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# Cation Deficient Layered Ruddlesden–Popper-Related Oxysulfides $La_2LnMS_2O_5$ (Ln = La, Y; M = Nb, Ta)

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The structures of the new oxysulfide Ruddlesden–Popper phases $La_2LnMS_2O_5$ (Ln = La, Y; M = Nb, Ta) are reported together with an iodide-containing variant: $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ ($0 \leq x < 0.11$). Structures were refined against powder-neutron or single-crystal X-ray diffraction data. All of these compounds exhibit an intergrowth structure with NaCl-type slabs [$La_2S_2$] alternating regularly with perovskite-type oxide slabs [$LnMO_5$] or [$La_{1-x}Nb_{1+x}O_5I_{2x}$]. In the oxide slabs, the trivalent and pentavalent cations are disordered on the long-length scale probed by diffraction methods, but bond length considerations suggest that they must be ordered at least on the length scale of the unit cell. The [$LnMO_5$] block of the iodide-free compounds derive from the ideal [$Ti_2O_5$] blocks found in $Ln_2Ti_2S_2O_5$ (Ln = Nd–Er; Y) by the formal substitution of two $Ti^{4+}$ ions with one $Ln^{3+}$ and one $M^{5+}$ion. The unusual partial insertion of iodide in the perovskite voids of the [$LaNbO_5$] block in $La_3NbS_2O_5$ was found to be coupled to a La/Nb substitution, maintaining the charge balance within the $[La_{1-x}Nb_{1+x}O_5I_{2x}]^{2-}$ block. The $Nb^{5+}$ ions were found to be too resistant to reduction to undergo the intercalation of alkali metals observed in the $Ln_2Ti_2S_2O_5$ series.

## Introduction

In the past few years, oxychalcogenides have seen a renewed interest with the discovery of low-dimensional compounds that exhibit interesting electronic[1,2] and/or magnetic[3] properties. For oxychalcogenide and other mixed-anion systems, the anionic segregation often leads to interesting structural features[4] such as low dimensionality. Many families of oxychalcogenide compounds show original intergrowth structures based on the stacking of chalcogenide and oxide 2D blocks.[5−8] The Ruddlesden−Popper-related phases $Ln_2Ti_2S_2O_5$ (Ln = Nd−Er; Y) are good examples of such intergrowth structures with [$Ln_2S_2$] rock-salt-type layers alternating regularly with [$Ti_2O_5$] perovskite-type layers.[7,8] These compounds have been shown to have good photocatalytic activity,[9,10] and reductive intercalation of lithium or sodium within the structure led to a metal-insulator transition.[11,12]

Perovskite phases are of particular importance in solid-state chemistry as they often exhibit interesting physical properties such as superconductivity, magnetoresistance, ferroelectricity, or ionic conductivity. In that respect, it is of great interest to find new intergrowth compounds with perovskite-type blocks and study their structures and physical properties. We have investigated several quaternary systems containing rare-earth and transition elements. During our

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exploration of the La/Nb/S/O system, a new Ruddlesden−Popper phase $La_3NbS_2O_5$ was found. This article describes the structural chemistry of this and other closely related compounds and attempts at alkali metal intercalation.

## Experimental Section

**Synthesis.** Single-phase samples of $La_3MS_2O_5$ (M = Nb, Ta) were prepared by the reaction between $La_2O_3$ (Aldrich 99.99%), $La_2S_3$ (synthesized from the elements (La, Aldrich 99.9%; S, Alfa 99.9995%) as described in ref 13) and $M_2O_5$ ($Nb_2O_5$, Aldrich 99.99%; $Ta_2O_5$, Alfa 99.999%) in the molar ratio 5:4:3. Subsequently, powder samples of $La_2YMS_2O_5$ (M = Nb, Ta) were prepared by reacting $La_2O_3$, $Y_2O_3$ (Alfa 99.999%), $La_2S_3$, and $A_2O_5$ in the molar ratio 2:3:4:3. Prior to the synthesis of the quaternary and quinary solids, the oxides were dried overnight at 900 °C in air, and the appropriate mixtures were ground together in an argon-filled dry box. Pellets (13 mm diameter) were placed in alumina crucibles, which were loaded in predried silica ampoules. The pellets were heated at 1000 °C for three periods of 3 days with intermediate regrinding in the dry box until single-phase products had been produced according to the results of PXRD measurements. $La_3NbS_2O_5$ and $La_3TaS_2O_5$ were yellow-orange in color; the Y-containing compounds appeared gray in color. The products were found not to be air sensitive.

Crystals of the iodide-containing material $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$ were obtained when the reaction product from a preliminary attempt at the syntheses of a phase of composition $La_4Nb_2S_4O_7$ was reheated at 1000 °C for 10 days in an evacuated silica tube containing a small amount of iodine ($<$5 mg/cm$^3$). A powder sample of $La_{2.97}Nb_{1.03}S_2O_5I_{0.06}$ contaminated by up to 12.5% by the mass of $LaNbO_4$ was also obtained by the iodine transport method on a mixture of composition $La_3NbS_2O_5$ ($La_2O_3$, $La_2S_3$, $NbO_2$, S in the ratio 2:1:2:1).

