Structures and Properties of Functional Metal Selenites and Tellurites

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Metal selenites and tellurites are a class of very important compounds. In this paper, the structures and properties of metal selenites or tellurites combining with transition-metal (TM) ions with the d0 electronic configuration or tetrahedral MO4 building blocks of post-transition main-group elements were reviewed. Most compounds in the alkali or alkaline-earth—d0 TM—SeIV (or TeIV)—O systems exhibit extended anionic architectures composed of distorted octahedra of (d0) TM cations and tellurite or selenite groups. The distortion of the octahedron is always away from the lone-pair cation, and some of them exhibit excellent second-order nonlinear optical properties due to the additive effects of two types of bond polarizations. Because of the high coordination number of LnIII ions, most of compounds in the Ln—d0 TM—SeIV (or TeIV)—O systems are not second-harmonic-generation active; however, they are able to emit strong luminescence in the visible or near-IR region; also in most cases, the d0 TM cations are in tetrahedral geometry and are well separated from selenite or tellurite groups. It is also interesting to note that the selenite group is normally “isolated”, whereas the TeO4 (x = 3—5) can be polymerized into a variety of discrete polynuclear anionic clusters or extended architectures via Te—O—Te bridges.

Introduction

Noncentrosymmetric (NCS) compounds exhibit many interesting and useful properties such as ferroelectricity, piezoelectricity, and second-order nonlinear optical (NLO) behavior.1 With inorganic materials, the macroscopic acen-
tricity is often a manifestation of the asymmetric coordination environments of the cations. One of the important classes of NCS compounds is based on cations susceptible to second-
order Jahn–Teller (SOJT) distortion.2 Such a type of distortion can occur in two different types of cations, d0 transition metals (TM; Ti4+, V4+, Nb5+, Mo6+, W6+, etc.) and cations with stereoeactive lone pairs (Se4+, Te4+, Sb3+, etc.), both in asymmetric coordination environments. With the octahedrally coordinated d0 TM cations, SOJT effects occur when the empty d orbitals of the metal mix with the filled p orbitals of the ligands. In extended structures, this mixing results in a host of nearly degenerate electronic configurations that can be removed through the spontaneous distortion of the d0 TM.2 The d0 TM cation can be distorted toward either a face (local C3 direction), an edge (local C2 direction), or a corner (local C4 direction) of the MO6 octahedron. The situation with the lone-pair cations is more complex. The structural distortion and polarization was thought to be through the mixing of the metal cation s and p orbitals. Recently, it is believed that the oxide anion also plays an important role in the lone-pair formation. The interaction of the s and p orbitals of the metal cation with the oxide anion p states is critical for lone-pair formation. No matter how the lone pair is created, its structural consequences are profound because the lone pair “pushes” the oxide ligands toward one side of the cation, resulting in a highly asym-
metric coordination environment.3 Studies have shown that compounds containing both types of cations may have a large second-harmonic-generation (SHG) efficiency due to the “constructive” addition of these polarizations, which will be discussed in more detail later.

Tetrahedral groups such as silicates, phosphates, and germanates are very important building units in zeolites and other porous materials that have been widely used as

Some of phosphates such as KDP (KH2PO4) and KTP (KTiOPO4) are also very important second-order NLO materials. Therefore, the combination of these tetrahedral groups with the lone pair containing a TeIV or SeIV cation may also result in new inorganic compounds with novel structural topologies and SHG properties.

It should also be pointed out that the transition-metal oxyhalides of SeIV or TeIV display many types of novel structures and interesting magnetic properties such as low-dimensional magnets, etc. Transition-metal tellurium(IV) or selenium(IV) oxyhalides can be regarded as “chemical scissors”. The later TM cations form bonds to both oxygen and halide, while lone-pair cations tend to form bonds only to oxygen anions. This chemical difference can be utilized to reduce the dimensionality of the TM arrangements with interesting magnetic properties. It is amazing that many compounds in above systems can be generally formulated as Mn+((QO3)nX2), where M, Q, and X represent the TM, Se (or Te), and the halide anion, respectively. Our exploration of the missing members in the nickel system afforded four new compounds, namely, Ni4Cu(Te5O13)Cl2, Dy2Cu(Te5O13)Br2, and Nd4Cu(Te5O13)Cl2. The halide anion may be involved in metal coordination or remain isolated.

In this paper, our discussion will be focused on only two important systems: combination of TeIV or SeIV with d0 TMs or with the tetrahedral groups of main-group elements such as SiO4, GeO4, BO4, PO4, etc. Our group and many other groups have been exploring new NCS compounds in these two systems during the past few years (Table 1).

Part I. Combination of d0 TM Ions with SeIV or TeIV

1. Alkali (or Alkaline Earth)—d0 TM—SeIV (or TeIV)—O System. This system contains a large number of compounds, some of which possess good SHG properties (Table 1). The TM ions with the d0 electronic configuration are mostly Mo6+, Nb5+, and Ta5+, but there are also some examples involving V5+, Nb5+, and Ta5+.

Five compounds with four different structural types were reported in alkali-metal—molybdenum(VI) selenium(IV) oxide systems A2MoSeO6 (A = Na+, K+, Rb+) and A2(MoO3)3(SeO3) (A = NH4+, Cs+). The first three compounds feature a 3D anionic network, a 0D anionic dimer, and a 1D anionic chain, respectively. The 3D anionic structure of Na2MoSeO6 (NCS space group P213) is based on alternative linkages of MoO6 octahedra (distorted toward a face) and SeO3 groups, forming tunnels of Mo2Se2 four-membered rings and MoSe4 eight-membered rings; the sodium cations occupy the larger tunnels. Na2MoSeO6 revealed a weak SHG intensity of about 10 × SiO2. The structure of K2MoSeO6 contains two edge-sharing Mo6 octahedra, each of which is further chelated by a SeO3 group, forming [Mo2Se2O12]6− clusters that are separated by K+ ions.


In Rb₂MoO₆O₆, the MoO₆ octahedra are interconnected into a 1D chain via corner-sharing, the SeO₄ groups are hanging on both sides of the chain, and each of them shares an edge with a MoO₆ octahedron.¹⁰ The last two compounds (space group P6₃) are isostructural and feature a 2D hexagonal tungsten bronzelike anionic layer of MoO₆ octahedra capped on one side by pyramidally coordinated SeIV;¹⁰ such a layer maintained up to the melting temperature (around 450 °C).¹¹ The Mo₆⁺ ions are distorted toward a face of the MoO₆ octahedron in A₂Mo₃TeO₁₂ (A = NH₄⁺, Cs⁺), whereas they are distorted toward an edge in A₂Mo₆Te₂O₁₄·6H₂O (A = Rb⁺, K⁺). The Te₄⁺ cations in both types of compounds adopt the same asymmetric coordination environments and are bonded to three O atoms.

Three types of compounds were found in the alkali–Mo₆⁺–Te⁴⁺–O systems, namely, (NH₄)₂WTe₂O₈, Rb₂W₂TeO₉, and A₂W₃TeO₁₂ (A = K⁺, Rb⁺, Cs⁺).¹² (NH₄)₂WTe₂O₈ crystallizes in the noncentrosymmetric (NCS) polar space group P2₁ (No. 4). It exhibits a 2D structure comprising of WO₆ octahedra connected to Te₄O₆ tetrahedra and 1D vanadium-oxide helical chains.

