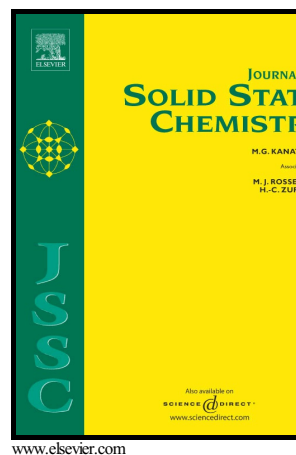


$\text{Cs}_7\text{Sm}_{11}[\text{TeO}_3]_{12}\text{Cl}_{16}$  and  $\text{Rb}_7\text{Nd}_{11}[\text{TeO}_3]_{12}\text{Br}_{16}$ ,  
the new tellurite halides of the tetragonal  
 $\text{Rb}_6\text{LiNd}_{11}[\text{SeO}_3]_{12}\text{Cl}_{16}$  structure type

Dmitri O. Charkin, Cameron Black, Lewis J.  
Downie, Dmitry E. Sklovsky, Peter S. Berdonosov,  
Andrei V. Olenov, Wuzong Zhou, Philip Lightfoot,  
Valery A. Dolgikh



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# **Cs<sub>7</sub>Sm<sub>11</sub>[TeO<sub>3</sub>]<sub>12</sub>Cl<sub>16</sub> and Rb<sub>7</sub>Nd<sub>11</sub>[TeO<sub>3</sub>]<sub>12</sub>Br<sub>16</sub>, the new tellurite halides of the tetragonal Rb<sub>6</sub>LiNd<sub>11</sub>[SeO<sub>3</sub>]<sub>12</sub>Cl<sub>16</sub> structure type**

Dmitri O. Charkin,<sup>[a]</sup> Cameron Black,<sup>[b]</sup> Lewis J. Downie<sup>[b]</sup>, Dmitry E. Sklovsky<sup>[a, c]</sup>, Peter S. Berdonosov<sup>[a]</sup>, Andrei V. Olenev<sup>[a, c]</sup>, Wuzong Zhou<sup>[b]</sup>, Philip Lightfoot<sup>[b]</sup> and Valery A. Dolgikh<sup>[a]</sup>

a Department of Chemistry, Moscow State University, 119991, GSP-1, Moscow, Russia E-mail: berdonosov@inorg.chem.msu.ru

b EaStCHEM and School of Chemistry, University of St Andrews, Purdie Building, St. Andrews, Fife, KY169ST, UK

c SineTheta LTD, Moscow, 119991, Russia

\* Corresponding author FAX +7 494 939 0998 E-mail: berdonosov@inorg.chem.msu.ru

**Abstract:** Two new rare-earth – alkali – tellurium oxide halides were synthesized by a salt flux technique and characterized by single-crystal X-ray diffraction. The structures of the new compounds Cs<sub>7</sub>Sm<sub>11</sub>[TeO<sub>3</sub>]<sub>12</sub>Cl<sub>16</sub> (**I**) and Rb<sub>7</sub>Nd<sub>11</sub>[TeO<sub>3</sub>]<sub>12</sub>Br<sub>16</sub> (**II**) (both tetragonal, space group *I4/mcm*) correspond to the sequence of [MLn<sub>11</sub>(TeO<sub>3</sub>)<sub>12</sub>] and [M<sub>6</sub>X<sub>16</sub>] layers and bear very strong similarities to those of known selenite analogs. We discuss the trends in similarities and differences in compositions and structural details between the Se and Te compounds; more members of the family are predicted.

