

A mixed-valent niobium oxysulfide, $\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$

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Dilanthanum triniobium disulfide octaoxide, $\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$, crystallizes in the orthorhombic space group $Pnmm$ and is isostructural with the $\text{Ln}_2\text{Ta}_3\text{X}_2\text{O}_8$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd , and $X = \text{S}$ and Se) family of tantalum compounds. Nb^{4+} and Nb^{5+} ions co-exist in the structure and occupy different crystallographic sites. While the Nb^{4+} ions are found in mixed oxygen and sulfur octahedra, the Nb^{5+} ions are found in oxygen-only octahedra.

Comment

Oxychalcogenides containing electropositive elements, like rare earth or alkaline earth metals, combined with transition metals often exhibit a lamellar structure, with segregation in the oxide and sulfide layers. The $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Sm}$ and Pr) family of compounds (Boyer *et al.*, 1999; Goga *et al.*, 1999) is a good example of such intergrowth structures, with Ln_2S_2 rock-salt-type layers alternating regularly with Ti_2O_5 perovskite-type layers. The structure of the $(\text{Sr}_{n+1}\text{M}_n\text{O}_{3n-1})$ - (Cu_2S_2) ($M = \text{Sc}, \text{Fe}, \text{Ni}$ and Cu) family of compounds (Zhu & Hor, 1997; Otschi *et al.*, 1999) can also be described as an intergrowth of perovskite- and fluorite-type layers. Recently, a niobium oxysulfide, namely $\text{La}_{10.8}\text{Nb}_5\text{S}_{10}\text{O}_{20}$, was reported to have an intergrowth structure in which Ln_2S_2 rock-salt-type layers alternate with a complex mixed lanthanum and niobium oxysulfide layer (Boyer-Candalen & Meerschaut, 2000). In a quest for a much simpler intergrowth structure in the $\text{La}/\text{Nb}/\text{S}/\text{O}$ system, we have found the title compound, $\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$, as a by-product. The observed systematic conditions ($k + l = 2n$ for $0kl$ and $h + l = 2n$ for $h0l$) allow only two possible space groups, *viz.* $Pnn2$ (No. 34) and $Pnmm$ (No. 58), and the intensity statistics indicate a centrosymmetric space group. Subsequently, we realized that $\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$ was isostructural with the $\text{Ln}_2\text{Ta}_3\text{X}_2\text{O}_8$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd , and $X = \text{S}$ and Se) family of tantalum compounds (Brennan *et al.*, 1991; Brennan & Ibers, 1992). Using the reported atomic parameters and space group $Pnmm$, the refinement led to an R factor of 2.58% for the observed reflections and 80 parameters. At this stage, examination of the Fourier difference

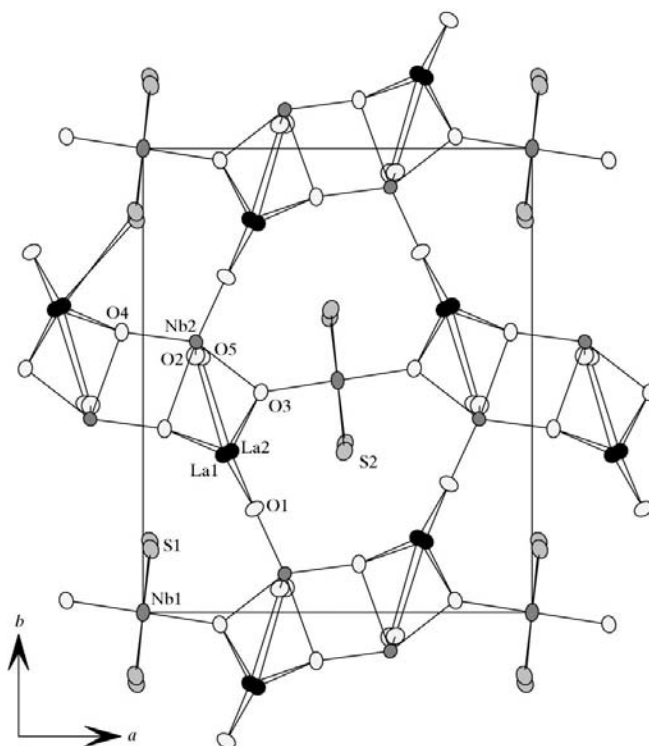


Figure 1

A view of the structure of $\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$ along the c axis. Displacement ellipsoids are shown at the 80% probability level.

