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Anionic Templating: Synthesis, Structure, and Characterization of Novel Three-Dimensional Mixed-Metal Oxychlorides $Te_4M_3O_{15}\cdot Cl$ ($M = Nb^{5+}$ or Ta^{5+})

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Two new three-dimensional oxychlorides are reported, $Te_4M_3O_{15}\cdot Cl$ ($M = Nb^{5+}$ or Ta^{5+}). The isostructural materials were synthesized by chemical transport reactions utilizing TeO_2, M_2O_5, and MCl_5 ($M = Nb^{5+}$ or Ta^{5+}) as reagents. The compounds exhibit a three-dimensional cationic tunnel framework, with Cl^- anions occupying the tunnels. Crystal data: monoclinic, space group $C2/c$, $a = 18.9944(7)$ Å, $b = 7.8314(3)$ Å, $c = 21.1658(8)$ Å, $\beta = 116.6400(10)°$, $Z = 8$ ($T = 295$ K).

Because of their intercalation behavior, high-temperature superconductivity, optical properties, as well as novel crystal chemistry, metal oxychlorides are of great interest.[1−10] For example, a variety of amines have been intercalated into FeOCl, TiOCl, VOCl, and LnOCl (Ln = Ho, Er, Tm, and Yb).[1−3] In addition, $(Ca,Na)_2CuO_2Cl_2$[11] and $(Ca,Na)_2CaCu_2O_4Cl_2$[12] have been shown to be high T_c materials, whereas $BiSeO_3Cl$ is SHG active.[6] Metal oxychlorides are synthesized either through solid-state techniques,[13,14] hydrothermal methods,[15] chemical transport reactions,[16] or, in the case of LnOCl, a two step pyrohydrolysis procedure.[2,17] Structurally, except for the Sillen[18] and other layered phases,[7,19] the chloride anion is usually part of the framework, that is, directly bonded to one of the metal cations. Even in situations where the chloride is "free", a layered framework is usually observed.[20−21] We report in this communication the synthesis, structure, and characterization of two new three-dimensional oxychlorides, $Te_4M_3O_{15}\cdot Cl$ ($M = Nb^{5+}$ or Ta^{5+}). Similar to the Sillen and other layered phases, the chloride anions in our materials are not bonded to any of the metal cations. However, unlike the layered phases, the materials reported herein exhibit a three-dimensional channel structure with the chloride anion residing in the middle of the channel. To the best of our knowledge, only the naturally occurring mineral francisite, $Cu_3Bi(SeO_3)_2O_2Cl$,[22] shares this three-dimensional cationic channel topology.

Polycrystalline $Te_4Nb_3O_{15}\cdot Cl$ and $Te_4Ta_3O_{15}\cdot Cl$ were obtained by standard solid-state techniques. Under an atmosphere of dry nitrogen, TeO_2 (4.9 mmol, 99+ %, Aldrich), Nb_2O_5 (1.8 mmol, 99.99%, Aldrich; or Ta_2O_5, 99%, Aldrich), and $NbCl_5$ (0.7 mmol, 99%, Aldrich; or $TaCl_5$, 99.8%, Alfa) were thoroughly ground and put into a quartz tube, which was evacuated and sealed. The tube was heated to 700 °C (60 °C h^{-1}), held for 24 h, and cooled to room temperature. White polycrystalline powders, subsequently shown to be $Te_4Nb_3O_{15}\cdot Cl$ and $Te_4Ta_3O_{15}\cdot Cl$, were recovered. Single crystals of $Te_4Nb_3O_{15}\cdot Cl$ ($Te_4Ta_3O_{15}\cdot Cl$) were grown by transport reaction. TeO_2 (1.0 mmol), Nb_2O_5 (Ta_2O_5) (2.0 mmol), and $NbCl_5$ ($TaCl_5$) (0.2 mmol) were placed in a quartz tube (length = 12 cm, o.d. = 1.3 cm) that was

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evacuated and sealed. The tube was put in a tube furnace with a thermal gradient of 100 °C (cold zone 630° and hot zone 730 °C). Colorless block shaped crystals were observed in the cold zone (20% yield based on TeO_2) after 5 days. Crystals of $Te_4Nb_3O_{15}$•Cl were of much better quality than those of $Te_4Ta_3O_{15}$•Cl; thus, the former were used for single-crystal analysis.[23] Because both compounds can be made in bulk, powder X-ray diffraction was used to demonstrate the materials are isostructural.[27]

$Te_4Nb_3O_{15}$•Cl has a three-dimensional structure consisting of NbO_6 octahedra linked to asymmetric TeO_3 polyhedra. Each Nb^{5+} is bonded to six oxygen atoms with bond distances ranging from 1.781(8) to 2.228(8) Å, whereas each Te^{4+} cation is connected to three oxygen atoms with bond distances ranging from 1.853(8) to 1.909(8) Å. The Te^{4+} cations are in a highly asymmetric coordination environment attributable to their nonbonded electron pair. Each Nb^{5+} is linked through oxygen to four Te^{4+} and two additional Nb^{5+} cations, whereas each Te^{4+} cation is connected through oxygen to three other Nb^{5+} cations. Thus, in connectivity terms, the framework can be described as a $[4(TeO_{3/2})^+3(NbO_{6/2})^-]^+$ cation, with charge balance retained by the Cl^- anion. Bond valence calculations resulted in values ranging from 5.06 to 5.15 and from 3.74 to 3.93 for Nb^{5+} and Te^{4+}, respectively.[28,29]

The connectivity of the NbO_6 octahedra and TeO_3 polyhedra produce eight-membered ring (8-MR) channels that run along the [010] direction (see Figure 1). The walls of the channel consist of four NbO_6 octahedra and four TeO_3 polyhedra that alternate and are linked through oxygen atoms. The nonbonded electron pair on Te^{4+} points into the center of the channel, where the Cl^- anion resides (see Figure 2). The Cl^- anions are in an approximate square planar environment, surrounded by four Te^{4+} cations at a distance of 3.26(1) Å. The rings are connected along the [010] direction through corner linked NbO_6 octahedra, thus forming cationic channels. The 8-MR channels are separated along the [001] direction by columns of corner-shared NbO_6 octahedra.