**Keywords:** lanthanides • tellurium • Structure elucidation • crystal engineering • layered compounds

The targeted synthesis of inorganics with the so-called open-framework structures, intergrowth structures or compounds combining different structural slabs, containing channels or other tailored interiors, is considered one of the key problems of modern inorganic chemistry. The rapid development of this area is supported, first, by diversity of the framework architectures, and, second, with the promising future of these compounds which can be used as high-performance catalysts, molecular sieves, nanostructured materials, nonlinear optical materials, *etc.* [1-5]. As yet, *a priori* construction of the desired structure motifs and prediction of the best chemical compositions is not feasible in general, not the least due to complexity and versatility of both the architectures and the compositions themselves. Significant developments have been achieved in the area of hybrid metal-organic frameworks [6, 7] where both the metal cation and the organic linkers or templates determine the resulting structures. An alternative approach has been developed for the pure inorganics, which is based on the so-called “salt-inclusion solids”. These marry two chemically dissimilar constituents, which are usually the covalent and ionic sub-frameworks, in one structure [8-12]. In fact, these “salt inclusions” often act as templates for pores, channels, or interlayer spaces of the covalent framework. The desired chemical dissimilarity of the sub-frameworks can be achieved by employing systems containing cations and anions that differ significantly in their Lewis acidity *vs.* basicity. For instance, such differences are present in the systems containing cations of transition and alkali (or alkaline earth) metals, as well as oxide and halide (excluding fluoride) anions. It is also known that lone-pair cations like  $\text{Sb}^{\text{III}}$ ,  $\text{Bi}^{\text{III}}$ ,  $\text{Se}^{\text{IV}}$ ,  $\text{Te}^{\text{IV}}$ , or  $\text{I}^{\text{V}}$ , often act as “bordering” agents of the frameworks covering the walls of their interiors (pores, channels, *etc.*) [12], often together with the “terminating” agents like halide anions [13]. They are also known to induce non-centrosymmetry, particularly when several such cations contribute to the same compound.

These relationships are elegantly exemplified by the crystal chemistry of systems containing dissimilar cations and anions (mostly lone-pair cations together with Group 1, 2, or 3 cations, or halide and oxide anions). A large group of compounds therein adopt layered structures [14-24]; those containing  $\text{Se}^{\text{IV}}$  and  $\text{Te}^{\text{IV}}$  exhibit particularly complex architectures briefly reviewed in [14]. A variety of these are layered and contain  $[\text{M}_{11+x}(\text{ChO}_3)_{12}]^{n+}$  2D frameworks ( $\text{M} = \text{Ln}$  or  $\text{Bi}$ , in some cases partially substituted by  $\text{Mn}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ca}$ ,  $\text{Sr}$ , or  $\text{Li}$ ,  $x = 0$  or  $1$ ;  $\text{Ch} = \text{Se}$  or  $\text{Te}$ ,  $n = 8, 9$ , or  $12$ ). These slabs interleave with either sheets formed by halide anions, or more complex cation-deficient metal-halide layers chopped from the structures of  $\text{CsCl}$ ,  $\text{FeSe}$  (common formula  $[\text{M}_{8-y}\text{X}_{16}]$ ;  $\text{M} = \text{alkali metal}$  or  $\text{Cu}^{\text{I}}$ ;  $y = 1$  or  $2$ ;  $\text{M} = \text{Zn}$ ,  $y = 5$ ) or  $\text{NaCl}$  ( $[\text{M}_{8-y}\text{X}_{24}]$ ,  $\text{M} = \text{Cd}$ ,  $y = 2$ ); mixed-layer structures are also possible. Known compositions, layer sequences, and symmetry of the crystal structures are briefly summarized in **Table 1**. First

observed among selenites, this family has been recently extended by us into the realm of tellurites; we also successfully introduced novel NaCl-type  $[\text{Cd}_6\text{Cl}_{24}]$  metal-halide blocks [14]. Except for some small symmetrical and compositional differences, the structures of the Ln-Se-O and Ln-Te-O metal-oxide frameworks were found to be essentially similar. This prompted us to find tellurium representatives for other structures so far observed only among compounds of Se. Shleid et al [23] have prepared and structurally characterized a Eu - Cs - Te oxyhalide,  $\text{Cs}_7\text{Eu}_{11}[\text{TeO}_3]_{12}\text{Cl}_{16}$  and noted that the tellurium compounds of the like were yet very rare. In the current paper, we describe some more representatives and demonstrate that the family may indeed be extended much further.