### Table 1. Te⁴⁺ and Se⁴⁺ Compounds Showing NCS Structures and SHG Properties

<table>
<thead>
<tr>
<th>compound</th>
<th>space group</th>
<th>structural feature</th>
<th>SHG efficiency</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TeO₃</td>
<td>P₄12/2</td>
<td>3D network of corner-sharing TeO₃ groups</td>
<td>5 × SiO₂</td>
<td>3b</td>
</tr>
<tr>
<td>Te₂O₅</td>
<td>P2₁</td>
<td>3D network of corner-sharing Te₄O₄ groups and Te₆O₆ octahedra</td>
<td>400 × SiO₂</td>
<td>3b</td>
</tr>
<tr>
<td>Te₅O₆</td>
<td>Iₐ</td>
<td>3D network of corner-sharing Se₄O₆ and Te₄O₆ groups</td>
<td>400 × SiO₂</td>
<td>3a, 3b</td>
</tr>
<tr>
<td>Te₅SeO₇</td>
<td>Pmn2₁</td>
<td>2D layer composed of Se⁴⁺O₄ tetrahedra and Te₄⁺O₄ groups</td>
<td>200 × SiO₂</td>
<td>3b</td>
</tr>
<tr>
<td>Bi₂Te₃O₇</td>
<td>Abm2</td>
<td>3D network of corner-, edge-, or face-sharing BiO₆, BiO₅, and TeO₃ groups</td>
<td>300 × SiO₂</td>
<td>3c</td>
</tr>
<tr>
<td>Na₂MoSeO₆</td>
<td>P₂₁3</td>
<td>3D anionic structure based on alternative linkages of MoO₆ octahedra and SeO₄ groups</td>
<td>10 × SiO₂</td>
<td>10a</td>
</tr>
<tr>
<td>Na₂Mo₅TeO₁₆</td>
<td>P₂</td>
<td>1D chain consisting of MoO₁₂ trimers that are connected TeO₄– anions</td>
<td>500 × SiO₂</td>
<td>11a</td>
</tr>
<tr>
<td>(NH₄)₂TeO₅</td>
<td>P₆₃</td>
<td>2D layer consisting of WO₆ octahedra connected to TeO₄ polyhedra</td>
<td>250 × SiO₂</td>
<td>12a</td>
</tr>
<tr>
<td>Na₂W₂TeO₅</td>
<td>Iₐ</td>
<td>3D structure built from a corrugated 2D tungsten oxide layer further interconnected by TeO₆ groups</td>
<td>500 × SiO₂</td>
<td>12b</td>
</tr>
<tr>
<td>Rb₂W₆TeO₁₄</td>
<td>P31c</td>
<td>2D tungsten oxide layer capped by TeO₆ groups on one side</td>
<td>200 × SiO₂</td>
<td>13b</td>
</tr>
<tr>
<td>Cs₂W₆TeO₁₄</td>
<td>P₆₃</td>
<td>2D tungsten oxide layer capped by TeO₆ groups on one side</td>
<td>400 × SiO₂</td>
<td>13b</td>
</tr>
<tr>
<td>BaMo₆TeO₉</td>
<td>P₂₁</td>
<td>2D layer built by dimers of edge-sharing MoO₆ octahedra that are interconnected by TeO₆ groups</td>
<td>600 × SiO₂</td>
<td>14b</td>
</tr>
<tr>
<td>Ba₂W₆TeO₁₄</td>
<td>P₂₁</td>
<td>2D layer built by dimers of edge-sharing WO₆ octahedra that are interconnected by TeO₆ groups</td>
<td>500 × SiO₂</td>
<td>14b</td>
</tr>
<tr>
<td>Cd₂V₂Te₃O₁₅</td>
<td>P₂₁₂₁</td>
<td>3D network in which the cadmium tellurite layers are further interconnected by both “isolated” VO₆ tetrahedra and 1D vanadium-oxide helical chains</td>
<td>1.4 × KDP</td>
<td>23</td>
</tr>
<tr>
<td>B₃SeO₇</td>
<td>P₂₁₂₁</td>
<td>3D network composed of B₂O₅⁺⁺ anions interconnected by Se⁴⁺ atoms</td>
<td>2.2 × KDP</td>
<td>27</td>
</tr>
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</table>

2D tungsten oxide layer of corner-sharing WO₆ octahedra with W₃ and W₆ rings. The TeO₃ groups in K₂W₁TeO₁₂ act as interlayer linkers to form a 3D structure. In Rb and Cs compounds, the TeO₃ groups only cap on the same side of the W₃ rings; therefore, the compounds are 2D. The K compound is centrosymmetric, whereas the Rb and Cs compounds are acentric and revealed strong SHG efficiencies of 200 and 400 × SiO₂, respectively. These can be explained by the different radii of the alkali-metal ions; the larger one will have larger interlayer O•••O separations, which allows a similar capping of TeO₃ groups and the formation of noncentrosymmetric structures.¹²c

The AE²⁺−MoO₃⁺ (W⁶⁺)−Se⁴⁺ (Te⁴⁺)−O systems are still less explored.¹⁴ Two compounds in the Ba−Mo−Se−O system were reported, BaMoO₃(SeO₃) and BaMoO₃(SeO₃)₂. BaMoO₃(SeO₃) exhibits a layered structure in which MoO₆ octahedra, with the A₂(MoO₃)₃(SeO₃)₂ (A=K, Rb, Cs) octahedron (distorted toward a face) are bridged by Se⁴O₃ groups, forming Mo₃Se₂ four-membered rings and Mo₆Se₃ six-membered rings. BaMoO₃(SeO₃)₂ is acentric (Cmc₂₁) and features a 3D network composed of pairs of corner-sharing MoO₆ octahedra bridged by SeO₃ groups. The MoO₆ octahedron is distorted toward an edge (the local C₂ direction).¹₄a BaMo₂TeO₉ and Ba₃W₂TeO₉ are isostructural and crystallized in the polar space group P2₁; their structures feature an anionic layer composed of MoO₆ octahedra linked to the asymmetric TeO₃ polyhedra. The MoO₆ octahedra in BaMo₂TeO₉ are distorted toward a face (along the local C₃ [111] direction) with three short and three long Mo−O distances. The WO₆ octahedra in Ba₂W₂TeO₉ exhibit two types of distortion: toward a face as discussed above and toward an edge with two short, two normal, and two long W−O bonds. Two MoO₆ octahedra form a dimer via a M−O−M bridge and such dimeric units are further interconnected by TeO₃ groups via M−O−Te bridges. BaMo₂TeO₉ and Ba₃W₂TeO₉ revealed extremely strong SHG responses of 600 and 500 × SiO₂, respectively.¹₄b

Several phases were reported in A−V⁵⁺−Se⁴⁺−O systems: AVSeO₅ (A=Rb, Cs), A(MO₃)₂(SeO₃) (A=K⁺, Rb⁺, Cs⁺, NH₄⁺), and the V⁵⁺/V⁴⁺ mixed-valent K₂V₂SeO₅.¹⁵ A(MO₃)₂(SeO₃) (A=K⁺, Rb⁺, Cs⁺, NH₄⁺) are isostructural with A₂(MoO₃)₂(SeO₃)₂ (A=NH₄⁺, Cs⁺),¹⁰b featuring hexagonal layers of corner-sharing VO₆ octahedra, with the SeO₃ groups capping on one side of the vanadium(V) oxide layer; the interlayer distances are much shorter than those of the corresponding Mo compounds because of the much fewer cations needed to balance the charge.¹₅a,b The structure of the polar AVSeO₅ (A=Rb, Cs; space group P2₁) is a 3D anionic network formed by alternative linkages of VO₆ square pyramids and SeO₃ groups via corner-sharing, creating two types of helical tunnels along the b axis composed of four- and eight-membered rings. The alkali-metal ions occupy the large tunnels.¹⁵b K₂VeO₅ contains both V⁵⁺ and V⁴⁺ ions, in octahedral and tetrahedral coordination environments, respectively. Its structure features a double layer of [V₂SeO₇]− composed of corner-sharing VO₆ octahedra, VO₄ tetrahedra, and SeO₃ groups.¹⁵c

Only one compound was reported for the alkaline earth−V⁵⁺−Se⁴⁺−O family. Ba₃(VO₃)₂(SeO₃)₂·H₂O exhibits a 2D-layered structure consisting of layers of VO₆ square pyramids linked to SeO₃ polyhedra, with the Ba²⁺ cations and water molecules occupying the interlayer region.¹⁶ Each layer consists of eclipsed 12-membered V₆Se₆ rings and smaller eight-membered V₄Se₄ rings. Each V₅⁺ is bonded to five O atoms in a distorted square-pyramidal environment with two “short” [1.642(9) and 1.647(9) Å] and three “normal” bonds [1.952-(8)−2.006(9) Å]. Three of the five O atoms are further bonded to Se⁴⁺ cations, whereas the two “short” V−O bonds remain terminal. The selenite groups adopt two types of binding modes: tridentate bridging with three Se−O−V bridges and bidentate with only two Se−O−V bridges.

