The Mixed Lanthanum Dichalcogenide β-LaS$_{1.86(1)}$Se$_{0.14(1)}$: Synthesis, Crystal Structure, Raman Spectrum and Optical Band Gap

Christian Bartsch and Thomas Doert

Department of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany

Reprint requests to PD Dr. Thomas Doert. Fax: +49 351 463 37287.
E-mail: thomas.doert@chemie.tu-dresden.de

The ternary lanthanum sulfide selenide β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ was obtained by reaction of the elements in an NaCl flux. The new compound adopts the β-LnS$_2$ structure type and crystallizes in the orthorhombic space group *Pnma* (no. 62) with lattice parameters of $a = 814.77(1)$, $b = 1638.46(1)$ and $c = 413.88(1)$ pm. Raman lines indicate the presence of mixed $(S_{1-y}Se_y)^{2-}$ dianions with $y \approx 0.14$, besides the well known S_2^{2-} dianions. The band gap of β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ is 2.5 eV as determined by optical spectroscopy.

Key words: Polychalcogenides, Rare Earth Metal, Crystal Structure, Raman Spectra

Introduction

LnS$_2$ disulfides of trivalent rare earth metals (Ln = Y, La–Nd, Sm, Tb–Lu) are dimorphic. They either adopt the monoclinic *alpha* type (space group $P2_1/a$, no. 14) with lattice parameters $a \approx 800$ pm, $b \approx 400$ pm, $c \approx 800$ pm and $\beta \approx 90°$, or the orthorhombic *beta* type (space group *Pnma*, no. 62) with lattice parameters of $a \approx 800$ pm, $b \approx 1600$ pm and $c \approx 400$ pm [1, 2]. Diselenides LnSe$_2$ of the same metals on the other hand are only known in the *alpha* type structure (*cf.* [3], *e. g.*). The two structures are polytypes resulting from a different packing of their fundamental building blocks: puckered [LnX] double slabs and planar layers [X] of chalcogen atoms. With trivalent Ln metals, the puckered double slabs can be written as [$Ln^{3+}X^{2-}$], thus carrying an overall charge of $+1$. This charge has to be compensated by the planar chalcogen layer, which is realized by forming X_2^{2-} dianions (X = S, Se) in both structure types. In accordance with the localization of electrons, all disulfides and diselenides of trivalent Ln atoms are semiconductors.

We recently investigated a complete Vegard series of ternary lanthanum sulfide selenides LaS$_{2-x}$Se$_x$ ($0 \leq x \leq 2$) [4]. These mixed sulfide selenides, which have been prepared by metathesis reactions from anhydrous lanthanum chloride and alkali metal polychalcogenides, adopt the α-LnS$_2$ structure with a pronounced site preference of the crystallographically independent chalcogen positions. Raman spectroscopic measurements evidence mixed $(S_{1-y}Se_y)^{2-}$ chalcogen dianions for this material. Performing the synthesis in a slightly modified way, however, yields a ternary lanthanum sulfide selenide LaS$_{1.86(1)}$Se$_{0.14(1)}$ adopting the orthorhombic *beta*-type structure. This compound is presented in the following.

Results and Discussion

β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ crystallizes in the orthorhombic space group *Pnma* (no. 62) with lattice parameters of $a = 814.77(1)$ pm, $b = 1638.46(1)$ pm and $c = 413.88(1)$ pm. Crystallographic data and the results of the structure determination are listed in Tables 1 and 2, interatomic distances of β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ in Table 3.

The crystal structure of β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ is built up from puckered double slabs [LaS]$^+$ and planar chalcogenide layers composed of a herringbone pattern of X_2^{2-} dianions stacked alternately along [010] (Fig. 1). The La and S atoms of the double slabs occupy the *Wyckoff* site 8d. The planar layer comprises two crystallographically independent chalcogen positions (both *Wyckoff* site 4c) so that each X_2^{2-} dianion is formed by an $X2$ and an $X3$ atom. Both positions, $X2$ and $X3$, show very similar occupancies by sulfur and selenium (Table 2). In contrast, no evidence for a partial selenium occupation

Table 1. Crystallographic data of β-LaS$_{1.85(1)}$Se$_{0.15(1)}$.