### Experimental Section

**Synthesis.** The synthesis conditions were similar to those employed previously [14]. In a typical run, 1 mmol of  $\text{TeO}_2$  and rare-earth oxide halide  $\text{LnOX}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ,  $\text{Ln} = \text{La} - \text{Dy}$ ), together with 5 - 7 mmol of the corresponding alkali halide  $\text{MX}$  ( $\text{M} = \text{Rb}, \text{Cs}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ), were thoroughly ground, placed into silica tubes (inner diameter 7-8 mm), evacuated to  $\sim 10^{-2}$  torr, and flame-sealed so that the total ampoule length was 70-80 mm. Tubes were heated to  $850^\circ\text{C}$  in 120 hrs, soaked for 150 hrs, and cooled to  $650^\circ\text{C}$  in 120 hrs, after which the furnace was switched off. The intermediate  $650^\circ\text{C}$  step seems to be necessary to prevent formation of colored by-products which are most likely alkali metal halotellurates(IV),  $\text{M}_2\text{TeX}_6$ , as deduced from instant discoloration upon dissolving the salt fluxes and formation of tiny colorless crystals contaminating the samples. The use of smaller amounts of initial charges and tube diameters results only in microcrystalline powders of the target compounds. Routine XRD patterns of the ground samples provided about 10-12 lines most of which were indexable using primitive tetragonal unit cells with  $a \sim 4\text{\AA}$  and  $c \sim 13\text{\AA}$  which are the  $1/4 \times 1/4 \times 1$  (or  $1/2$ ) subcells for the target compounds. Due to closeness of scattering factors for Ln and Te, the intensities of the superstructural lines are expected to be rather low. Considering the intensities of lines not indexed using the above-mentioned subcell, the yields generally exceed 80% and the samples were multiphasic. For the later rare-earths, the patterns could be interpreted in favor of compounds similar to  $\text{HoTeO}_3\text{Cl}$  [25]. Not all samples were found to contain good quality single crystals and reproducibility of their growth is yet low, contrary to the phase content of the insoluble residues where the target phases dominate. Hence, in the current paper, we restrict ourselves to the description of two new compounds,  $\text{Rb}_7\text{Nd}_{11}[\text{TeO}_3]_{12}\text{Br}_{16}$  (**I**) and  $\text{Cs}_7\text{Sm}_{11}[\text{TeO}_3]_{12}\text{Cl}_{16}$  (**II**) for which good-quality crystals could be obtained. Similar to [14], we note that the use of  $\text{LnOX}$  precursors is important for the preparation of the target compounds: annealing mixtures of  $\text{Ln}_2\text{O}_3$  and  $\text{TeO}_2$  in  $\text{CsCl}$  fluxes results in preparation of rare-earth tellurites, for example [26], with no halide incorporated.

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**Single-crystal X-ray studies.** X-ray data for **II** were collected on a STOE STADI-VARI

Pilatus 100K diffractometer. Raw intensity data were treated with the STOE X-Area Version 1.66 software package according to a standard procedure. Data were corrected for Lorentz and polarization factors. Absorption correction was introduced based on the real crystal shape, utilizing X-Red32 and X-Shape Version 2.12.2 programs, implemented into X-Area package.

The crystal structure of **II** was solved in a centrosymmetric space group  $I4/mcm$  (140) by charge-flipping method, using the SUPERFLIP [27] program integrated into JANA2006 software package [28]. All atoms, including oxygen, were localized, and the model was then successfully refined in anisotropic mode by a full-matrix least-squares method on  $F^2$  (SHELX [29]).

For **I**, the X-ray data collection and cell refinement were performed on a Rigaku SCX Mini instrument and by using Rigaku Crystal Clear software. The collected data set was corrected for Lorentz and polarization factors as well as for absorption by Multi-scan [30]. The crystal structure of **I** was refined basing on atomic positions, found during the refinement of **II** utilizing SHELX [29] software. It should be notified that for compound **I** the refinement lead to relatively high value of the residual electronic density peaks (**Table 2**). It probably was the result of pure quality of measured crystal or/and imperfectness of the absorption correction introduced. Several attempts to refine the crystal structure of **I** were performed utilized data, collected on different crystals but all of them lead to same results.

Data collection and refinement parameters are summarized in **Table 2** and selected interatomic distances are listed in **Table 3**. Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de); [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)) deposition numbers are 429504 for **I** and 429505 for **II**.

## Results and Discussion

**Description of crystal structures.** Our results demonstrate that tellurium analogs of the alkali rare-earth(III) oxoselenates(IV) halogenide ie.  $Cs_7Sm_{11}[TeO_3]_{12}Cl_{16}$  (**I**) and  $Rb_7Nd_{11}[TeO_3]_{12}Br_{16}$  (**II**) involving CsCl-derived metal-halide blocks, do indeed exist. Despite the differences in composition and alkali–rare earth combinations both compounds are isostructural. The unit cell of **II** is presented in **Fig S1** supporting information.

The HRTEM investigation of the samples confirmed the unit cells determined by the XRD studies. **Fig. 1(a)** shows a typical image of **I** when viewed down the [001] zone axis. The corresponding FFT pattern is shown as the inset. The  $d$ -spacings measured are A: 3.92 Å, B: 3.92 Å and C: 10.8 Å. The strong diffraction spots, e.g A and B, imply that the basic substructure

in the *ab* plane is *ca.* 4 Å × 4 Å with a fourfold superstructure indicated by weak spots, e.g. C, leading to a true lattice of *ca.* 16 Å × 16 Å. **Fig. 1(b)** is the HRTEM image along the [1-10] direction. The diffraction spots D and E corresponding to *d*-spacings of 6.16 and 2.75 Å, respectively, can be indexed as (004) and (440). No stacking faults were observed along the [001] direction.