Reports on A(Åe)−Nb⁵⁺ (or Ta⁵⁺)−Se⁴⁺ (or Te⁴⁺)−O systems are still rare.¹⁷ The structural backbone of Na₁₁ Nb₅ Te₆ O₁₈ may be considered as two sets of corner-shared NbO₆ octahedral chains. The “first” chain consists of one row of corner-shared NbO₆ octahedra that are linked by TeO₃ and TeO₄ polyhedra, whereas the “second” chain consists of two rows of corner-shared NbO₆ octahedra that are linked by TeO₃ groups. Each of these chains of octahedra runs parallel to the [010] direction. The “first” and “second” chains are linked by the TeO₃ and TeO₄ groups, along the [100] and [010] directions, resulting in the 3D topology. The Te⁴⁺ cation that connects the two chains is partially occupied. The Na⁺ cations reside in the spaces between the two chains. The second compound, Na Nb₅ Te₆ O₁₈, also exhibits a 3D structure consisting of corner-linked NbO₆ octahedra that are connected to asymmetric TeO₃ and TeO₄ groups. Similar to Na₁₁ Nb₅ Te₆ O₁₈, the structural backbone of Na Nb₅ Te₆ O₁₈ may also be considered as an infinite chain of corner-shared NbO₆ octahedra. The chain consists of three corner-shared NbO₆ octahedra running along the [001] direction. These octahedra are infinite, through additional corner-sharing, in the [010] direction. The TeO₃ and TeO₄ groups serve to link these NbO₆ octahedra. The Na⁺ cations reside in the spaces between the NbO₆ octahedra. In both compounds, the distortion of the NbO₆ octahedron is along the local C₁ direction.¹⁷ The crystal structures of Ba₃M₆Te₂O₂₃ (M=Nb, Ta) are dominated by the [M₂O₆]¹²⁻ anionic network with incorporated Ba²⁺ and Te⁴⁺ ions. Tunnels based on M₆, M₆Te and M₆Te₂ rings are formed along the [010] direction; the Ba²⁺ ions occupy the tunnels of eight-membered rings.¹⁷b

2. Ln⁻d⁰ TM−Te⁴⁺ or Se⁴⁺−O Systems. Only three compounds, namely, LaNbTe₆O₁₈ and La₃M₆Te₂O₂₃ (M=Nb, Ta), were reported by the Halasyamani group before our group’s work on this research field.¹⁸ La Nb Te₆ O₉ consists of 1D corner-linked chains of NbO₆ octahedra that are

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connected by TeO$_3$ polyhedra. La$_2$M$_2$Te$_6$O$_{23}$ (M = Nb, Ta) also has a 1D crystal structure, consisting of different types of chains that run parallel to the c axis. One chain consists of corner-linked MO$_6$ octahedra. Each MO$_6$ octahedron shares additional corners with TeO$_3$ and TeO$_2$ groups. The TeO$_3$ polyhedra are separated from each other, but the TeO$_2$ groups are connected through an O atom into the TeO$_4$ “chain”, which is broken at random intervals because of the defects on the bridging O atoms. The other chain is the isolated TeO$_4$ chain that is also broken at random intervals because of the defects. In all three compounds, the Nb$^{5+}$ or Ta$^{5+}$ cation is distorted toward an edge with two “short”, two “normal”, and two long M$^{5+}$–O bonds; the short ones are terminal and the long ones are connected to a Te$^{4+}$ cation, whereas the remaining two bonds are involved in the M$^{5+}$–O–M$^{5+}$ bridges. In all three compounds, Te$^{4+}$ cation is in an asymmetric coordination environment attributable to its stereoactive lone pair.

We think that a slight change of the radius of the Ln$^{III}$ ion may induce a completely different structure; in other words, the “lanthanide contraction” may play an important role in the structures formed. Furthermore, lanthanide compounds are capable of emitting strong luminescence in the visible and near-IR regions; both oxyanions of d$^0$ TM and Te$^{IV}$ (or Se$^{IV}$) are good activators for luminescence of the Ln$^{III}$ ions. Like corresponding alkalai or alkaline-earth compounds, Ln$^{III}$ compounds with NCS structures may also be formed. Therefore, systematic investigation of the lanthanide selenium(IV) or tellurium(IV) oxides with additional TM ions with a d$^0$ electronic configuration may give rise to new lanthanide NLO materials or luminescent materials. Solid-state reactions of lanthanide(III) oxide (and/or lanthanide(III) oxychloride), MoO$_3$ (or WO$_3$) and TeO$_2$ at high temperature led to 12 new compounds with 8 different types of structures, namely, Nd$_3$MoSe$_2$O$_{10}$, Gd$_2$MoSe$_3$O$_{12}$, La$_2$MoTe$_4$O$_{12}$, Nd$_2$MoTe$_3$O$_{12}$, Ln$_2$MoTe$_4$O$_{14}$ (Ln = Pr, Nd), La$_2$WTe$_2$O$_{18}$, Nd$_2$W$_2$Te$_2$O$_{18}$, and Ln$_2$MTe$_2$O$_{12}$Cl$_4$ (Ln = Pr, Nd; M = Mo, W).

Nd$_3$MoSe$_2$O$_{10}$ can also be formulated as Nd$_3$(MoO$_4$)$_2$(SeO$_3$)$_2$. Its structure features a 3D network in which the Nd$^{III}$ ions are interconnected by SeO$_3^{2–}$ anions and MoO$_4$ tetrahedra (Figure 1). Both Nd1 and Nd2 are eight-coordinated by eight O atoms with Nd–O distances in the range of 2.407(7)–2.540(7) Å. The Mo$^{VI}$ atom is in a slightly distorted tetrahedral coordination environment with Mo–O distances in the range of 1.740(7)–1.816(6) Å. The interconnection of Nd1 atoms via bridging selenite groups leads to a (001) layer, whereas Nd2 atoms are bridged by MoO$_4$ tetrahedra to form a (002) layer. The above two types of layers are further interconnected via Nd–O–Se bridges into a 3D network (Figure 1). The lone pairs of the Se$^{IV}$ cations are oriented toward the cavities of the structure.

When the molar ratio of Se/Ln was increased to 3:2, Gd$_2$MoSe$_3$O$_{12}$ with a different structure was obtained.

Figure 1. View of the structure of Nd$_3$MoSe$_2$O$_{10}$ down the a axis. The MoO$_4$ tetrahedra are shaded in cyan. Nd, Se, and O atoms are drawn as green, yellow, and red circles, respectively.

Figure 2. View of the structure of Gd$_2$MoSe$_3$O$_{12}$ down the b axis. The MoO$_4$ tetrahedra are shaded in cyan. Gd, Se, and O atoms are drawn as green, yellow, and red circles, respectively.