Formula	LaS$_{1.86(1)}$Se$_{0.14(1)}$
M_r	206.97
Crystal size, mm^3	$0.05 \times 0.05 \times 0.04$
Color	black
Crystal system; space group	orthorhombic; *Pnma*
a, pm	814.8(3)
b, pm	1637.9(7)
c, pm	414.2(2)
V, pm$^3 \cdot 10^{-6}$	552.7(4)
Z	8
$\rho_{calc.}$ g cm^{-3}	4.96
$F(000)$, e	722.8
μ(MoK_α), mm^{-1}	17.5
Absorption correction	numerical, SADABS [11]
T_{min} / T_{max}	0.541 / 0.640
hkl range	$-14 \leq h \leq 14$, $-29 \leq k \leq 29$, $-7 \leq l \leq 7$
2θ range, deg	4.84 – 65.48
Reflections measured / unique	10623 / 1815
R_{int} / R_σ	3.23 / 2.67
Refinement method	SHELXL-97 [12], full-matrix least-squares on F^2
Restrictions / parameters	0 / 40
R_1 / wR_2 [$I \geq 2\sigma(I)$]	0.020 / 0.052
R_1 / wR_2 (all data)	0.025 / 0.058
GoF (F^2)	1.15
Extinction parameter	0.0054(2)
$\Delta\rho_{fin}$ (max / min), 10^6 e$^-$ pm^{-3}	1.70 / -1.63

Fig. 1. Crystal structure of LaS$_{1.86(1)}$Se$_{0.14(1)}$ (top) and projection of the chalcogenide layer (bottom). The distance within the dichalcogenide dianions (pm) and the selenium content (%) of the mixed sites $4c$ are shown; atoms are displayed at a 99.99 % probability level.

of the S1 position (site $8c$) in the double slabs is found. In accordance with its higher electronegativity, sulfur obviously prefers the positions closer to lanthanum. The same site preference of S and Se has been found for the series of α-LaS$_{2-x}$Se$_x$ compounds ($0 < x < 2$) [4].

The structure of the title compound is well known from the binary phase β-LaS$_2$, *e. g.* [1, 2]. Lanthanum is surrounded by nine chalcogen atoms forming a capped square antiprism. In accordance with the small amount of incorporated selenium, the lattice parameters of β-LaS$_{1.85(1)}$Se$_{0.15(1)}$ are only slightly larger than those of the binary sulfide β-LaS$_2$ with $a =$ 813.98(5), $b =$ 1637.85(9) and $c =$ 414.36(3) pm. Interestingly, the La–X distances are nearly unaffected thereof (Table 3). The La–S distances within the double slabs are equal within an uncertainty interval of 3σ for both compounds, and the distances between lanthanum and the chalcogen positions in the planar layer show only minor differences. The distance in the dichalcogenide dianions is 214.0(1) pm, which is slightly larger than that observed in β-LaS$_2$ (211.5(3) pm) or other binary rare earth metal disulfides [1, 2]. On the other hand, the shortest distances between two dianions of the chalcogenide lay-
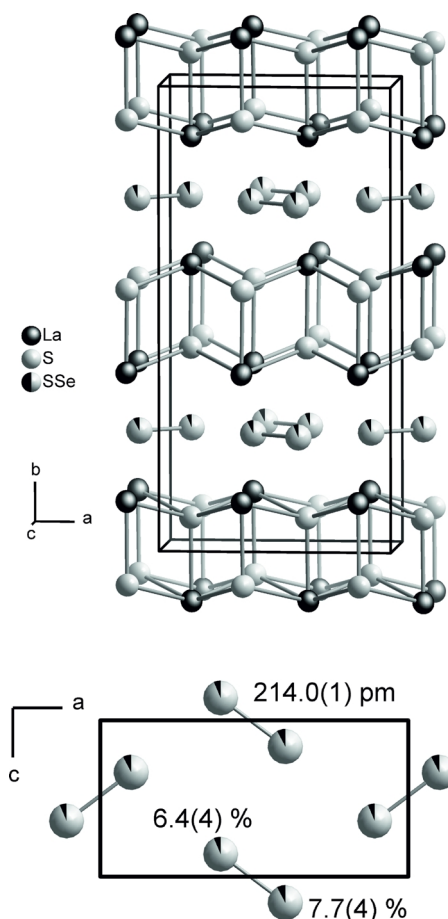
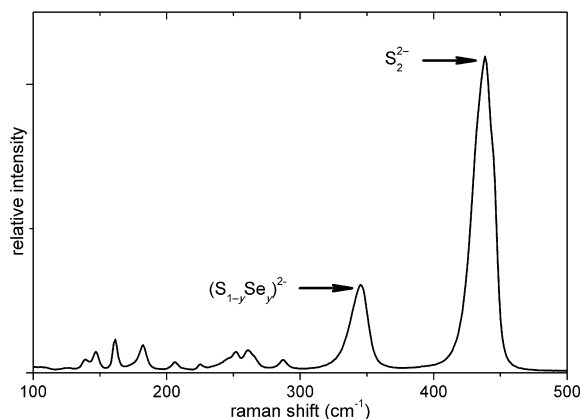ers even shrink moderately (307.9(1) pm compared to 309.7(2) pm).