The structures of the compounds **I** and **II** contain four independent *Ln* atoms, three alkali metal atoms and two tellurium atoms per unit cell. Three out of four *Ln* atoms reside in oxygen environments: Ln(1) in a square-antiprismatic coordination Ln(1)O<sub>8</sub>, Ln(2) and Ln(3) in less-symmetrical ten-vertex polyhedra LnO<sub>10</sub>. The fourth *Ln* atom has a mixed oxygen and halogen coordination and resides in an Archimedean antiprism Ln(4)O<sub>4</sub>X<sub>4</sub> with oxygen and halogen atoms forming two opposite bases of the antiprisms. These bonding preferences and chemical affinity of *Ln* atoms corresponds to the Lewis acid/base strength (La(Sm<sup>3+</sup>) = 0.36 valence units (v.u.), La(Nd<sup>3+</sup>) = 0.40 v.u. [31], Lb(O<sup>2-</sup>) = 0.5 v.u., Lb (Cl<sup>-</sup>) = 0.17 v. u. [32]. The Ln–O bond distances (**Table 3**) are of the same order as those in chemically related compounds (e.g. *d*(Sm–O) = 2.35 – 2.48 Å in Sm<sub>2</sub>Mn[Te<sub>5</sub>O<sub>13</sub>]Cl<sub>2</sub>, *d*(Nd–O) = 2.39 – 2.60 Å in Nd<sub>4</sub>Cu[Te<sub>5</sub>O<sub>15</sub>]Cl<sub>3</sub>) [33].

The structures of **I** and **II** host three alkali cation sites, which are characterized by different environments (**Table 3**). Two of these are coordinated by halide anions forming distorted MX<sub>8</sub> cubes while the third one corresponds to an almost regular M(3)O<sub>8</sub> cube. The generated distances of Rb–O 2.614 Å and Cs–O 2.604 Å seem somewhat below the common range; however, in [CsEu<sub>11</sub>(TeO<sub>3</sub>)<sub>12</sub>][Cs<sub>6</sub>Cl<sub>16</sub>] the same distances were observed for Cs–O bonds [23] and a number of structures containing similarly short distances were published, for example [34-37].

The polyhedra of Ln(1) – Ln(3) and M(3) (LnO<sub>8</sub>, LnO<sub>10</sub> and MO<sub>8</sub>) form the metal-oxygen layers by sharing their edges; they reside at *z* = ¼ and *z* = ¾ (**Fig 2a**). The Ln(4)O<sub>4</sub>X<sub>4</sub> polyhedra decorate these layers forming a loose net as shown on **Fig 2b**. The Te atoms are surrounded by three oxygen atoms at 1.86 – 1.91 Å, forming TeO<sub>3</sub>*E* moieties (*E* is the lone pair of Te(IV)). Their oxygen atoms also form the vertices of the LnO<sub>*n*</sub> and MO<sub>8</sub> polyhedra. The TeO<sub>3</sub>*E* groups form the second net of decorations over the metal-oxide slab (**Fig 2a**); they reside near the holes in the metal – oxygen layers formed by LnO<sub>8</sub>, LnO<sub>10</sub> and MO<sub>8</sub> polyhedra. Their orientation and distribution probably allow to situate the “halophilic” lone pairs of Te<sup>IV</sup> between the Ln(4)O<sub>4</sub>X<sub>4</sub> antiprisms (**Fig. 2**).

The decorated layers interleave with CsCl-like layers comprised of M(1)X<sub>8</sub> and M(2)X<sub>8</sub> cubes. The M–X distances do not differ much from related structures *d*(Cs–Cl) = 3.42 – 3.65 Å in Cs<sub>3</sub>La<sub>11</sub>[SeO<sub>3</sub>]<sub>12</sub>Cl<sub>12</sub> [24], 3.60 Å in Pb<sub>0.6</sub>Bi<sub>1.4</sub>Cs<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> [38], or 3.56 Å in CsCl [39]. The metal-halide layers are situated around *z* = 0 and *z* = ½. One quarter of the cubes are vacant; the stuffed and empty cubes are ordered (**Fig. 2, c**). The four halogen atoms from the Ln(4)O<sub>4</sub>X<sub>4</sub> antiprisms