Gd$_2$MoSe$_3$O$_{12}$ can also be formulated as Gd$_2$(MoO$_4$)$_2$(SeO$_3$)$_3$, which can be considered as one O$^{2–}$ anion of Nd$_2$MoSe$_2$O$_{10}$ being replaced by the third selenite group. The structure of Gd$_2$MoSe$_3$O$_{12}$ features a 3D network of gadolinium(III) selenite, with the MoO$_6$ octahedra occupying the cavities of the network. Both Gd atoms in the asymmetric unit are eight-coordinated, with Gd–O distances ranging from 2.337(5) to 2.485(5) Å. Unlike that in Nd$_2$MoSe$_2$O$_{10}$, the Mo$^{VI}$ atom in Gd$_2$MoSe$_3$O$_{12}$ is octahedrally coordinated by three O atoms from three selenite groups and three O$^{2–}$ anions (Figure 2). The MoO$_6$ octahedron is distorted toward a face (local C$_3$ direction), exhibiting three “long” and three “short” Mo–O bonds. The magnitude of the distortion (Δd$_{0}$) is 1.492. The interconnection of the Gd$^{III}$ ions by selenite groups results in a 3D network with tunnels running along the b axis. The MoO$_6$ octahedra are located at the tunnels formed by gadolinium(III) selenite (Figure 2).

The structure of La$_3$MoTe$_2$O$_{12}$ is composed of two La$^{3+}$ ions, one MoO$_4^{2–}$ anion, and one Te$_2$O$_4^{4–}$ anion. It can be considered as two selenite groups in Nd$_2$MoSe$_2$O$_{10}$ being replaced by a Te$_2$O$_4^{4–}$ anion. The La$^{3+}$ ion is nine-coordinated by seven O atoms from four Te$_3$O$_8^{4–}$ anions and...
two O atoms from two MoO$_4^{2-}$ anions. The La—O distances range from 2.451(8) to 2.821(8) Å. The trinuclear Te$_3$O$_8^{4-}$ anion is formed by one TeO$_4$ group corner-sharing with two TeO$_3$ groups. The MoVI cation is in a slightly distorted tetrahedral coordination geometry, with the Mo—O distances ranging from 1.754(8) to 1.793(11) Å. The interconnection of the La$^{3+}$ by chelating and bridging Te$_3$O$_8^{4-}$ anions led to a 3D network with tunnels along the $a$ axis. These tunnels are formed by 10-membered rings (six La and four Te). The MoO$_4$ polyhedra are located at the above tunnels and connected with the La$^{3+}$ ions via corner-sharing (Figure 3).

Nd$_2$MoTe$_3$O$_{12}$ can be formulated as Nd$_2$(MoO$_4$)(TeO$_3$)(Te$_2$O$_5$); it can also be considered as the Te$_3$O$_8^{4-}$ anion in La$_2$MoTe$_3$O$_{12}$ being replaced by a tellurite and a ditellurite group. Different from the La$^{3+}$ ion in La$_2$MoO$_4$(Te$_3$O$_8$), the Nd$^{3+}$ ion in Nd$_2$(MoO$_4$)(TeO$_3$)(Te$_2$O$_5$) is eight-coordinated by eight O atoms, with the Nd—O distances in the range of 2.324(4)–2.603(4) Å. The Te$^{IV}$ cations of the tellurite and ditellurite groups are coordinated by three O atoms in an asymmetric environment. The Te—O distances are in the range of 1.838(4)–1.987(2) Å. The interconnection of Nd$^{III}$ ions by bridging tellurite and ditellurite groups afforded a layered architecture (Figure 4). The MoO$_4$ tetrahedron was capped on four Nd$^{III}$ ions of the 2D layer with the terminal O1 atom toward the interlayer space (Figure 4). The interlayer distance is about 8.85 Å.$^{19a}$

The use of more TeO$_2$ in the syntheses led to Ln$_2$MoTe$_4$O$_{14}$ (Ln = Pr, Nd). Both compounds are isostructural and feature a 3D network in which the Ln$^{III}$ ions are interconnected by 1D Te$_4$O$_{10}^{4-}$ chains and MoO$_4$ tetrahedra (Figure 5). Therefore, Ln$_2$MoTe$_4$O$_{14}$ (Ln = Pr, Nd) can also be formulated as Ln$_2$(MoO$_4$)(Te$_4$O$_{10}$) (Ln = Pr, Nd). Among two unique Ln$^{III}$ atoms in the asymmetric unit, one is eight-coordinated by eight tellurite O atoms whereas the other is eight-coordinated by six tellurite O atoms and two O atoms from two molybdate anions. The Mo$^{VI}$ atom is in a slightly distorted tetrahedral coordination environment with Mo—O distances in the range of 1.733(4)–1.779(4) Å. The Te$^{IV}$ atoms are three- or four-coordinated by O atoms in an asymmetric environment. The Te—O distances are in the range of 1.826(3)–2.457(3) Å. The TeO$_3$ and TeO$_4$ groups are interconnected via corner-sharing into a novel 1D Te$_4$O$_{10}^{4-}$ anionic chain (Scheme 1). The interconnection of Nd1 and Nd2 atoms via bridging Te$_4$O$_{10}^{4-}$ anionic chains led to neodymium(III) tellurium(IV) oxide layers, which are further interconnected by MoO$_4$ tetrahedra into a 3D network with apertures along the $a$ axis. The aperture is formed by 10-membered rings containing six Ln$^{III}$ ions, two MoO$_4^{2-}$ anions, and two TeO$_4$ groups. The lone pairs of the Te$^{IV}$ atoms are oriented toward the apertures of the structure (Figure 5). It is worth comparing the structures of Ln$_2$MoTe$_4$O$_{14}$ (Ln = Pr, Nd) with those of La$_2$MoTe$_3$O$_{12}$ and Nd$_2$MoTe$_3$O$_{12}$. All four compounds contain MoO$_4$ tetrahedra; however, their Te—O architectures are completely different: La$_2$MoTe$_3$O$_{12}$ features discrete Te$_2$O$_5^{2-}$ anions, whereas Nd$_2$MoTe$_3$O$_{12}$ contains both TeO$_4^{2-}$ and dimeric Te$_2$O$_5^{2-}$ anions, and 1D Te$_4$O$_{10}^{4-}$ anions are formed in Ln$_2$MoTe$_4$O$_{14}$ (Ln = Pr, Nd). Nd$_2$MoTe$_3$O$_{12}$ features a layered structure with MoO$_4$ tetrahedra hanging between two

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**Figure 3.** View of the structure of La$_2$MoO$_4$(Te$_3$O$_8$) down the $a$ axis. The MoO$_4$ tetrahedra are shaded in cyan. La, Te, and O atoms are drawn as green, yellow, and red circles, respectively.

**Figure 4.** View of the structure of Nd$_2$(MoO$_4$)(TeO$_3$)(Te$_2$O$_5$) down the $c$ axis. The MoO$_4$ tetrahedra are shaded in cyan. Nd, Te, and O atoms are drawn as green, yellow, and red circles, respectively.

**Figure 5.** View of the structure of Ln$_2$MoTe$_4$O$_{14}$ down $a$-axis. The MoO$_4$ tetrahedra are shaded in cyan. Ln, Te, and O atoms are drawn as green, yellow, and red circles, respectively.
La$_2$MoTe$_3$O$_{12}$ can also be formulated as the interlayer space (Figure 6). In Ln$_5$MoTe$_7$O$_{23}$Cl$_3$ (Ln = Pr, Nd), the MoO$_4$ tetrahedron serves as a bridge between two lanthanide(III) tellurium(IV) oxide layers.