Attempts at reductive intercalation of lithium into $La_3NbS_2O_5$, analogous to reactions on the isostructural $Ln_2Ti_2S_2O_5$, were carried out by reacting the powder with *n*-BuLi in hexane at temperatures between 20 and 60 °C for up to 1 month. The products were washed three times with dry hexane and dried under vacuum before being removed to the dry box. All such attempts failed to result in any changes in the PXRD pattern. The orange/yellow powder turned grayish in color possibly indicating some surface reaction. This suggests that $Nb^{5+}$ is too resistant to reduction for a series of intercalation reactions similar to those described for $Ln_2Ti_2S_2O_5$[11,12] to be possible.

**Chemical Analysis.** The precise composition of small crystals contained in a powder sample of $La_3NbS_2O_5$ was checked by electron microprobe analysis performed at BRGM-CNRS laboratory (Orleans, France). We found a formulation $La_{2.94(4)}Nb_1S_{2.12(5)}O_{4.6(4)}$ that compares very well with the structural formulation $La_3NbS_2O_5$. Both samples obtained by iodine transport experiments were also analyzed with a chemical EDX-equipped scanning electron microscope JEOL 5800LV. Analysis of a large single crystal led to a composition $La_{2.9}Nb_1S_2O_{4.8}I_{0.2}$, very close to the structural formulation $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$. Analysis of the powder sample $La_{2.97}Nb_{1.03}S_2O_5I_{0.06}$ revealed a La/Nb/S ratio 3.0:1:1.8 and showed the presence of iodide and oxygen in the sample.

**Powder-Neutron and X-ray Diffraction.** Powder neutron diffraction (PND) measurements on single-phase powders of $La_3MS_2O_5$ and $La_2YMS_2O_5$ were made on 2 g samples, using the diffractometer POLARIS at the ISIS Facility (Rutherford Appleton Laboratory, U.K.). Diffraction patterns were measured by the time-of-flight method in the *d*-spacing range $0.5 < d < 8$ Å, using detector banks at mean scattering angles $2\theta$ of 35, 90, and 145° for a total integrated proton current at the production target of 600 $\mu$Ahr for 2 g of $La_3NbS_2O_5$, 400 $\mu$Ahr for 2 g of $La_3TaS_2O_5$, 400 $\mu$Ahr for 2 g of $La_2YNbS_2O_5$, and 400 $\mu$Ahr for 2 g of $La_2YTaS_2O_5$. These PND data were analyzed using the Rietveld profile refinement suite GSAS.[14] The background for each data bank was fit using a 10 term shifted Chebyschev function, and the peak profiles in each data bank were modeled using a convolution of back-to-back exponentials with a pseudo-Voigt function.

PND measurements on $La_{2.97}Nb_{1.03}S_2O_5I_{0.06}$ were performed on the high-resolution 3T-2 double-axis diffractometer in the Orphee reactor of the Laboratoire Léon Brillouin (Saclay, France). The data were collected at room temperature on a bank of $^3$He detectors with a step size of 0.05°. A monochromatic neutron beam ($\lambda = 1.225$ Å) was used, and a cylindrical vanadium sample holder (5 mm in diameter) was filled with 0.8 g of powder. The small sample size resulted in a fairly low signal/noise ratio. This sample was analyzed using simultaneous Rietveld refinement against PXRD and PND data using *FullProf*[15] and *WinPlotr*.[16] In this analysis, the background was defined by a linear interpolation between user-selected points. A pseudo-Voigt function was used for the X-ray peak profile and a pure Gaussian profile for the neutron profile. The March−Dollase model was used for preferred orientation (001 direction) in all of the refinements. The relative weights of the X-ray and neutron patterns was 60:40.

Powder X-ray diffraction (PXRD) patterns for Rietveld analysis were collected from a Siemens D5000 diffractometer (Cu K$\alpha$ radiation, $\lambda =$1.540598 and 1.544390 Å; $\theta/2\theta$ geometry; Kevex punctual detector). All of the powders were sieved at 200 $\mu$m to obtain a plane-sample surface and minimize preferred orientation.

**Single-crystal X-ray diffraction (SCXRD).** Data collection on an orange plate-like crystal of $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$ with dimensions $60 \times 90 \times 100$ $\mu$m$^3$ was carried out at room temperature on a Kappa CCD diffractometer using graphite-monochromatized Mo radiation ($\lambda = 0.71069$ Å). A set of 706 frames was collected in $\phi$ and $\omega$ scans mode, with a rotation of 1° and an exposure time of 15 s per frame; the crystal-to-detector distance was 30 mm. The data were corrected for Lorentz and polarization effects. Intensities were corrected for absorption (18.7 mm$^{-1}$) through the face-indexed option (min. and max. transmission coefficient = 0.2049 and 0.8446). The initial set of 5341 reflections was averaged according to the 4/*mmm* point group, leading to 320 independent reflections (= all data), with $R_{int} = 0.0589$. The structure was solved by direct methods (*SHELXS*[17]) and refined with the program JANA 2000 by a full-matrix least-squares technique based on $F^2$ against all data.[18]