As the scattering data yield only an average model of the crystal structure, it is not possible to determine if the planar chalcogenide layer contains mixed (S$_{1-y}$Se$_y$)$^{2-}$ dianions or only the homonuclear species S$_2^{2-}$ and, to a small extent, Se$_2^{2-}$. Evidence for the existence of mixed diatomic anions (S$_{1-y}$Se$_y$)$^{2-}$ was, however, found in Raman spectroscopic measurements. In accordance with literature data for binary disulfides [2, 5], the Raman spectrum of β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ exhibits the characteristic line for the stretching mode of the S$_2^{2-}$ dianion at about 440 cm^{-1}, Fig. 2. Besides, another pronounced Raman line is visible at *ca.* 340 cm^{-1} (Fig. 2)

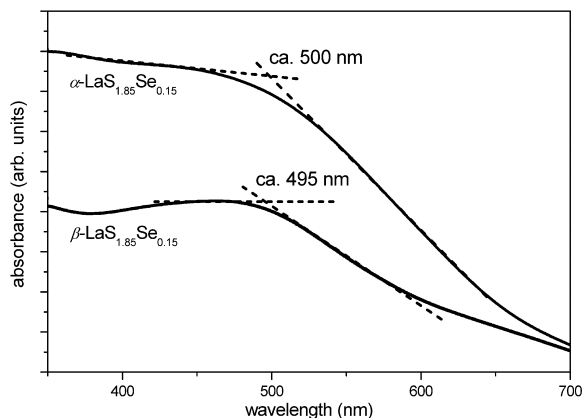| Atom	Site	x	y	z	sof	U_{eq}
La1	8d	0.37083(2)	0.11174(1)	0.28091(3)	1	72.2(5)
S1	8d	0.12515(7)	0.06735(4)	0.7601(1)	1	79(1)
S2	4c	0.3993(1)	1/4	0.8326(2)	0.936(4)	104(2)
Se2	4c	0.3993(1)	1/4	0.8326(2)	0.064(4)	104(2)
S3	4c	0.1091(1)	1/4	0.3564(2)	0.923(4)	102(2)
Se3	4c	0.1091(1)	1/4	0.3564(2)	0.077(4)	102(2)

Table 2. Site, occupancy (sof) and isotropic displacement parameters ($\times 10^4$ pm^2) for β-LaS$_{1.86(1)}$Se$_{0.14(1)}$.