The above synthetic methods were also applied to the Ln$^{III}$–W$^{VI}$–Te$^{IV}$–O systems. La$_2$WTe$_6$O$_{18}$ was obtained when we attempted to prepare the W$^{VI}$ analogue of La$_2$MoTe$_7$O$_{12}$. La$_2$WTe$_6$O$_{18}$ can also be formulated as La$_3$(WO$_6$)(Te$_3$O$_7$)$_2$. The La1 atom is 10-coordinated by seven O atoms from two Te$_3$O$_7^2^-$ anions and three O atoms from three WO$_4$ tetrahedra. The La–O distances range from 2.487(4) to 2.884(8) Å. The W$^{VI}$ atom is tetrahedrally coordinated by four O atoms, with the W–O distances ranging from 1.724(6) to 1.786(1) Å. The Te$^{IV}$ atom is coordinated by four O atoms with Te–O distances in the range of 1.850(4)–2.193(1) Å. The TeO$_4$ groups are further interconnected into a Te$_3$O$_7^2^-$ layer via corner-sharing (Scheme 1). Within the layer, three-membered rings and “pear-shaped” six-membered rings are found. Similar Te$_3$ and “pear-shaped” Te$_6$ rings have been reported in Cd$_2$Cl$_6$(TeO$_4$)$_2$.

The interconnection of La$^{III}$ ions by bridging WO$_4^{2-}$ anions led to a 2D [La$_2$WO$_4$]$^{4+}$ layer along the $ab$ plane. One [La$_2$WO$_4$]$^{4+}$ layer and two Te$_3$O$_7^2^-$ layers are further interconnected into a thick layer in the $ab$ plane via La–O–Te bridges (Figure 6). The thickness of the layer is about 7.65 Å, and the interlayer opening width is about 3.0 Å. This type of layer can also be viewed as the [La$_2$WO$_4$]$^{4+}$ layer being sandwiched between two Te$_3$O$_7^2^-$ anionic layers. The lone-pair electrons of Te$^{IV}$ atoms are oriented toward the interlayer space (Figure 6).

Nd$_2$W$_2$Te$_2$O$_{13}$ with a different structure was obtained in our attempts to prepare the Nd$^{III}$ analogue of La$_2$WTe$_6$O$_{18}$. Nd$_2$W$_2$Te$_2$O$_{13}$ features a 3D network structure in which the W$_2$O$_{10}$ dimers occupy the large apertures formed by neodymium telluride (Figure 7). Among two unique Nd$^{III}$ ions in the asymmetric unit, one is eight-coordinated whereas the other one is nine-coordinated. The Nd–O distances range from 2.333(5) to 2.681(5) Å. Unlike that in La$_2$WTe$_6$O$_{18}$, both of the W$^{VI}$ cations in Nd$_2$W$_2$Te$_2$O$_{13}$ are octahedrally coordinated. W1 is coordinated by two O atoms from two tellurite groups and four terminal O atoms, whereas W2 is coordinated by one O atom from a tellurite group and five terminal O atoms. A pair of WO$_6$ octahedra is interconnected via edge-sharing into a W$_2$O$_{10}^{8-}$ dimer. Both of the WO$_6$ octahedra are severely distorted. The W1 atom is distorted toward a face (local C$_3$ direction) with three “short” [1.743(6)–1.834(5) Å] and three “long” [2.033(5)–2.300(5) Å] W–O bonds, whereas the W2 atom is distorted toward an edge (C$_2$) with two “short” [1.745(6) and 1.767(6) Å], two “normal” [1.900(5) and 1.930(5) Å], and two “long” [2.172(5) and 2.232(5) Å] W–O bonds. Again both W$^{VI}$ cations are distorted away from the O atoms that bonded to the Te$^{IV}$ cations. The magnitudes of the distortion (∆) are 1.118 and 0.945 Å respectively for W1O$_6$ and W2O$_6$. The interconnection of the Nd$^{III}$ ions by the tellurite groups resulted in a 3D network with two types of apertures along the $a$ axis (Figure 7). The large apertures with a narrow-long shape are formed by 10-membered rings composed by four TeO$_3$ groups and six Nd$^{III}$ ions, and the small ones are formed by four-membered rings composed of two Nd1 and two Te1O$_2$ groups. The W$_2$O$_{10}$ dimers are located at the large apertures (Figure 7). In Nd$_2$W$_2$Te$_2$O$_{13}$, each W$_2$O$_{10}$ dimer connects with two TeO$_3$ groups (one in a unidentate fashion, and the other in a bidentate bridging fashion) to form a [W$_2$Te$_2$O$_{13}$]$^{6-}$ anion. Therefore, the structure of Nd$_2$W$_2$Te$_2$O$_{13}$ can also be viewed as the Nd$^{III}$ ions being interconnected by [W$_2$Te$_2$O$_{13}$]$^{6-}$ anions via Nd–O–Te and Nd–O–W bridges (Figure 7).

When chloride anion was introduced into the Ln–Mo (W)–Te–O system, isostructural Ln$_3$MTe$_2$O$_3$Cl$_3$ (Ln = Pr, Nd; M = Mo, W) were obtained. These compounds feature a 3D network of a lanthanide(III) molybdenum(VI) tellurium(IV) oxychloride with large apertures occupied by isolated Cl anions and the lone-pair electrons of Te$^{IV}$ (Figure 8). Ln$_3$MTe$_2$O$_3$Cl$_3$ can also be formulated as Ln$_3$(MO$_4$)(Te$_3$O$_9$)(TeO$_3$)$_2$Cl$_3$. The asymmetric unit of Ln$_3$MTe$_2$O$_3$Cl$_3$ contains three unique Ln$^{III}$ ions, one M$^{VI}$ cation, and four Te atoms. Two Ln$^{III}$ ions are 8-coordinated, whereas the third one is 10-coordinated. The Ln–Cl distances are significantly longer than those of the Ln–O bonds. The M$^{VI}$ cation is in...
...sublevels if both the lower and upper levels of $^4F_{3/2}$ are of $^4I_{9/2}$ and $^4F_{3/2}$ transitions at 10 K, whereas Nd$_2$W$_2$Te$_2$O$_{13}$ displays eight and nine subbands at 10 K upon excitation at 288 nm. The lifetimes for the $^4I_{9/2} \rightarrow ^4I_{11/2}$ transition were measured to be 0.21 and 0.20 ms and 3.2 and 3.6 $\mu$s respectively for Nd$_2$MoSe$_2$O$_{10}$ and Nd$_2$MoTe$_4$O$_{14}$ and for Nd$_2$MoTe$_3$O$_{12}$ and for Nd$_2$MoTe$_4$O$_{14}$ and Nd$_2$W$_2$Te$_2$O$_{13}$. The three Pr$^{III}$ compounds are capable of emitting luminescent light in the blue, green, and red regions. Pr$_5$MoTe$_7$O$_{23}$Cl$_3$ and Pr$_5$WTe$_7$O$_{23}$Cl$_3$ display four sets of emission bands at 491 nm (very strong, $^3P_0 \rightarrow ^1H_4$), 534 nm (moderate, $^3P_0 \rightarrow ^1H_3$), 619 nm (moderate, $^3P_0 \rightarrow ^1H_4$), 649 nm (strong, $^3P_0 \rightarrow ^3F_2$), and 735 nm (weak, $^3P_0 \rightarrow ^3F_0$) under $\lambda_{ex}$ = 448 nm. Under the same experimental conditions, the corresponding emission bands for Pr$_2$MoTe$_4$O$_{14}$ are much weaker. Because of the so-called “crystal-field effect” as well as multiple Pr$^{3+}$ sites, a few transition bands were split into several subbands. \(^{19}\)

3. TM$^{-d^0}$ TM–Te$^{IV}$ or Se$^{IV}$–O Systems. Reports on compounds in the TM–Mo$^{V}$–Te$^{IV}$/Se$^{IV}$–O systems are much fewer than those of the alkali and alkaline-earth ones.\(^{20}\) The structure of Cd(VO$_2$)$_3$(SeO$_3$)$_2$$^+$H$_2$O can be described as a pillarized layered architecture. The layer is composed of dimers of VO$_3$ square pyramids and dimers of CdO$_6$ decahedra connected to one another by sharing corner and/or edge O atoms, whereas the pillars are composed of distorted VO$_6$ octahedra connected to one another via corner- and edge-sharing with capping selenite groups; the lone-pair electrons of the Se$^{IV}$ atoms are oriented toward the narrow-shaped tunnels along the $b$ axis.