## Results

Recent exploration of the La/Nb/S/O system carried out by some of us led to the discovery and characterization of

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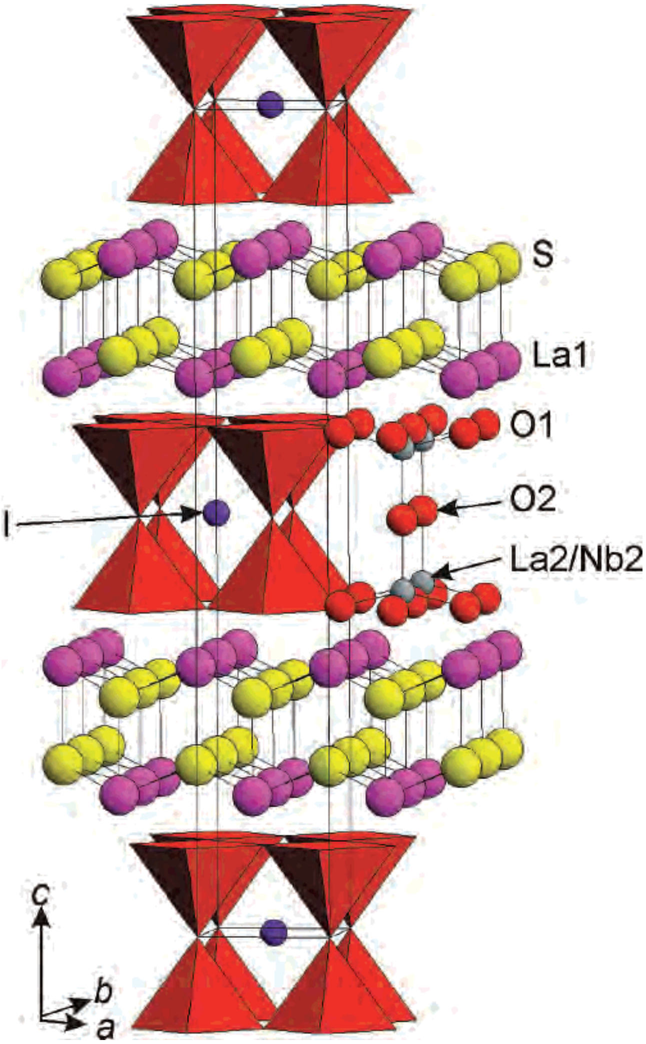

**Figure 1.** Idealized structure of the Ruddlesden−Popper-related phases $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ ($0 \leq x \leq 0.11$) In $La_3NbS_2O_5$, $La_2S_2$ rock-salt-type layers separate $LaNbO_5$ perovskite-type blocks in which lanthanum and niobium atoms (La2 and Nb2) share the same crystallographic site. The different sizes of these cations result in the atom O2 being displaced away from the mirror plane perpendicular to the crystallographic *c* axis on which it lies in the idealized structure. In $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ ($0 \leq x \leq 0.11$), the perovskite voids are partially filled with iodine, as indicated.

the new compound $La_{\sim 10.8}Nb_5S_{10}O_{20}$.[19] This compound exhibits a complex intergrowth structure with rock-salt-type layers [$La_2S_2$]. During this work, another unknown layered oxysulfide was identified but not fully characterized.[19] In the hope of finding a new intergrowth compound containing perovskite-type blocks, the La−Nb−S−O quaternary system was further investigated. First attempts to obtain crystals in the La−Nb−S−O system by the iodine vapor transport method (Experimental Section) led to the discovery of large platy orange crystals. EDX analysis revealed a new phase containing La, Nb, S, O, and I in the ratio 2.9:1.0:2:4.8:0.2. The structure of this compound was determined from SCXRD data (below), and the refinement produced a formula $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ with $x \approx 0.11$, very close to the result of EDX analysis. This structure determination showed that the product $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ ($x \approx 0.11$) had a structure closely related to that of $Sm_2Ti_2S_2O_5$.[7,8] Another synthesis attempt with iodine (Experimental Section) led to a powder sample corresponding to a similar phase but with a lower content of iodine, namely $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ with $x \approx 0.03$.

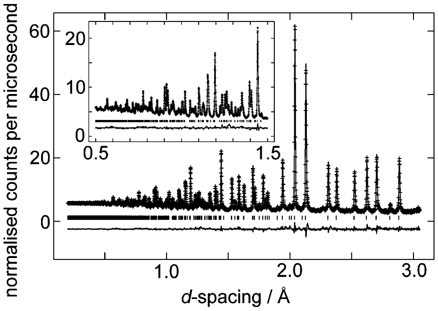

**Figure 2.** The refinement of $La_3NbS_2O_5$ against POLARIS PND data (145° detector bank). The measured (points), calculated (line), and difference (lower line) profiles are shown. The tick marks show the positions of allowed reflections.