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also belong to the  $MX_8$  cubes. The interplay between the  $\{MLn_{11}[TeO_3]_{12}\}^{10+}$  and  $[M_6\Box_2Cl_{16}]^{10-}$  layers is illustrated by the fact that the vacancies in the latter exactly correspond to the decorating  $Ln(4)O_4X_4$  antiprisms in the former (**Fig. 2, d**) probably to avoid too short separations between  $Ln^{3+}$  and  $M^+$  cations (3.1 – 3.2 Å). The same is also the case for the  $M_7Ln_{11}[SeO_3]_{12}Cl_{16}$  compounds [15-17, 21-23], as well as the most likely reason why, in the structures where the  $\{\Box(M,Ln)_{11}[SeO_3]_{12}\}^{8+}$  slabs are separated by only halide sheets [17-20], the  $LnO_4X_4$  antiprisms never stack in “eclipsed”, only in “staggered” motif. The complete structures of the new tellurites may be considered as a sequence of metal –oxygen and metal-halide slabs as shown on **Fig 3**.

**Differences vs. similarities in the structures of Se and Te compounds.** The structures of the new compounds add one more global similarity to the crystal chemistry of layered Ln--Se and Ln--Te oxide halides. New differences, however, are found, of which the first concerns chemistry: while for selenites, the structures involving metal-halide slabs have been hitherto found only among oxide chlorides and not oxide bromides (**Table 1**) such restrictions seem not to exist for the tellurium compounds.

The second difference concerns structure details: the compounds  $M_7Ln_{11}[TeO_3]_{12}X_{16}$  are not direct structural analogs of  $M_7Ln_{11}[SeO_3]_{12}Cl_{16}$  [15, 16] but rather of  $Rb_6LiLn_{11}[SeO_3]_{12}Cl_{16}$  [21-23] where all cationic positions in the metal-oxide slabs are filled. It is likely that increase of the metrics when proceeding from Se to Te compounds makes it possible for large cations like  $Rb^+$  or  $Cs^+$  to enter cubic voids not only in the metal-halide, but also in the metal-oxide part of the structure. Both structures contain two metal-halide and metal-oxide slabs per unit cell due to the doubled  $c$  parameter.

The structures of **I** and **II** share the same space group not only with  $Rb_6LiLn_{11}[SeO_3]_{12}Cl_{16}$  but also with  $Cd_6Gd_{12}[TeO_3]_{12}Cl_{24}$  [14] forming a link between the hitherto described tetragonal selenium and tellurium compounds. All these correspond to the same type of superstructure, corresponding to doubling of the  $c$  axis, and demonstrate the topologically equal motif of the  $[(M,Ln)_{12}(ChO_3)_{12}]$  slabs. We had noticed in [14] that the doubling of the  $c$  axis in the structure of  $Cd_6Gd_{12}[TeO_3]_{12}Cl_{24}$  is caused by the motif of  $LnO_4X_4$  antiprisms decorating the slab of  $LnO_n$  polyhedra; this motif is, as expected, identical over the structures under discussion. Therefore, within tetragonal symmetry and  $2\times c$  superstructure the global features of the  $[(M,Ln)_{12}(ChO_3)_{12}]$  slabs seem to be transferable between structures containing different metal-halide slabs and even chalcogens. Unfortunately, direct comparisons between structures of **I**, **II**,  $Rb_6LiNd_{11}[SeO_3]_{12}Cl_{16}$  and  $Cd_6Gd_{12}[TeO_3]_{12}Cl_{24}$  are not feasible due to different nature of rare-earth and halide elements involved. However, the Sm–O, Sm–Cl, and Te–O distances in the slightly different structures of  $Cs_7Sm_{11}[TeO_3]_{12}Cl_{16}$  and  $Cd_6Sm_{12}[TeO_3]_{12}Cl_{24}$  are transferable

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within a few per cent. This is particularly so for the Te–O distances, which are almost the same for the structures of **I** and **II** (see **Table 3**). It is curious to note that *a* cell parameters for these two compounds are also very close and probably dictated by the composition of the metal-oxide slab. The Cs–Cl and Rb–Br distances demonstrate a considerable scatter (3.42 – 3.76 Å) and the range of ~0.3 Å is similar to that compared to Rb–Cl in Rb<sub>6</sub>LiLn<sub>11</sub>[SeO<sub>3</sub>]<sub>12</sub>Cl<sub>16</sub> (3.31 – 3.66 Å [21- 23]). This scatter can be attributed to different coordination modes of the halide anions which may be bonded to alkali and rare-earth cations or neighbor the alkali vacancy or lone pair of the chalcogen. Thus, the behavior of the CsCl layers is, in general, also transferable from selenites to tellurites; this suggests that other structures, as yet observed among selenites only, may meet their tellurium analogs.

