}O_{9.4}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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(5) Crystals of $Na_{1.4}InTe_{3.6}O_{9.4}$ were prepared hydrothermally by combining Na_2CO_3 (0.318 g, 3.00×10^{-3} mol), $In(NO_3)_2 \cdot xH_2O$ (0.301 g, 1.00×10^{-3} mol), TeO_2 (0.638 g, 4.00×10^{-3} mol), and 2 mL of deionized water. The reaction mixture was loaded into a 23 mL Teflon-lined stainless steel autoclave. The autoclave was subsequently sealed and heated to 230 °C for 5 days, before being cooled to room temperature at a rate of 6 °C h^{-1}. After cooling, the autoclave was opened, and the product was recovered by filtration and washed with water. Inductively coupled plasma analysis for $Na_{1.4}InTe_{3.6}O_{9.4}$ exhibits a Na/In/Te ratio of 1.47:1.00:3.54.

(6) A colorless block crystal of dimensions 0.014 mm × 0.025 mm × 0.029 mm for $Na_{1.4}InTe_{3.6}O_{9.4}$ was used for structural determination. Data were collected on a Bruker SMART BREEZE CCD X-ray diffractometer at room temperature using graphite-monochromated Mo Kα radiation. The data were integrated using the *SAINT* program,[9] with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to variation in the path length through the detector faceplate. A semiempirical absorption correction was made on the hemisphere of data with the *SADABS* program.[10] The structures were solved by direct methods using *SHELXS-97*[11] and refined using *SHELXL-97*.[12] Crystal data: monoclinic, space group *P2/c* (No. 13), a = 11.2026(5) Å, b = 6.7162(3) Å, c = 13.0527(6) Å, β = 107.457(2)°, V = 936.84(7) Å^3, Z = 4, ρ_{calc} = 5.333 g cm^{-3}, $2\theta_{max}$ = 50.08°, λ = 0.71073 Å, T = 298.0(2) K, total data 12314, unique data 1657, observed data [I > 2σ(I)] = 1385, μ = 13.609 mm^{-1}, 140 parameters, R_{int} = 0.0654, observed $R(F)/R_w(F)$ = 0.0299/0.0675 on |F^2|.

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(8) Crystal data for $NaIn(TeO_2)_3$: orthorhombic, space group *Pbca* (No. 61), a = 10.67300(5) Å, b = 8.26500(3) Å, c = 13.5683(2) Å, V = 1196.89(3) Å^3, Z = 8, ρ_{calc} = 5.428 g cm^{-3}, $2\theta_{max}$ = 56.62°, λ = 0.71073 Å, T = 298.0(2) K, total data 12525, unique data 1482, observed data [I > 2σ(I)] = 1234, μ = 13.542 mm^{-1}, 92 parameters, R_{int} = 0.045, observed $R(F)/R_w(F)$ = 0.0253/0.0533 on |F^2|.

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6238

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