We deem that the combination of the lone-pair electrons of Se$^{IV}$ or Te$^{IV}$ with the distorted MoO$_6$ octahedron may lead to new compounds in TM–Mo$^{VI}$ or V$^{V}$–Se$^{IV}$/Te$^{IV}$–O systems with novel structures and unusual physical properties, such as magnetic or optical properties. So far, no nickel molybdenum(VI) selenite or tellurite has been structurally characterized. Our exploration of new phases in nickel

molybdenum(VI) selenite or tellurite systems led to three new compounds, namely, Ni$_3$(Mo$_2$O$_8$)(XO$_3$) (X = Se, Te)$_{21}$ and Ni$_3$(MoO$_4$)(TeO$_3$)$_{22}$.

Ni$_3$(Mo$_2$O$_8$)(XO$_3$) (X = Se, Te) display two different types of 3D structures containing [Mo$_4$O$_{16}$]$^{8-}$ and [Ni$_6$O$_{22}$]$^{32-}$ clusters or 1D nickel oxide chains (Figure 9). The structure of Ni$_3$(Mo$_2$O$_8$)(SeO$_3$) features a 3D network in which [Ni$_6$O$_{22}$]$^{32-}$ clusters and SeO$_3^{2-}$ anions. All three Ni$^{II}$ ions in the asymmetric unit are octahedrally coordinated by six O atoms, with Ni−O distances ranging from 1.983(4) to 2.160(4) Å. Both Mo$^{VI}$ cations are octahedrally coordinated by six O atoms. The Mo−O bond distances are in the range of 1.719(4)−2.304(4) Å. The Mo$^{V}$ cations are distorted toward an edge (local C$_2$ direction) with two “short”, two “normal”, and two “long” Mo$^{6+}$−O bonds. The magnitudes of the distortions ($\Delta d$) were calculated to be 1.18 and 1.29 Å respectively for Mo1 and Mo2. The four Mo$^{VI}$ octahedra are interconnected by edge-sharing to form a cyclic [Mo$_4$O$_{16}$]$^{8-}$ tetranuclear cluster unit (Figure 9a). Six Ni$_6$ octahedra are interconnected into a hexanuclear [Ni$_6$O$_{22}$]$^{32-}$ cluster unit through edge-sharing (Figure 9b). The intracluster Ni⋯Ni separations between a pair of edge-sharing Ni$_6$ octahedra are in the range of 3.034(1)−3.245(1) Å (Figure 9b). The [Ni$_6$O$_{22}$]$^{32-}$ cluster units are bridged by SeO$_2^{2-}$ groups to form a 2D nickel selenite layer parallel to the ab plane. Neighboring nickel selenite layers are further interconnected by the [Mo$_4$O$_{16}$]$^{8-}$ clusters via Mo−O−Ni bridges into a 3D network structure. The lone-pair electrons of the Se$^{IV}$ atoms are oriented toward the cavities of the structure. The structure of Ni$_3$(Mo$_2$O$_8$)(TeO$_3$) is different from that of Ni$_3$(Mo$_2$O$_8$)(SeO$_3$), although their chemical formulas are comparable. It features a 3D structure in which the corrugated nickel oxide anionic chains are bridged by [Mo$_4$O$_{16}$]$^{8-}$ cluster units and TeO$_3^{2-}$ anions. As in Ni$_3$(Mo$_2$O$_8$)(SeO$_3$), the Ni$^{II}$ and Mo$^{VI}$ cations are octahedrally coordinated by six O atoms. Similar to that in Ni$_3$(Mo$_2$O$_8$)(SeO$_3$), the four Mo$^{VI}$ octahedra in Ni$_3$(Mo$_2$O$_8$)(TeO$_3$) are interconnected via edge-sharing to form a [Mo$_4$O$_{16}$]$^{8-}$ tetranuclear cluster unit. Two NiO$_6$ and one Ni$_2$O$_6$ octahedra are interconnected via edge-sharing into a [Ni$_3$O$_{13}$]$^{20-}$ trinuclear unit. Such neighboring trinuclear units are further interconnected through edge-sharing into a corrugated [Ni$_3$O$_{11}$]$^{16-}$ anionic chain along the b axis with a Ni1−O2−Ni1 bond angle of 84.65(9)$^\circ$ (Figure 9c). This nickel oxide chain can also be viewed as Ni$_2$O$_6$ octahedra being grafted onto the corrugated chain of Ni$_1$O$_6$ through edge-sharing. It is interesting to note that [Ni$_6$O$_{22}$]$^{32-}$ clusters are formed in Ni$_3$(Mo$_2$O$_8$)(SeO$_3$), whereas corrugated [Ni$_3$O$_{11}$]$^{16-}$ anionic chains are observed in Ni$_3$(Mo$_2$O$_8$)(TeO$_3$). Both nickel oxide building units are based on Ni$_3$O triangles. The Ni$_3$O triangles in [Ni$_6$O$_{22}$]$^{32-}$ clusters are condensed via sharing Ni−Ni edges, whereas those in [Ni$_3$O$_{11}$]$^{16-}$ anionic chains are observed in Ni$_3$(Mo$_2$O$_8$)(TeO$_3$). Both nickel oxide building units are based on Ni$_3$O triangles. The Ni$_3$O triangles in [Ni$_6$O$_{22}$]$^{32-}$ clusters are condensed via sharing Ni−Ni edges, whereas those in [Ni$_3$O$_{11}$]$^{16-}$ anionic chains are observed in Ni$_3$(Mo$_2$O$_8$)(TeO$_3$). Both nickel oxide building units are based on Ni$_3$O triangles. The Ni$_3$O triangles in [Ni$_6$O$_{22}$]$^{32-}$ clusters are condensed via sharing Ni−Ni edges, whereas those in [Ni$_3$O$_{11}$]$^{16-}$ anionic chains are observed in Ni$_3$(Mo$_2$O$_8$)(TeO$_3$). Both nickel oxide building units are based on Ni$_3$O triangles.
thickness of the layer is about 12.1 Å. Such layers are further interconnected by the [Mo4O16]8− clusters via Mo−O−Ni bridges into a 3D network structure. The lone-pair electrons of the TeIV atoms are oriented toward the tunnels of the structure.

When we increased the molar ratio of TeO2/MoO3 to 2:1, a new Ni−Mo−Te−O phase with NCS structure (space group $P2_12_12_1$), Ni3(MoO2)(TeO3)$_2$, was obtained recently. Its structure features a novel 3D network of nickel(II) oxide with larger 1D tunnels along the $a$ axis. The MoO$_4$ tetrahedra and TeO$_3$ groups cap the walls of the tunnels (Figure 10a). Among three unique NiII ions in the asymmetric unit, two are octahedrally coordinated, whereas the third one is in a square-pyramidal geometry. NiO$_6$ octahedra are interconnected by edge-sharing along the $a$ axis into a 1D chain, whereas NiO$_5$ polyhedra are corner-sharing along the $a$ axis into a 1D chain. These two types of chains are further interconnected via corner-sharing into a 3D open framework of nickel oxide, forming 1D helical tunnels along the $a$ axis, which are based on Ni$_{12}$ rings (Figure 10a). Unlike those in Ni$_3$(Mo$_2$O$_8$)(SeO$_3$) and Ni$_3$(Mo$_2$O$_8$)(TeO$_3$), the MoVI cation is in a tetrahedral environment and there are no Mo−O−Mo or Mo−O−Te bridges. The MoO$_4$ tetrahedra and TeO$_3$ groups cap walls of the tunnels; the lone-pair electrons of the TeIV cations and terminal O atoms of the MoO$_4$ tetrahedra are pointing toward the center of the tunnel (Figure 10b).