While the global features of the {(M,Ln)<sub>12</sub>[ChO<sub>3</sub>]<sub>12</sub>} slabs seem to be transferable, the modes of filling the cubic position in all three structures are different. In the Cd compounds, it is filled by Ln<sup>3+</sup> cations. In the compound of alkali metals, this is not feasible, perhaps due to expected too large non-stoichiometry in the non-existent {Ln<sub>12</sub>[ChO<sub>3</sub>]<sub>12</sub>}[M<sub>4</sub>X<sub>16</sub>] composition; such a small amount of alkali cations is probably not enough to prevent a system of two consecutive halide layers from collapse. But if, in the selenium compounds, the cubic void can be filled only by the smallest (Li<sup>+</sup>) in the tellurium compounds, the largest (Cs<sup>+</sup>) can also contribute. The generated Rb–O and Cs–O bond distances seem somewhat small, though a number of structures containing similarly short distances were published recently. A possible solution is that Rb<sup>+</sup> and Cs<sup>+</sup> are, at least partially, distributed over several positions together with Ln<sup>3+</sup>. Such attempts were made during the refinement and indeed do allow somewhat lower R-factors and difference electron densities. Nevertheless, they were finally abandoned due to low refined alkali content; for the Cs/Sm couple, the difference in scattering factors is really unfavorable. The same question was raised by Lipp and Schleid [21] in discussion of the structure of Rb<sub>6</sub>LiPr<sub>11</sub>[SeO<sub>3</sub>]<sub>12</sub>Cl<sub>16</sub>, where the void looks on the contrary too large for Li<sup>+</sup>. As yet, it is possible to imagine that the alkali cations actually reside mostly in the cubic position, but at least partially in the other positions. Evidently, more investigations including lighter alkali cations, more easily discernible from Ln<sup>3+</sup>, are necessary to elucidate the cation distribution in these complex structures. These studies are now in progress.

## Conclusions

We have predicted and successfully realized the new tellurium analogs of the layered rare-earth selenium halides involving CsCl-related metal-halide slabs. These compounds appear to be isostructural to some previously known multi-cation selenites and Cs<sub>7</sub>Eu<sub>11</sub>[TeO<sub>3</sub>]<sub>12</sub>Cl<sub>16</sub>, though they differ somewhat in details from their direct compositional analogs. These variations in composition and structure indicate the trends in similarities and differences between selenium



and tellurium compounds and outline new directions for further expansion and development of this non-trivial family of layered oxide halides.

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**Figure 1.** HRTEM images from **I** viewed down the (a) [001] and (b) [1-10] zone axes. The diffraction spots can be indexed into the tetragonal unit cell with  $a = 15.8875$  and  $c = 25.7374$  Å, A: (400) B: (040) C: (110) D: (004) and E: (440). The insets are the corresponding FFT patterns.

**Figure 2.** **a)** The network of the metal-oxide polyhedra; **b)** the same net covered with Nd<sup>4+</sup> along the [0 0 1] and [0 1 0] direction of the  $\text{Rb}_7\text{Nd}_{11}(\text{TeO}_3)_{12}\text{Br}_{16}$  structure **c)**  $\text{M}_6\text{X}_8$  slab in the  $\text{Rb}_7\text{Nd}_{11}(\text{TeO}_3)_{12}\text{Br}_{16}$  structure **d)** the view along [0 0 1] showing vacancies in  $\text{M}_6\text{X}_8$  slab under the  $\text{Nd}_4\text{O}_4\text{X}_4$  prisms

**Figure 3.** Slab structure of  $\text{Rb}_7\text{Nd}_{11}(\text{TeO}_3)_{12}\text{Br}_{16}$

#### Highlights

- Two new rare-earth – alkali – tellurium oxide halides were synthesized.
- They adopt slab structure of rare earth-tellurium-oxygen and CsCl-like slabs.
- The Br-based CsCl-like slabs have been observed first in this layered family.

**Table 1.** Compositions, space groups and cell constants for layered rare-earth chalcogenite halides comprising  $[(A, Ln)_{11+x}(ChO_3)_{12}]^{n+}$  slabs (A = uni- or divalent metal;  $n = 8, 9, 12$ ). The formulae are unified in order to illustrate the layer composition and sequences.