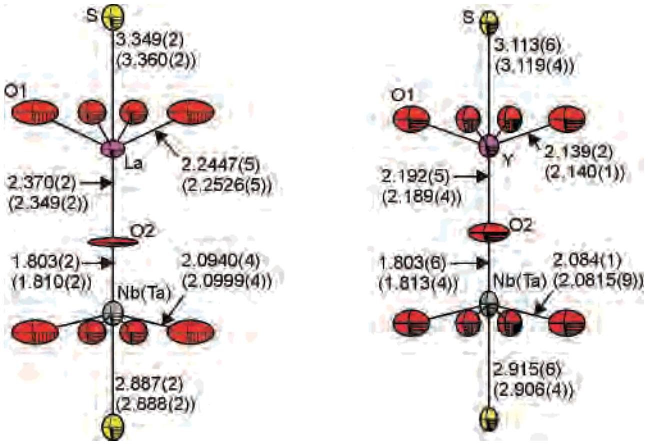

**Figure 3.** Local coordination geometries in the oxide slabs of $La_3NbS_2O_5$ (left) and $La_2YNbS_2O_5$ (right) derived from refinements against POLARIS PND data with displacement ellipsoids shown at the 99% level. Interatomic distances are given in angstroms. The comparative values for the tantalum analogues are shown in parentheses.

Subsequently, the reaction of $La_2O_3$, $La_2S_3$ and $Nb_2O_5$ in the ratio 5:4:3 as discussed in the experimental section led to a pure iodide-free powder sample of $La_3NbS_2O_5$. Following similar synthesis routes, a whole family of compounds of the composition $La_2LnMS_2O_5$ (Ln = La, Y; M = Nb, Ta) was obtained as pure powder samples (Experimental Section). The structures of these compounds refined from PND data are also closely related to the $Sm_2Ti_2S_2O_5$ structure type. In the discussion hereafter, we will first focus these iodine-free samples, and then we will describe the more-complex iodine-containing samples.

**Structures of $La_2LnMS_2O_5$. (Ln = La, Y; M = Nb, Ta).** Powder-neutron diffraction data of phase-pure $La_3NbS_2O_5$ revealed tetragonal symmetry with cell parameters $a$ = 4.0781(2) Å, $c$ = 25.230(1) Å, $V$ = 419.61(3) Å$^3$, and systematic absences consistent with a body-centered Bravais Lattice. Structure refinement was carried out using, as a starting model, the structure of the cation-defective Ruddlesden−Popper phase $Sm_2Ti_2S_2O_5$[7,8] (space group *I*4/*mmm* (No.

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**Table 1.** Results of PND Refinements at 295 K for $La_3NbS_2O_5$, $La_3TaS_2O_5$, $La_2YNbS_2O_5$, and $La_2YTaS_2O_5$

| compound | $La_3NbS_2O_5$ | $La_3TaS_2O_5$ | $La_2YNbS_2O_5$ | $La_2YTaS_2O_5$ |
|---|---|---|---|---|
| radiation | Neutron | | | |
| | POLARIS | | | |
| instrument | | | | |
| physical form | orange powder | orange powder | off-white powder | off-white powder |
| $T$ (K) | 295 | 295 | 295 | 295 |
| space group | $I4/mmm$ | $I4/mmm$ | $I4/mmm$ | $I4/mmm$ |
| fw | 653.7 | 741.8 | 603.74 | 691.78 |
| $a$ (Å) | 4.0781(2) | 4.09423(5) | 4.0523(2) | 4.0522(2) |
| $c$ (Å) | 25.230(1) | 25.1937(4) | 24.451(1) | 24.450(1) |
| $V$ (Å)$^3$ | 419.61(3) | 422.32(1) | 401.50(5) | 401.47(3) |
| $Z$ | 2 | 2 | 2 | 2 |
| $R_{wp}$ | 0.0237 | 0.0230 | 0.0239 | 0.0235 |
| $R_{F^2}$ | 0.150 | 0.155 | 0.090 | 0.090 |
| $\chi^2$ | 2.297 | 1.452 | 3.374 | 3.262 |

**Table 2.** Atomic Coordinates and Isotropic Atomic Displacement Parameters for $La_3NbS_2O_5$ from Powder-Neutron Diffraction

| formula | | | $La_3NbS_2O_5$ | | |
|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $100 \times U_{iso/eq}$/Å$^2$ | s.o.f. |
| La1 | 0 | 0 | 0.32487(2) | 0.67(2) | 1 |
| La2 | 0 | 0 | 0.07354(5) | 0.65(4) | 0.5[a] |
| Nb2 | 0 | 0 | 0.09185(6) | 0.65(4) | 0.5[a] |
| S | 0 | 0 | 0.20628(6) | 0.74(4) | 1 |
| O1 | 0 | $^1/_2$ | 0.11073(3) | 1.63(3) | 1 |
| O2 | 0 | 0 | 0.02039(6) | 2.34(7) | 0.5[a] |

[a] Not refined.