SHG measurements indicate that its SHG signal is very weak. Both Ni$_3$(Mo$_2$O$_8$)(SeO$_3$) and Ni$_3$(Mo$_2$O$_8$)(TeO$_3$) obey the Curie–Weiss law above 60 K with Weiss constants ($\theta$) of 15.4(2) and 5.5(1) K respectively for Se and Te compounds, indicating significant ferromagnetic interactions between

Figure 10. 3D network of nickel(II) oxide in Ni$_3$(MoO$_2$)(TeO$_3$)$_2$ (a) and view of the structure of Ni$_3$(MoO$_2$)(TeO$_3$)$_2$ along the $a$ axis. The NiO$_6$ and NiO$_5$ polyhedra are shaded in green, and MoO$_4$ tetrahedra are shaded in cyan. Te atoms are drawn as yellow circles.

Figure 11. View of the structure of Cd$_4$V$_2$Te$_3$O$_{15}$ down the $a$ axis. The CdO$_6$ and VO$_4$ polyhedra are shaded in blue and green, respectively. Te and O atoms are drawn as yellow and red circles, respectively.

Figure 12. View of the structure of Cd$_6$V$_2$Se$_5$O$_{21}$ down the $b$ axis. The CdO$_6$, CdO$_7$ and CdO$_8$ polyhedra are shaded in cyan and VO$_4$ tetrahedra in green. Se and O atoms are drawn as pink and red circles, respectively.
magnetic centers. It is expected that the magnetic interactions should be dominated by the magnetic interactions between NiII ions within the hexanuclear [Ni6O22]32− cluster in Ni3(Mo2O8)(SeO3) and the 1D [Ni3O11]16− anionic chain in Ni3(Mo2O8)(TeO3). Long-range magnetic ordering is observed below 28 and 56 K.

We also extended our studies to TM ions with a d10 electronic configuration such as ZnII and CdII ions.23 ZnII or CdII compounds may display semiconducting properties, and they are also able to emit blue light. Solid-state reactions of zinc(II) or cadmium(II) oxide, V2O5, and TeO2, at high temperature lead to two novel quaternary compounds, namely, Zn3V2TeO10 and Cd4V2Te3O15.23 Very recently Cd6(V2O6)(SeO3)5 and CdWTeO6 were also isolated.24

The structure of Zn3V2TeO10 is a complicated 3D network constructed by the interconnection of ZnO5, ZnO6, V2O4, and TeO4 polyhedra via corner- and edge-sharing. Cd4V2Te3O15 with an acentric structure features a 3D network in which the cadmium tellurite layers are further interconnected by both “isolated” VO4 tetrahedra and 1D vanadium oxide helical chains (Figure 11). Cd4V2Te3O15 displays a SHG efficiency of about 1.4 times that of KDP. It is stable up to 840 °C and shows little absorption in 0.6–10.0 μm. Luminescent measurements indicate that both compounds exhibit broad emission bands in the blue-light region.23

Cd6V2Se5O21 was obtained by solid-state reactions of cadmium(II) oxide, V2O5, and SeO2. Its structure is composed of a 3D open framework of cadmium(II) selenite and 1D vanadium(V) oxide chains of corner-sharing VO4 tetrahedra. The vanadium(V) oxide chains are inserted at the large tunnels of cadmium(II) selenite via V–O–Cd bridges. The CdII ions are coordinated by six, seven, or eight O atoms (Figure 12).24a

CdWTeO6 crystallized in triclinic Pj1; its structure features a complicated 3D network of corner/edge-sharing CdO6 octahedra, CdO7 pentagonal bipyramids, WO6 octahedra, and TeO3 groups (Figure 13). There are three CdII, two WVI, and two TeIV sites in its asymmetric unit. Two CdII sites lying on the center of symmetry are octahedrally coordinated, and the third CdII ion in a general position is seven-coordinated in a pentagonal-bipyramidal geometry. The CdO6 octahedra form 1D chains along the b axis via edge-sharing; these 1D chains are capped by TeO2 groups. The WO6 octahedra are distorted toward a face (local C3 direction). Neighboring WO6 octahedra are interconnected via corner-sharing into 1D chains also along the b axis. These tungsten oxide chains are further capped by TeO2 groups on one side, and they are further bridged by CdO4 polyhedra via edge- and corner-sharing into a 2D layer parallel to the ab plane (Figure 13b). Two such layers are interconnected into a double layer via Cd–O–W bridges. The above two types of building units are alternating and interconnected along the c axis via corner-sharing (Te–O–Cd, Cd–O–W, and Cd–O–Cd bridges) into a 3D architecture (Figure 13a).24b

Part II. Metal Tellurites and Selenites Containing Tetrahedral Groups of Main-Group Elements

So far such compounds are still rare. With respect to tellurite phosphate oxides, a few materials have been reported, namely, Te$_2$O$_5$(HPO$_4$)$_2$, Te$_2$O$_{10}$(PO$_4$)$_2$, Ba$_2$TeO$_4$(PO$_4$)$_2$, BaTeMO$_4$(PO$_4$)$_2$ (M = Nb$^{5+}$ or Ta$^{5+}$), and A$_2$TeMoO$_6$(PO$_4$)$_2$ (A = K, Rb, Cs, TI). Structurally these materials are different; BaNbTeO$_4$(PO$_4$)$_2$ contains 2D layers, whereas Te$_2$O$_5$(HPO$_4$)$_2$ and Te$_2$O$_{10}$(PO$_4$)$_2$ exhibit 3D structures consisting of asymmetric TeO$_4$ and TeO$_5$ polyhedra that are linked through corner-sharing.$^{25a-c}$ Ba$_2$TeO$_4$(PO$_4$)$_2$ displays a novel 1D chain structure that is composed of PO$_4$ tetrahedra and TeO$_5$ polyhedra. Te$^{4+}$ cations are in asymmetric coordination environments attributable to their lone pairs. Two TeO$_2$ rings form a dimeric unit via edge-sharing; two neighboring TeO$_2$ units are further interconnected via a pair of phosphate groups into a 1D chain along the b axis, and each Te$^{4+}$ atom is also bonded to the third phosphate group through one Te$^-$–O$^-$–P bridge.$^{25d}$ The isostructural mixed-metal phosphates, BaMTeO$_6$(PO$_4$) (M = Nb$^{5+}$, Ta$^{5+}$), have novel layered crystal structures consisting of Mo$^{6+}$O$_6$ corner-sharing octahedral chains that are connected to TeV$^{4+}$O$_4$ polyhedra and phosphate tetrahedra. The phosphate groups act as pendant groups between two neighboring layers. The Nb$^{5+}$ cation distorts along the local C$_4$ direction of its octahedron with a “short–long–short–long” Nb–O–Nb bond motif. Furthermore, the Nb$^{5+}$ cation displaces away from the oxide ligands that are bonded to Te$^{4+}$ or P$^{5+}$ cations, attributable to the structural rigidity of the TeO$_2$ and PO$_4$ polyhedra. $^{25e}$ A$_2$Mo$_2$TeO$_6$(PO$_4$)$_2$ displays a pillared layered architecture composed of Mo$_2$P$_2$O$_4$ layers and TeO$_2$ groups as the pillars. Within the Mo$_2$P$_2$O$_4$ layer, the Mo$_6$ octahedra (distorted toward an edge) and PO$_4$ tetrahedra are interconnected via corner-sharing, forming MoO$_3$P$_4$ four-membered rings and MoO$_4$P$_4$ eight-membered rings.$^{25f}$