	Composition	Space group	Cell parameters				Ref.
			a, Å	b, Å	c, Å	angle, °	
1	[Sm <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][K <sub>7</sub> Cl <sub>16</sub> ]	<i>Pnan</i>	15.6334	15.664	25.074		15
2	[Pr <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Cs <sub>7</sub> Cl <sub>16</sub> ]	<i>Cmca</i>	51.698	15.999	15.986		15
3		<i>Pna2<sub>1</sub></i>	15.911	15.951	25.860		16
4	[Nd <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Cs <sub>7</sub> Cl <sub>16</sub> ]	<i>Pban</i>	15.941	15.954	51.656		16
5	[Cs <sub>0.5</sub> Sm <sub>10.5</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Br <sub>8</sub> ]	<i>Bbab</i>	15.797	15.797	17.963		17
6	[MnNd <sub>10</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Cl <sub>8</sub> ]	<i>P2/c</i>	15.889	15.872	19.361	$\beta = 114.0$	18
7	[CoNd <sub>10</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Cl <sub>8</sub> ]	<i>P2/c</i>	15.699	15.700	19.171	$\beta = 114.0$	19
8	[NiNd <sub>10</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Cl <sub>8</sub> ]	<i>P2/c</i>	15.818	15.787	19.276	$\beta = 114.2$	18
9	[CuNd <sub>10</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Cl <sub>8</sub> ]	<i>P2/c</i>	15.775	15.769	19.231	$\beta = 114.0$	19
10	[CaNd <sub>10</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Cl <sub>8</sub> ]	<i>Ccca</i>	15.588	17.419	15.681		20
11	[SrNd <sub>10</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Cl <sub>8</sub> ]	<i>Ccca</i>	15.773	17.622	15.836		20
12	[LiPr <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Rb <sub>6</sub> Cl <sub>16</sub> ]	<i>I4/mcm</i>	15.9058		24.787		21
13	[LiNd <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Rb <sub>6</sub> Cl <sub>16</sub> ]	<i>I4/mcm</i>	15.8169		24.772		22
14	[LiEu <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ][Rb <sub>6</sub> Cl <sub>16</sub> ]	<i>I4/mcm</i>	15.6460		24.734		23
15	[CsEu <sub>11</sub> (TeO <sub>3</sub> ) <sub>12</sub> ][Cs <sub>6</sub> Cl <sub>16</sub> ]	<i>I4/mcm</i>	15.8488		25.790		23
16 <sup>a</sup>	[La <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ] <sub>2</sub> [Cl <sub>8</sub> ][Cs <sub>6</sub> Cl <sub>16</sub> ]	<i>Cmca</i>	43.176	16.073	16.037		24
17 <sup>a</sup>	[La <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ] <sub>2</sub> [Cl <sub>8</sub> ][Cu <sub>6</sub> Cl <sub>16</sub> ]	<i>P<math>\bar{1}</math></i>	15.795	15.824	20.386	$\alpha = 96.1$ $\beta = 106.5$ $\gamma = 90.0$	18
18 <sup>a</sup>	[La <sub>11</sub> (SeO <sub>3</sub> ) <sub>12</sub> ] <sub>2</sub> [Cl <sub>8</sub> ][Zn <sub>3</sub> Cl <sub>16</sub> ]	<i>P<math>\bar{1}</math></i>	16.087	16.141	20.732	$\alpha = 107.3$ $\beta = 95.1$ $\gamma = 90.0$	18
19	[Sm <sub>12</sub> (TeO <sub>3</sub> ) <sub>12</sub> ][Cd <sub>6</sub> Cl <sub>24</sub> ]	<i>P4/nbm</i>	15.842		13.079		14
20	[Eu <sub>12</sub> (TeO <sub>3</sub> ) <sub>12</sub> ][Cd <sub>6</sub> Cl <sub>24</sub> ]	<i>P4/nbm</i>	15.7742		13.113		14
21	[Gd <sub>12</sub> (TeO <sub>3</sub> ) <sub>12</sub> ][Cd <sub>6</sub> Cl <sub>24</sub> ]	<i>I4/mcm</i>	15.7626		26.410		14

[a] Entries correspond to mixed-layer structures

**Table 2.** Crystal Data and Structure Refinement for Cs<sub>7</sub>Sm<sub>11</sub>(TeO<sub>3</sub>)<sub>12</sub>Cl<sub>6</sub> (I) and Rb<sub>7</sub>Nd<sub>11</sub>(TeO<sub>3</sub>)<sub>12</sub>Br<sub>16</sub> (II)