139)), in which NaCl-type slabs [$Sm_2S_2$] alternate regularly with perovskite-type slabs [$Ti_2O_5$], which contain empty 12-coordinate sites (voids) similar to those normally occupied by large cations in perovskites. The refined structure is shown in Figure 1. Unsatisfactory refinements, as judged by the agreement factors and the visual fit to the data were obtained if the La2 and Nb2 atoms replacing the titanium atoms of $Sm_2Ti_2S_2O_5$ in the oxide slab were located at identical positions 0 0 $z$. Furthermore, it was necessary to locate atom O2 in the central plane of the oxide slab on a split position 0 0 $\pm z$. The large $d$-spacing range accessible on POLARIS enabled the refinement to be carried out with all of the atoms described using anisotropic displacement ellipsoids. The refinement results are presented in Figure 2 and Table 1, and part of the structural model is depicted in Figure 3. Atomic coordinates are given in Table 2, atomic anisotropic displacement parameters are included as Supporting Information (Table S1), and selected bond distances are given in Table 3.

The $La_3TaS_2O_5$, $La_2YNbS_2O_5$ and $La_2YTaS_2O_5$ compounds were prepared for comparison with $La_3NbS_2O_5$, in particular to investigate the effect of changing the size of the trivalent ion located on the distorted-octahedral sites in the oxide layer. The results of refinement against POLARIS PND data, using the structure of $La_3NbS_2O_5$ as a starting model, are summarized in Table 1. The best powder pattern fit, the tables of atomic coordinates, and the anisotropic displacement parameters are included as Supporting Information (Figure S1 and Tables S2−S7). In the Y-containing materials, it was initially assumed that Y solely occupies the distorted-octahedral site (the La2 site in $La_3NbS_2O_5$). Attempts to distribute $Y^{3+}$ and $La^{3+}$ ions statistically over the La1 and La2 sites produced significantly poorer agreement factors. Refinements of the La/Y distibution converged on the ordered model with $Y^{3+}$ ions located solely on the distorted-octahedral sites in the oxide layer. The refined interatomic distances around these sites (Figure 3 and Table 3) are between 0.1 and 0.25 Å shorter in $La_2YMS_2O_5$ than in $La_3MS_2O_5$, consistent with the difference of 0.13 Å in the 6-coordinate radii of $La^{3+}$ and $Y^{3+}$.[20] For, $La_2YNbS_2O_5$ and $La_2YTaS_2O_5$, a stable refinement was once again obtained using a split site model for yttrium and niobium or tantalum, although the difference in the $z$ coordinates of the two sites was only 45% of that in the $La_3MS_2O_5$ compounds. An alternative model with yttrium and niobium or tantalum located on a single crystallographic site with a displacement ellipsoid slightly elongated in the $c$ direction produced refinements, which were only marginally poorer. The local environments in the oxide slabs are shown in Figure 3. In all of the compounds, O2 occupies a site split by the mirror plane perpendicular to the principal axis as described above, and the refinements showed that the ellipsoid was flattened in the $z$ direction and enlarged in the $xy$ plane compared with the ellipsoids for the other atoms. Attempts to locate O2 on sites split around the mirror planes containing the principal axis did not lead to improvement in the quality of the fit. The ellipsoid of O1 is slightly elongated in the direction of the two octahedral metal atoms to which it is bonded. These observations are discussed further below.

**Structure Determination and Refinement of Iodine-Containing Samples.** SCXRD analysis of the crystals of $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$ revealed tetragonal symmetry with cell parameters $a = 4.0639(6)$ Å, $c = 25.735(5)$ Å, $V = 425.0(1)$ Å$^3$, and systematic absences consistent with a body-centered Bravais Lattice. Structure solution by direct methods in space group $I4/mmm$ (No. 139) produced a crystal structure that resembles that of the cation-defective Ruddlesden−Popper phases $Sm_2Ti_2S_2O_5$.[7,8] Structure refinement revealed several notable structural features. First, the distorted octahedral site, similar to that occupied by titanium in $Sm_2Ti_2S_2O_5$, is fully occupied in $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ by both La2 and Nb2 atoms (located on slightly different 0 0 $z$ sites) in a manner that is not ordered on the scale probed by the diffraction experiment. Second, O2 in the central plane of the oxide slab is located on a site 0 0 $\pm z$ split by a mirror plane. These observations are similar to those made during refinement of the structure of $La_3Nb_1S_2O_5$. Conversely, the