So far, there is no reports on metal selenites or tellurites containing additional SiO$_2$ or GeO$_2$ tetrahedra. Our exploration into the unexplored RE–Ge/Si–Te$^{IV}$–O systems afforded two novel lanthanum(III) tellurites with additional SiO$_2$ or GeO$_2$ tetrahedra, namely, La$_2$(Si$_{5.2}$Ge$_{2.8}$O$_{18}$)(TeO$_3$)$_4$ and La$_2$(Si$_{13}$O$_{18}$)(TeO$_3$)$_4$. The structure of La$_2$(Si$_{15}$Ge$_{2}$O$_{18}$)(TeO$_3$)$_4$ features a 3D network of the [Si$_{15}$Ge$_2$O$_{18}$]$^{12+}$ tetrahedral layers and the [La$_2$(TeO$_3$)$_4$]$^{24+}$ layers that alternate along the b axis. The germanate–silicate layer consists of corner-sharing XO$_4$ (X = Si, Ge) tetrahedra, forming four- and six-membered rings. The structure of La$_2$(Si$_{13}$O$_{18}$)(TeO$_3$)$_4$ is a 3D network composed of the [Si$_{13}$O$_{18}$]$^{2-}$ double layers and the [La$_2$(TeO$_3$)$_4$]$^{24+}$ layers that alternating along the a axis. The [Si$_{13}$O$_{18}$]$^{2-}$ double layer is built by corner-sharing silicate tetrahedra, forming four-, five-, and eight-membered rings. $^{25g}$


The TeO$_2^{2-}$ anions in both compounds are only involved in the coordination with the La$^{3+}$ ions to form a lanthanum(III) tellurite layer.$^{26}$

We also developed a new SHG material, Se$_2$B$_2$O$_7$, by the combination of BO$_4$ tetrahedra with SeO$_3^{2-}$ groups.$^{27}$ The structure of Se$_2$B$_2$O$_7$ features a 3D network composed of dimers of corner-sharing BO$_4$ tetrahedra and SeO$_3$ groups (Figure 14). The open framework of Se$_2$B$_2$O$_7$ can also be described as an interesting mixed (3,4)-connected net of the B and Se atoms (linked by –O– bridges). Right-handed helical tunnels along the c axis are formed. These tunnels are based on Ba$_2$Se$_4$ 10-membered rings. The lone pairs of the Se$^{IV}$ cations are oriented toward the above tunnels. Se$_2$B$_2$O$_7$ is stable up to 300 °C. It exhibits a SHG efficiency of about 2.2 times that of KDP (KH$_2$PO$_4$). Se$_2$B$_2$O$_7$ is transparent in the range of 300–2000 nm, and it exhibits an optical band gap of 4.64 eV.$^{27}$

Conclusions and Outlook

Several factors have strong effects on the structural topologies of the resulting compounds. The slight change of the ionic radius of the cation such as the A$^1$ or Ln$^{III}$ ion could lead to a completely different structure such as, for example, A$_3$W$_3$TeO$_{12}$ (A = K$^+$, Rb$^+$, Cs$^+$)$^{26c}$ and Ln$_2$MoTe$_3$O$_{12}$ (Ln = La, Nd).$^{26b}$ Also metal tellurites usually show structures different from the corresponding selenites because of the larger ionic radius of Te$^{IV}$ than Se$^{IV}$, such as, for example, Ni$_3$(Mo$_2$O$_8$)(QO$_3$) (Q = Se, Te).$^{21}$ In some cases, isomerism exists for some metal tellurites. Recently, we obtained a cubic phase of Ga$_2$Te$_3$O$_9$ ($I4_3d$) and a hexagonal phase of Ga$_2$Te$_3$O$_9$ ($P6_3/m$) in the same hydrothermal reaction; the cubic phase is SHG active (1 × KDP) and is densely packed, whereas the centrosymmetric hexagonal phase has a much lower density and features a 3D network with large tunnels along the c axis.$^{28}$ Molar ratios of the starting materials, synthetic methods, and reaction temperatures are also very important factors.

Several trends are obvious. The combination of the two types of cations susceptible to SOJT distortion, d$^0$ TM and lone-pair cation (Te$^{IV}$ or Se$^{IV}$), not only gives rise to a rich structural chemistry but also affords many NCS compounds with good SHG properties. As for the direction of the out-of-center distortion, it was found that V$^{5+}$ and Nb$^{5+}$ usually displace toward an edge or corner, whereas Mo$^{6+}$ and W$^{6+}$ ions are more likely distorted toward an edge or face. The V$^{5+}$ cation may adopt the square-pyramidal geometry besides a tetrahedron and a octahedron. Also it is not as stable as other d$^0$ TM cations, and sometimes it is reduced to V$^{4+}$ during the reaction. The bond polarization follows the following order: Te$^{IV}$ > Se$^{IV}$ and Mo$^{6+}$ > V$^{5+}$ > W$^{6+}$ > Nb$^{5+}$ > Ta$^{5+}$. It is observed that Ln$^{III}$ compounds are seldom acenitic and the d$^0$ TM cations are more likely tetrahedrally coordinated; this may be due to the higher coordination number for the Ln$^{III}$ ions than the A$^1$ and A$^{II}$ cations. It is
worth mentioning that the Se$^{IV}$ cation exists mostly as a SeO$_3$ group (in some cases as the diselinite group), whereas Te$^{IV}$ can be three-, four-, or five-coordinated, and the most amazing aspect is that these TeO$_x$ ($x = 3-5$) polyhedra can be polymerized into many types of polynuclear clusters or extended skeletons (Scheme 1) besides a ditellurite anion; such a polymerization is hardly observed in the organically templated or organically covalently bonded metal tellurites. Inorganic solids with various polymeric tellurium(IV) oxide anions include a Te$_3$O$_8$$^{4-}$ trimer in La$_2$MoTe$_3$O$_{12}$, a Te$_5$O$_{11}$$^{6-}$ tetramer in Er$_2$Te$_5$O$_{11}$, a Te$_5$O$_{13}$$^{6-}$ pentamer in Ln$_3$MTe$_7$-O$_2$Cl$_3$ (Ln = Pr, Nd; M = Mo, W), a 1D Te$_4$O$_{10}$$^{4-}$ in Ln$_2$Mo-Te$_2$O$_{14}$ (Ln = Pr, Nd), a 1D Te$_5$O$_{13}$$^{2-}$ in [Cd$_2$(Te$_5$O$_{13}$)]$^{-}$-{CdCl$_6$}, a 1D Te$_7$O$_{17}$$^{6-}$ in Cd$_2$Cl$_6$(Te$_7$O$_{17}$), layered Te$_5$O$_2$$^{2-}$ in La$_3$WTe$_6$O$_{18}$, a 2D Te$_4$O$_6$$^{2-}$ in K$_2$Te$_4$O$_9$·3H$_2$O, and a 2D Te$_2$O$_2$$^{2-}$ in Ln(Te$_2$O$_3$)X (Ln = Nd, X = Cl, Br; Ln = Gd, X = Cl).29-30b,c Certainly more examples will be discovered in the future, and extensive theoretical studies are needed to understand its origin.

There are also many fertile lands for our exploration in the field of metal selenites and tellurites. Systematic investigation on the Ln$^{III}$—V$^5+$ (Nb$^{V+}$, Ta$^{V+}$, Ti$^{IV+}$)—Te$^{IV}$ (or Se$^{VI}$)—O systems is expected to afford many compounds with new structural types as well as excellent luminescent materials. The mixing of two types of charge-balancing cations such as Ln—AE, AE—A, and Ln—A could change the overall charges of the anionic networks in addition to breaking the packing limitation for the single-type cation; thus, a variety of new structures can be obtained. The combination of lone-pair Te$^{IV}$ or Se$^{IV}$ with borate is also quite promising in the search for new SHG materials. In order to exhibit good second-order NLO properties, the above two types of bond polarizations should be “adductive”, which is still a great challenge for a synthetic chemist. To fully address these problems, strong interactions between synthetic and theoretical chemists are necessary.

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