Formula	Cs <sub>7</sub> Sm <sub>11</sub> (TeO <sub>3</sub> ) <sub>12</sub> Cl <sub>16</sub>	Rb <sub>7</sub> Nd <sub>11</sub> (TeO <sub>3</sub> ) <sub>12</sub> Br <sub>16</sub> .
Crystal system		Tetragonal
Space group		<i>I4/mcm</i> (140)
<i>a</i> , Å	15.8875(11)	16,1179(3)
<i>c</i> , Å	25.7374(18)	25.9348(7)
<i>V</i> , Å <sup>3</sup>	6496.4(10)	6737.5(3)
<i>Z</i>		4
Instrument	Rigaku SCX Mini	STOE STADI-VARI Pilatus 100K
Wavelength, Å		0.71073
Data collection	173(2)	293(2)
temperature, K		
Data/restraints/parameters	1551 / 0 / 110	1588 / 0 / 109
Refinement method		Full-matrix least-squares on F <sup>2</sup>
Goodness-of-fit on F <sup>2</sup>	1.068	0.941
R ( <i>I</i> > 2σ( <i>I</i> ))	R1 = 0.0567 wR2 = 0.1576	R1=0.0331 wR2=0.0541
R (all data)	R1 = 0.0736 wR2 = 0.1675	R1=0.0636 wR2=0.0606
Largest diff. peak and hole (e/Å <sup>3</sup> )	6.309 / -7.427	3.153 / -2.603
ICSD number	429504	429505

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**Table 3.** Selected bond distances for **I** and **II**, Å

<b>I</b>			<b>II</b>		
Sm(1)-O(3)	× 8	2.398(10)	Nd(1)-O(3)	× 8	2.420(7)
Sm(2)-O(1)	× 2	2.382(10)	Nd(2)-O(1)	× 2	2.402(7)
Sm(2)-O(4)	× 2	2.462(11)	Nd(2)-O(3)	× 2	2.525(7)
Sm(2)-O(3)	× 2	2.509(11)	Nd(2)-O(4)	× 2	2.527(7)
Sm(2)-O(2)	× 2	2.621(11)	Nd(2)-O(2)	× 2	2.647(8)
Sm(2)-O(5)	× 2	2.789(3)	Nd(2)-O(5)	× 2	2.8423(15)
Sm(3)-O(5)	× 2	2.452(16)	Nd(3)-O(5)	× 2	2.521(9)
Sm(3)-O(1)	× 4	2.500(10)	Nd(3)-O(1)	× 4	2.543(7)
Sm(3)-O(2)	× 4	2.618(11)	Nd(3)-O(2)	× 4	2.652(7)
Sm(4)-O(2)	× 2	2.329(11)	Nd(4)-O(2)	× 2	2.353(6)
Sm(4)-O(4)	× 2	2.362(11)	Nd(4)-O(4)	× 2	2.379(5)
Sm(4)-Cl(2)	× 2	2.910(6)	Nd(4)-Br(2)	× 2	3.113(1)
Sm(4)-Cl(3)	× 1	3.023(4)	Nd(4)-Br(1)	× 1	3.141(1)
Sm(4)-Cl(4)	× 1	3.042(7)	Nd(4)-Br(4)	× 1	3.203(2)
Te(1)-O(4)	× 2	1.890(11)	Te(1)-O(5)	× 1	1.866(9)
Te(1)-O(5)	× 1	1.898(16)	Te(1)-O(4)	× 2	1.895(5)
Te(2)-O(3)	× 1	1.865(11)	Te(2)-O(3)	× 1	1.866(6)
Te(2)-O(1)	× 1	1.877(11)	Te(2)-O(1)	× 1	1.889(6)
Te(2)-O(2)	× 1	1.901(10)	Te(2)-O(2)	× 1	1.901(6)
Cs(1)-Cl(3)	× 2	3.420(7)	Rb(1)-Br(1)	× 1	3.443(3)
Cs(1)-Cl(2)	× 4	3.476(5)	Rb(1)-Br(2)	× 4	3.480(2)
Cs(1)-Cl(4)	× 2	3.847(8)	Rb(1)-Br(4)	× 2	3.695(3)
Cs(2)-Cl(4)	× 4	3.477(6)	Rb(2)-Br(2)	× 1	3.494(2)
Cs(2)-Cl(1)	× 2	3.578(6)	Rb(2)-Br(4)	× 1	3.515(2)
Cs(2)-Cl(2)	× 2	3.766(6)	Rb(2)-Br(3)	× 1	3.552(3)
Cs(3)-O(4)	× 8	2.604(12)	Rb(2)-Br(2)	× 2	3.670(2)
			Rb(3)-O(4)	× 8	2.614(8)
			Rb(3)-O(5)	× 4	3.204(9)



Graphical abstract