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**Table 3.** Selected Interatomic Distances (Angstroms) in $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ ($x \approx 0$, 0.03 and 0.11), $La_3TaS_2O_5$, $La_2YNbS_2O_5$, and $La_2YTaS_2O_5$

| | | $La_3NbS_2O_5$ | $La_{2.97}Nb_{1.03}S_2O_5I_{0.06}$ | $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$ | $La_3TaS_2O_5$ | $La_2YNbS_2O_5$ | $La_2YTaS_2O_5$ |
|---|---|---|---|---|---|---|---|
| La1 | S1 (×4) | 2.9889(4) | 2.991(3) | 2.9844(5) | 3.0014(4) | 2.9747(4) | 2.9751(4) |
| | S1 | 2.992(2) | 2.970(13) | 3.005(2) | 2.982(2) | 3.002(1) | 3.000(1) |
| | O1 (×4) | 2.6072(5) | 2.612(7) | 2.612(3) | 2.6156(6) | 2.5990(4) | 2.5990(4) |
| La2/Y | S1 | 3.349(2) | 3.386(15) | 3.471(2) | 3.360(2) | 3.113(6) | 3.119(4) |
| | O1 (×4) | 2.2447(5) | 2.253(5) | 2.275(2) | 2.2526(5) | 2.139(2) | 2.140(1) |
| | O2 | 2.370(2) | 2.33(3) | 2.35(3) | 2.349(2) | 2.192(5) | 2.189(4) |
| | I (×4) | | 3.417(4) | 3.4248(8) | | | |
| Nb2/Ta | S1 | 2.887(2) | 2.874(16) | 2.934(3) | 2.888(2) | 2.915(6) | 2.906(4) |
| | O1 (×4) | 2.0940(4) | 2.087(3) | 2.0893(11) | 2.0999(4) | 2.084(1) | 2.0815(9) |
| | O2 | 1.803(2) | 1.85(3) | 1.92(3) | 1.810(2) | 1.803(6) | 1.813(4) |

observation of Fourier difference maps revealed that the voids in the perovskite slab, which are empty in $Sm_2Ti_2S_2O_5$ and in $La_3Nb_1S_2O_5$, are partially occupied in $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$. Initial attempts to locate some $La^{3+}$ ions in approximately 20% of the voids and to replace about 20% of the $S^{2-}$ ions by the $I^-$ ions revealed by EDX analysis were unsatisfactory ($R_{obs} \approx 0.2$). There was no indication that the heavier $I^-$ is present on the site occupied by $S^{2-}$, and furthermore, to achieve charge balance, this arrangement would result in an approximate composition $La_{3.6}Nb_{0.6}O_5S_{1.8}I_{0.2}$, which is a very La-rich composition compared with that suggested by EDX analysis on the single crystals. A second model in which approximately 20% of the voids were filled by $I^-$ and the La:Nb ratio was adjusted in favor of niobium to satisfy charge balance produced a far more satisfactory refinement ($R_{obs} = 0.0236$) and was in line with the results of EDX analysis. Refinement of the site occupancy factors of I, La2, and Nb2 was constrained to satisfy the charge balance according to the formula $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$. There was no clear indication that $I^-$ compensates for a deficiency of oxide on the O2 site: refinement of the occupancy of the split O2 site resulted in a value of 0.42(3) with no improvement in the $R$ values ($R_{obs} = 0.0235$), although a reliable refinement of this by X-ray diffraction is difficult, particularly given the large O2 displacement ellipsoid. The final formula of the compound as deduced from the refinement is $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$, in good agreement with EDX analysis. Subsequent refinement with the site occupancy factor for I decoupled from the La2/Nb2 ratio led to a similar composition within the standard deviations. The final refinement with all of the atoms apart from O2 refined anisotropically produced agreement factors $R_{obs} = 0.0236$ and $R_{wobs} = 0.0462$ for 294 reflections ($I > 2\sigma(I)$) and 23 parameters. The electron density residuals were +1.74 and −2.98 $e^-Å^{-3}$. Crystal data and structure refinement are reported in Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters are reported in Table 5. Anisotropic displacement parameters are given in the Supporting Information (Table S8). Table 3 gives selected bond distances.

**Table 4.** Crystallographic Data, Data Collection, and Refinement Data for a Crystal of $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ ($x \approx 0.11$)

| crystallographic data | |
|---|---|
| chemical formula | $La_{2.888(1)}Nb_{1.112(1)}S_2O_5I_{0.225(4)}$ |
| fw (g·mol$^{-1}$) | 676.6 |
| cryst syst | tetragonal |
| params | $a = 4.0639(6)$ Å |
| | $c = 25.735(5)$ Å |
| $V$ | 425.03(12) Å$^3$ |
| $Z$ | 2 |
| $D_{calcd}$ | 5.786 g/cm$^3$ |
| dimensions ($\mu$m$^3$) | 60 × 90 × 100 |
| **Data Collection and Reduction** | |
| $T$ | 293(2) K |
| wavelength (Å) | 0.71073 |
| Angular range $\theta$ (deg) | 5.08−34.95 |
| $h, k, l$ ranges | $-6 \le h \le 6$, $-6 \le k \le 5$, $-41 \le l \le 41$ |
| collected reflns | 5341 |
| independent reflns | 319 |
| observed reflns ($I > 2\sigma(I)$) | 294 |
| absorption correction | Gaussian |
| absorption coefficient | 16.947 mm$^{-1}$ |
| $T_{min}/T_{max}$ | 0.205/0.844 |
| $R_{int}$ | 0.0594 |
| **Refinement Data** | |
| refinement | Least-squares on $F^2$ |
| F(000) | 588 |
| data/restrictions/params | 319/0/23 |
| R obs [$I > 2\sigma(I)$] | R = 0.0236, wR = 0.0462 |
| R (all data) | R = 0.0280, wR = 0.0467 |
| extinction coefficient | 0.31(3) |
| electronic residues ($e^-$/Å$^3$) | 1.74 et −2.98 |