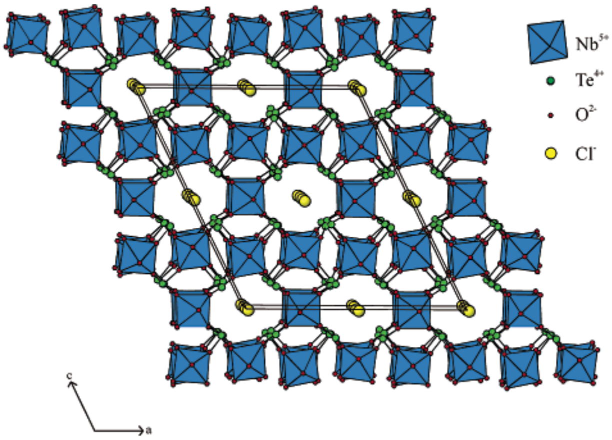

Figure 1. Polyhedral and ball-and-stick diagram of $Te_4Nb_3O_{15}$•Cl in the *ac*-plane.

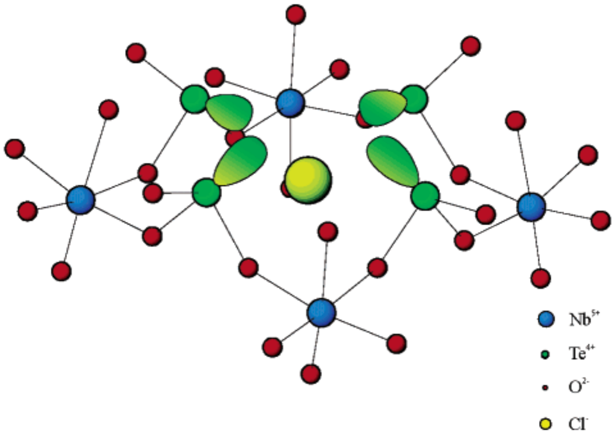

Figure 2. Ball-and-stick diagram of one ring of the 8-MR channel. Note how the Te^{4+} lone-pair (shown schematically) impedes the movement of the Cl^- anion.

Thermal analyses of both materials indicate the compounds are very robust with similar decomposition temperatures of 650 °C. For both materials, the chloride anion is initially lost at 650 °C. Immediately following this, the materials decompose and form $Te_3Nb_2O_{11}$[30] and $Te_2Ta_2O_9$[31] for $Te_4Nb_3O_{15}$•Cl and $Te_4Ta_3O_{15}$•Cl, respectively, as shown by powder X-ray diffraction measurements. The structural topology of the materials suggested the possibility for ion-exchange behavior. Initial ion-exchange experiments on polycrystalline $Te_4M_3O_{15}$•Cl (M = Nb^{5+} or Ta^{5+}) indicated that exchanging the Cl^- for other anions is difficult. If one examines the structures closely, it is not difficult to understand why no ion-exchange behavior is observed. Figure 2 shows one ring of the 8-MR channel with the lone-pair on the Te^{4+} cation represented schematically. A tetrahedral model is used to localize the lone-pair.[32] As can be seen, all of the lone-pairs point above the chloride, effectively preventing any mobility for the anion. Thus, the chloride anions are "locked" in place within the channel.

In summary, we have demonstrated that new three-dimensional oxychloride materials can be synthesized through

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(23) For $Te_4Nb_3O_{15}$•Cl, a colorless faceted crystal (0.15 × 0.20 × 0.25 mm^3) was used. Single-crystal data were collected on a Siemens SMART diffractometer equipped with a 1K CCD area detector using graphite monochromated Mo Kα radiation at 293 K. The data were integrated using the Siemens SAINT[24] program, with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in path length through the detector faceplate. ψ-Scan absorption corrections were applied. The structures were solved by direct methods using SHELXS-97[25] and refined using SHELXL-97.[26] Crystal data for $Te_4Nb_3O_{15}$•Cl: monoclinic, *C*2/*c*, a = 18.9944(7) Å, b = 7.8314(3) Å, c = 21.1658(8) Å, β = 116.6400(10)°, V = 2814.23(18) Å^3, Z = 8, $R(F)$ = 0.0369, GOF = 1.247.

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(27) For $Te_4Ta_3O_{15}$•Cl, a unit cell of a = 19.0249(7) Å, b = 7.7154(3) Å, c = 21.1662(9) Å, and β = 116.662(2)° was determined. The X-ray powder diffraction data for $Te_4Nb_3O_{15}$•Cl and $Te_4Ta_3O_{15}$•Cl have been deposited as Supporting Information.

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chemical transport techniques. We have been able to extend this family of materials utilizing MBr_5 ($M = Nb^{5+}$ or Ta^{5+}) as transport agents, thereby synthesizing $Te_4M_3O_{15}{\cdot}Br$ ($M = Nb^{5+}$ or Ta^{5+}). This recent synthesis suggests a general methodology has been developed for creating three-dimensional oxyhalide materials. We are in the process of growing crystals of the bromide phase, as well as synthesizing the fluoride and iodide analogues.

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Supporting Information Available: Experimental and calculated powder diffraction data for $Te_4Nb_3O_{15}{\cdot}Cl$ and $Te_4Ta_3O_{15}{\cdot}Cl$ and crystallographic information (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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