Table 3. Selected interatomic distances (pm) in β-LaS$_{1.86(1)}$Se$_{0.16(1)}$ and comparison to those of β-LaS$_2$ (X: mixed occupied chalcogen positions 4c of the planar layers).

Atoms	β-LaS$_{1.86(1)}$Se$_{0.15(1}$	β-LaS$_2$ [1]
La–S1$^{\#1}$	290.5(1)	290.5(2)
La––S1	291.1(1)	291.0(2)
La–S1$^{\#2}$	293.5(1)	293.8(1)
La–S1$^{\#3}$	303.1(1)	303.0(2)
La–S1$^{\#4}$	313.7(1)	313.7(2)
La–X2$^{\#3}$	293.8(1)	293.1(1)
La–X2	322.5(1)	323.3(1)
La–X3$^{\#4}$	303.6(1)	302.9(1)
La–X3	312.7(1)	313.0(1)
X2–X3$^{\#1}$	214.0(1)	211.2(3)
X2–X3	307.9(1)	309.7(2)

Symmetry code: $^{\#1}$: $x+1/2, y, -z+3/2$; $^{\#2}$: $-x+1/2, -y, z-1/2$; $^{\#3}$: $x, y, z-1$; $^{\#4}$: $x+1/2, y, -z+1/2$.

Fig. 3. Comparison of the UV/Vis spectra of α-LaS$_{1.83(1)}$Se$_{0.17(1)}$ (top) and β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ (bottom).

ture data [4, 6] we may assume that the S and Se occupancies obtained by X-ray structure analyses reflect the composition of the $(S_{1-y}Se_y)^{2-}$ dianions with $y \approx 0.14$ within the experimental error.

The band gap of β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ was determined by optical spectroscopy to 500 nm (2.5 eV). This is well in accordance with the band gap of a compound of similar composition adopting the *alpha* type structure, namely α-LaS$_{1.83(1)}$Se$_{0.17(1)}$, with 495 nm [4], Fig. 3. The band gap varies, thus, with the chemical composition and does not depend on the structure type.

Fig. 2. Raman spectrum of β-LaS$_{1.86(1)}$Se$_{0.14(1)}$; the signals due to the stretching modes of S$_2^{2-}$ and $(S_{1-y}Se_y)^{2-}$ dianions are indicated.

which can be attributed to the stretching mode of a mixed $(S_{1-y}Se_y)^{2-}$ anions. This line matches those for mixed $(S_{1-y}Se_y)^{2-}$ anions in the series α-LaS$_{2-x}$Se$_x$ where the respective Raman signature was found between 320 cm^{-1} and 290 cm^{-1} depending on the Se content of the compound [4]. Characteristic Raman lines for mixed $(S_{1-y}Se_y)^{2-}$ species were also observed for the pyrite type RuS$_{1-x}$Se$_x$ series [6]. The respective Raman line for a Se$_2^{2-}$ dianion is found at approximately 215 cm^{-1} [7]. By comparison with litera-

Conclusion

The ternary lanthanum sulfide selenide β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ was obtained by NaCl flux synthesis starting from the elements. The new compound adopts the β-LnS$_2$ structure type in space group *Pnma* (no. 62) with lattice parameters of $a = 814.77(1)$, $b = 1638.46(1)$ and $c = 413.88(1)$ pm. Raman lines indicate the presence of mixed $(S_{1-y}Se_y)^{2-}$ dianions with $y \approx 0.14$ besides S$_2^{2-}$ dianions. The band gap of β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ determined by optical spectroscopy is 2.5 eV. Both, Raman and UV/Vis spectra, show no significant differences between ternary members of the *alpha* and

beta series of LaS$_{2-x}$Se$_x$ compounds of the same composition.