**Table 5.** Atomic Coordinates and Equivalent or Isotropic Atomic Displacement Parameters for a Crystal of $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ ($x \approx 0.11$)

| atom | site | $x$ | $y$ | $z$ | $100 \times U_{iso/eq}$*/Å$^2$ | s.o.f. |
|---|---|---|---|---|---|---|
| La1 | 4$e$ | 0 | 0 | 0.32404 (2) | 1.145(11)* | 1 |
| La2 | 4$e$ | 0 | 0 | 0.07240 (6) | 1.41(3)* | 0.444(1) |
| Nb2 | 4$e$ | 0 | 0 | 0.09328 (7) | 1.54(4)* | 0.556(1) |
| I | 2$a$ | 0 | 0 | 0.5 | 2.33(8)* | 0.225(4) |
| S | 4$e$ | 0 | 0 | 0.20727(8) | 1.33(4)* | 1 |
| O1 | 8$g$ | 0 | 0.5 | 0.1122(2) | 2.44(11)* | 1 |
| O2 | 4$e$ | 0 | 0 | 0.0188 (12) | 10.1(7) | 0.5 |

To confirm the model established for $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$ from SCXRD measurements we carried out a combined refinement against PXRD and PND measurements on the powder sample obtained by an iodine vapor transport experiment (Table S9 and S10 in the Supporting Information). Free refinement of the occupancy factors for La2, Nb2, and I produced an Nb excess equal to La deficiency and equal to half the I occupancy, within standard deviation limits. The split O2 site was also found to be half-filled (i.e., there was no indication from this experiment of oxide deficiency). This supports our assumption that iodide incorporation is compensated by La/Nb nonstoichiometry. Final refinement with the $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ stoichiometry imposed, and the displacement parameter for I fixed at the value obtained from the refinement against PND data only, converged satisfactorily, producing a refined composition $La_{2.97(1)}Nb_{1.03(1)}S_2O_5I_{0.06(1)}$.

## Discussion

The crystal structures of iodine-free $La_3MS_2O_5$ and $La_2YMS_2O_5$ (M = Nb, Ta) are similar to the structures of the series $Ln_2Ti_2S_2O_5$ (Ln = Nd− Er; Y). Within $[La_2S_2]$ slabs, La1 atoms are coordinated by five sulfur atoms distributed in a square-pyramidal arrangement and by four oxygen atoms (O1) from the oxide slab, resulting in a monocapped square-antiprismatic coordination for La1. Within the perovskite-like oxide slab, the metal cations $La^{3+}$ or $Y^{3+}$ and $Nb^{5+}$ or $Ta^{5+}$ are accommodated in distorted-octahedral sites composed of five oxygen atoms (4 × O1 and 1 × O2) and one sulfur atom. Particularly in the cases of $La_3MS_2O_5$, the very different radii of the $La^{3+}$ and $Nb^{5+}$ (or $Ta^{5+}$) cations means that these cannot be accommodated on a single crystallographic site. The larger $La^{3+}$ cation is located closer to the central plane of the oxide slab than the $Nb^{5+}$ or $Ta^{5+}$ cation. This in turn requires that the oxide ion O2, which ideally lies on the mirror plane in the center of the oxide slab, must move away from its ideal site and away from the $La^{3+}$ ion to accommodate this $La^{3+}$ ion in a 6-coordinate site. This displacement of O2 must then preclude the presence of a second $La^{3+}$ ion coordinated to O2. The coordination requirements of $M^{5+}$ and $La^{3+}$ are thus only satisfied if the sequence M−O2−La is strictly observed along the *c* direction in each unit cell. The structural models derived from the diffraction results suggest that the orientation of the M−O2−La sequences is disordered on the long-length scale probed in the X-ray or neutron diffraction experiments. If the smaller $Y^{3+}$ is substituted for $La^{3+}$, these arguments still hold: O2 still occupies a split site, but is located closer to the mirror plane (i.e., the ideal position it adopts in the $Ln_2Ti_2S_2O_5$ series). However, the $Y^{3+}$ and $Nb^{5+}$ (or $Ta^{5+}$) sites are close enough to be modeled fairly satisfactorily, using a single site with an elongated displacement ellipsoid.