map revealed a residual peak ($4.52 \text{ e } \text{\AA}^{-3}$) at 0.63 \AA from atom Nb1. We then repeated the refinement with atom Nb11 at this site, constraining the sum of the site-occupancy factors of atoms Nb1 and Nb11 to be constant and the atomic displacement parameters of the two atoms to be identical. The refinement led to a better R factor (2.47%) for the observed reflections and 81 parameters. A projection of the structure of $\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$ is shown in Fig. 1. La atoms are located in a tricapped-trigonal-prismatic environment consisting of seven O and two S atoms. Atom Nb2 is located in a distorted octahedral environment consisting only of O atoms, while atoms Nb1 and Nb11 are located in distorted octahedral environments containing two O and four S atoms. As shown in Fig. 2, atom Nb1 is shifted from the center of the octahedron along the c axis. Consequently, two consecutive Nb1 atoms form, along this direction, either a short contact [$3.368(2) \text{ \AA}$] or an elongated contact [$4.301(2) \text{ \AA}$]. Atom Nb11 behaves in a similar manner, but this atom is shifted along the c axis in the opposite direction to atom Nb1 (Fig. 2). We observed a

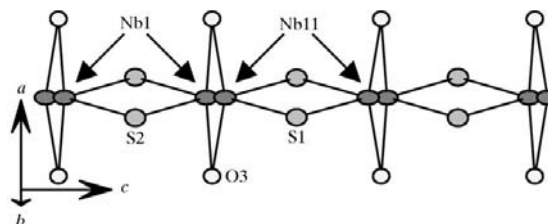


Figure 2

A view of the Nb1- or Nb11-atom chain running along the c axis. Displacement ellipsoids are shown at the 80% probability level.

superstructure that led to the doubling of the c parameter from 3.83 to 7.66 Å, which is a result of the displacement of atoms Nb1 or Nb11 from the center of the surrounding octahedron. Since atoms Nb1 and Nb11 are displaced along the c direction in opposite directions from the center of the octahedron by $c/2$, we believe that the Nb11-atom positions correspond to stacking faults. The shortest Nb1...Nb1 distance (3.368 Å) is comparable to the Nb2...Nb2 distance (3.328 Å) and is longer than the distance expected for a Peierls-like pair (~ 3 Å). Using the bond-valence method (Brown, 1981; Brese & Keeffe, 1991) and the refined Nb—O and Nb—S distances, we found bond-valence sums of 4.04 and 5.01 for atoms Nb1 and Nb2, respectively. These values are in excellent agreement with a charge equilibrium of $(\text{La}^{3+})_2(\text{Nb}^{4+})(\text{Nb}^{5+})_2(\text{S}^{2-})_2(\text{O}^{2-})_8$ and clearly attest that $\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$ is a mixed-valence compound with Nb^{4+} and Nb^{5+} ions in distinct crystallographic sites.

Experimental

$\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$ was obtained as a by-product during an exploration of the La/Nb/S/O system. Powdered La_2S_3 , Nb_2O_5 and La_2O_3 , weighed in a 4:3:2 ratio, were mixed finely and pressed into a pellet. The pellet was sealed in an evacuated silica tube and heated at 1273 K for 120 h. The intermediate reaction product was ground, mixed with a small amount of iodine to favor crystallization and reheated in a temperature-gradient furnace at 1273 K for 240 h. Small black needle-shaped crystals of the title compound were found at the cool end of the tube. Chemical analyses performed on these crystals using an EDS-equipped scanning electron microscope revealed an La/Nb/S ratio of close to 2:3:2.

Crystal data

$\text{La}_2\text{Nb}_3\text{S}_2\text{O}_8$	Mo $K\alpha$ radiation
$M_r = 748.67$	Cell parameters from 12 094 reflections
Orthorhombic, $Pnmm$	reflections
$a = 9.8698$ (2) Å	$\theta = 2.9\text{--}35.0^\circ$
$b = 11.7941$ (3) Å	$\mu = 13.58$ mm $^{-1}$
$c = 7.6686$ (1) Å	$T = 293$ (2) K
$V = 892.7$ (2) Å 3	Needle, black
$Z = 4$	$0.07 \times 0.03 \times 0.03$ mm
$D_x = 5.571$ Mg m $^{-3}$	

Data collection

Nonius KappaCCD diffractometer	2070 independent reflections
CCD φ scans	1811 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian	$R_{\text{int}} = 0.064$
(<i>JANA2000</i> ; Petricek & Dusek, 2000)	$\theta_{\text{max}} = 35.0^\circ$
$T_{\text{min}} = 0.511$, $T_{\text{max}} = 0.747$	$h = -15 \rightarrow 15$
20 315 measured reflections	$k = -18 \rightarrow 19$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$\Delta\rho_{\text{max}} = 1.38$ e Å $^{-3}$
$wR(F^2) = 0.052$	$\Delta\rho_{\text{min}} = -1.38$ e Å $^{-3}$
$S = 1.08$	Extinction correction: <i>SHELXL97</i>
2070 reflections	Extinction coefficient: 0.00085 (8)
81 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 3.1635P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: not used (isotypic); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXTL* (Bruker, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1017). Services for accessing these data are described at the back of the journal.

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