Experimental Section

Synthesis

All manipulations with the reagents were carried out under purified argon (Air Liquide, 99.999 %). Pieces of lanthanum, freshly filed from a rod (99.9 %, Strem), sulfur (99.95 %, Alfa Aesar; recrystallized from CS$_2$ and twice sublimed prior to use) and selenium (99.99 %, Fluka) in an atomic ratio La : S : Se = 1 : 1.9 : 0.1 together with a threefold excess of NaCl (99.9 %, Merck, dried under vacuum prior to use) were filled in a glassy carbon crucible which was inserted in a silica ampoule. The ampoule was flame sealed and placed in a furnace which was then heated to 850 °C with a heating rate of 2 K min^{-1}. After one week the samples were cooled to r. t. and rinsed with a 1 : 1 mixture of ethanol and water to remove the flux material. The product consists of red, plate-like, lustrous crystals.

Phase analyses

Phase purity of the reaction products was checked by X-ray powder diffraction (Panalytical, X'Pert PRO, Cu$K_{\alpha 1}$ radiation, Bragg-Brentano setup). Using silicon as internal standard and the LeBail method [8], the lattice parameters of the title compound were determined by profile fitting with the program JANA2006 [9].

Single-crystal structure determination

A complete X-ray data set of a suitable crystal of β-LaS$_{1.86(1)}$Se$_{0.14(1)}$ was recorded on a Bruker Apex2 CCD diffractometer with MoK_{α} radiation (graphite monochromator) at ambient temperature. Lp corrections were performed with the APEX SUITE software [9] and a numerical absorption correction was applied using SADABS [11]. Structure solution and refinement were performed with SHELXS/L-97 [12]. The occupancy factors of the mixed occupied chalcogen positions X2 and X3 were coupled to 1 as no indications for deficiencies were found.

Optical spectroscopy

The Raman spectra were recorded on single crystals with a Renishaw RM 2000 Raman microscope equipped with a 633 nm He/Ne Laser in the range from 100 nm to 500 nm.

The optical band gaps were determined by UV/Vis spectroscopy with a Varian Cary 4000 on powdered samples using BaSO$_4$ (Merck, white standard DIN 5033) as standard. Measurements were performed in the range from 350 nm to 900 nm. The band gap was determined as the onset-wavelength at the absorption edge.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-423352.

[1] Th. Schleid, P. Lauxmann, Chr. Graf, Chr. Bartsch, Th. Doert, *Z. Naturforsch.* **2009**, *64b*, 189.

[2] a) S. Bénazeth, M. Guittard, J. Flahaut, *J. Solid State, Chem.* **1981**, *37*, 44; b) B. LeRolland, P. Molinié, P. Colombet, P. F. McMillan, *J. Solid State Chem.* **1994**, *113*, 312.

[3] Th. Doert, Chr. Graf, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1101.

[4] Chr. Bartsch, Th. Doert, *J. Solid State Chem.*, submitted.

[5] a) I. G. Vasilyeva in *Handbook on the Physics and Chemistry of the Rare Earths*, (Eds.: K. A. Gschneidner Jr., L. Eyring, G. H. Lander), Vol. 32, Elsevier, Amsterdam **2001**, chapter 209 (Polysulfides), p. 567; b) A. Grzechnik, *Physica B* **1999**, *262*, 426.

[6] H. C. Lin, M. C. Lee, S. S. Lin, Y. S. Huang, *Solid State Commun.* **1992** *82*, 821.

[7] a) S. Strobel, A. Choudhury, P. K. Dorhout, Chr. Lipp,

T. Schleid, *Inorg. Chem.* **2008**, *47*, 4936; b) A. Heerwig, A. Isaeva, M. Ruck, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1131.

[8] A. LeBail, H. Duroy, J. L. Fourquet, *Mat Res. Bull.* **1988**, *23*, 447.

[9] V. Petříček, M. Dušek, L. Palatinus, JANA2006, The Crystallographic Computing System, Institute of Physics, University of Prague, Prague (Czech Republic) **2006**.

[10] APEX SUITE, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2008**.

[11] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2002**.

[12] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467; *ibid.* **2008**, *A64*, 112.