In the results of all four refinements of the iodine-free materials against PND data, the O2 ellipsoid was refined anisotropically and was found to be flattened in the *z* direction and enlarged in the *xy* plane compared with the ellipsoids for the other atoms. The ellipsoid of O1 is also anisotropic and is slightly elongated in the direction of the two octahedral metal atoms to which it is bonded. Both of these features are most pronounced (Figure 3) in the $La_3MS_2O_5$ examples, suggesting that they are a consequence of the disorder of the different-sized cations and are thus more pronounced when the difference in the sizes of the trivalent and pentavalent cations in the oxide slab is larger. Bond valence calculations carried out on $La_3NbS_2O_5$ using the *EUTAX* package[21] and performed using an artificial model in the non-centrosymmetric *I*4*mm* sub-group of *I*4/*mmm*, to allow the ordering of $La^{3+}$ and $Nb^{5+}$ ions in the oxide slabs, produced bond-valence sums of 4.02 and 4.03 for $La^{3+}$ and $Nb^{5+}$, respectively. The analogous calculation for $La_2YNbS_2O_5$ produced bond-valence sums of 3.79 and 4.28 for $Y^{3+}$ and $Nb^{5+}$, respectively. The apparent overbonding of $La^{3+}$ or $Y^{3+}$and underbonding of $Nb^{5+}$ is presumably relieved by the disorder in the oxide-ion positions described by the anisotropic displacement parameters, which is not accounted for in the bond-valence calculation. The discrepancy between the calculated bond-valence sums and the expected values is smaller in $La_2YNbS_2O_5$ than in $La_3NbS_2O_5$, and this mirrors the smaller size mismatch of the trivalent and pentavalent cations and the smaller anisotropy of the O1 and O2 displacement ellipsoids in the Y-containing cases.

In the samples that were prepared using iodine as a transport agent, iodide ions fill up to 20% of the voids in the perovskite-like oxide slabs. In the sample $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$ analyzed by SCXRD, this site is coordinated on average by four niobium ions at 3.74 and four lanthanum ions at 3.425 Å. This is somewhat similar to the coordination environment of some europium atoms in $Eu_{27}Ti_{20}I_{0.70}Cl_{1.30}S_{54}O_{12}$.[22] Eight O1 ions in the outer parts of the oxide slabs are 3.53 Å distant (a distance comparable to the sum of the $I^-$ and $O^{2-}$ ionic radii[20]). The four I−O2 contacts, however, are a short 2.91 Å. Whereas this distance is comparable to the I−O contact in the salt $[Ru_3(CO)_9H]I$ (2.92 Å),[23] this distance seems short for an oxide iodide material. One possibility that would minimize unfavorable repulsions is partial vacancy of oxide coupled with the presence of charge-compensating iodide ions, leading to a composition of approximately $La_3NbO_{4.9}S_2I_{0.2}$. Whereas the SCXRD refinement does not indicate any deficiency at the O2 site, this technique is insensitive to atoms of low atomic number, and, furthermore, the displacement ellipsoid of O2 is extremely large. However, the SCXRD refinement does indicate that the material is slightly niobium rich by an amount exactly required to compensate for the presence of iodide, without needing to invoke oxide deficiency. The large displacement parameter of O2 may be a consequence of the accommodation of iodide in the void site. Comparison of the displacement ellipsoids in $La_3NbS_2O_5$ (Table 2), in the impure sample of $La_{2.97}Nb_{1.03}S_2O_5I_{0.06}$ (Table S10 in the Supporting Information), and in $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$ (Tables 5 and S8 in the Supporting Information) supports this idea. It reveals that the ratio of the oxygen-equivalent isotropic displacement parameters *U*(O2)/*U*(O1) increases with the iodide content from 1.43 in $La_3NbS_2O_5$ to 2.88 in $La_{2.97}Nb_{1.03}S_2O_5I_{0.06}$ and 4.14 in $La_{2.89}Nb_{1.11}S_2O_5I_{0.22}$. This suggests a local reorganization of the oxide slab with an increase of the I−O2 contact on accommodation of iodide in the structure.

## Conclusions

In summary, we have synthesized new oxysulfide Ruddlesden−Popper-type phases $La_2LnMS_2O_5$ (Ln = La, Y; *M* = Nb, Ta). These compounds exhibit an intergrowth

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structure, with NaCl type slabs [$La_2S_2$] alternating regularly with perovskite-type slab [$LnMO_5$]. The structure derives from the ideal structure of $Sm_2Ti_2S_2O_5$ containing [$Ti_2O_5$] perovskite blocks by the formal substitution of 1 $La^{3+}$ and 1 $Nb^{5+}$ for 2 $Ti^{4+}$. Incorporation of iodide in the perovskite voids of $La_3NbS_2O_5$ was found to be coupled to La/Nb substitution on the metal site of the oxide block and leads to compounds with formula $La_{3-x}Nb_{1+x}S_2O_5I_{2x}$ that maintains the oxidation state equilibrium between $La^{3+}$, $Nb^{5+}$, $S^{2-}$, $O^{2-}$, and $I^-$. Attempts to introduce a mixed-valence $Nb^{4+}/Nb^{5+}$ in this compound either by lithium intercalation or by direct synthesis have been unsuccessful.

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**Supporting Information Available:** Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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