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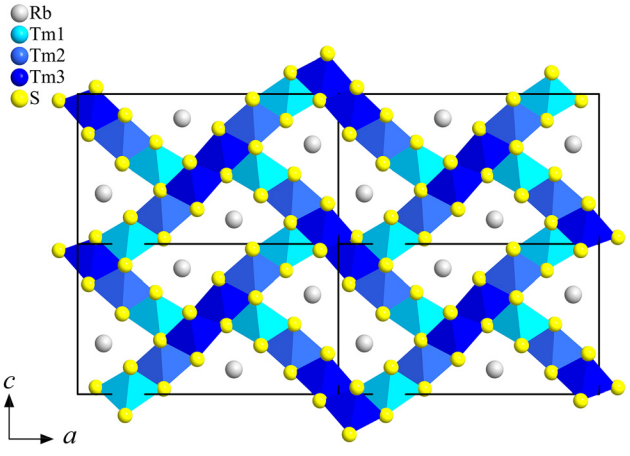
$RbTm_3S_5$: the first rubidium lanthanoid(III) sulfide with $CsEr_3Se_5$-type crystal structure



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Abstract

$RbTm_3S_5$, orthorhombic, *Pnma* (no. 62), a = 20.7225(16) Å, b = 3.9231(3) Å, c = 11.6958(9) Å, V = 950.83(13) Å^3, Z = 4, $R_{gt}(F)$ = 0.0263, $wR_{ref}(F^2)$ = 0.0666, T = 293 K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

1 Source of materials

$RbTm_3S_5$ was synthesized from a molten polysulfide flux containing Tm, Rb_2S_3, As_2S_3 and S in a molar ratio of 1:1:1:6. The reactants were filled in a sealed glassy ampoule and heated up to 823 K within 20 h. After 96 h the mixture cooled down to 523 K with −2 K h^{-1}, held at this temperature for another 120 h and finally cooled down with −2 K h^{-1} to 373 K, before the furnace was turned off. Rb_2S_3 was synthesized in liquid ammonia out of a stoichiometric 2:3-mixture of Rb and S. All chemicals and products were handled in an argon-filled glove box. Single crystals in the shape of orange-colored rods were selected manually and transferred into glass capillaries.

Table 1: Data collection and handling.

Crystal:	Rod, orange
Size:	0.09 × 0.06 × 0.05 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	33.85 mm^{-1}
Diffractometer, scan mode:	STOE STADIVARI, rotation mode ω-scans
θ_{max}, completeness:	30.3°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9698, 1563, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1512
$N(param)_{refined}$:	56
Programs:	Stoe & Cie,[1] SHELX,[2,3] DIAMOND[4]

2 Experimental details

Suitable single crystals of $RbTm_3S_5$ were selected for X-ray diffraction experiments on a STOE Stadi–Vari diffractometer (Stoe & Cie GmbH, Darmstadt, Germany) using monochomatized MoKα radiation (λ = 0.71073 Å). The crystal-structure solution could be obtained with SHELXS-2019/2 using Direct Methods, whereas the refinement was carried out with SHELXL-2019/2 by applying least-squares calculations on F^2.[2,3] The lowest and highest residual electron density almost coincide in terms of magnitude (2.4 and 2.5 e Å^{-3}), the quality of the structure solution is therefore not influenced by the calculated residual electron density of −2.5 e Å^{-3} at Tm3.

3 Comment

In the systems of lanthanoid sulfides containing alkali metals mainly three different compositions have been reported so far $ALnS_2$,[5,6] ALn_7S_{11}[7] and $A_3Ln_7S_{12}$[8] (A = Li – Cs, Ln = lanthanoid). Compared to the related selenides and tellurides it is noticeable that the composition ALn_3Ch_5 for Ch = S seems to be

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unknown, whereas the first representatives with *Ch* = Se and Te like $CsHo_3Te_5$ already exist for quite a while.[9] In this context, next to $CsSc_3S_5$[10] the new compound $RbTm_3S_5$ presented here is the first ternary lanthanoid(III) sulfide with this composition, adopting the $CsEr_3Se_5$-type crystal structure.[11,12]

The structure of the title compound is built up from edge-connected $[TmS_6]^{9-}$ octahedra with typical distances (d(Tm–S) = 2.58–2.81 Å) as known from thulium sulfides like *D*-type Tm_2S_3 (d(Tm–S) = 2.60–2.92 Å[13]) and empty channels along [010]. The size of these channels is defined by 5×4 octahedral units arranged in a herringbone-like pattern (see the figure). Tm1 and Tm2 each form infinite chains along [010], where one octahedron links its two neighbors via opposite edges. By connecting those chains, the sites of the empty channels are created. The channel corners are built from Tm3-centered sulfur octahedra, which are again edge-connected to each other in a way, that each $[(Tm3)S_6]^{9-}$ octahedron has four direct neighbors. This results in infinite chains along [010], which connect the chains of Tm1- and Tm2-centered sulfur polyhedra to erect a three-dimensional network 3D-{$[Tm_3S_5]^-$} with channels in [010] direction, where the Rb^+ cations find place in a sevenfold coordination environment of sulfur atoms, forming a capped trigonal prism (d(Rb–S) = 3.37–3.61 Å) with distances comparable to those in Rb_2S_5 (d(Rb–S) = 3.30–3.76 Å[14]), for example.

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References

1. X-Area: *The Stoe Single-Crystal Diffraction Software Package*; Stoe & Cie GmbH: Darmstadt, Germany.
2. Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Brandenburg, K. *DIAMOND*; Crystal Impact GbR: Bonn, Germany.
5. Ballestracci, R.; Bertaut, E. F. Étude Cristallographique de Sulfures de Terres Rares et de Sodium. *Bull. Soc. Fr. Mineral. Cristallogr.* **1964**, *87*, 512–517.
6. Bronger, W.; Brüggemann, W.; von der Ahe, M.; Schmitz, D. Zur Synthese und Struktur Ternärer Chalcogenide der Seltenen Erden $ALnX_2$ mit *A* = Alkalimetall und *X* = Schwefel, Selen oder Tellur. *J. Alloys Compd.* **1993**, *200*, 205–210.
7. Lin, H.; Li, L.-H.; Chen, L. Diverse Closed Cavities in Condensed Rare Earth Metal-Chalcogenide Matrixes: $CsLu_7Q_{11}$ and $(ClCs_6)RE_{21}Q_{34}$ (*RE* = Dy, Ho; *Q* = S, Se, Te). *Inorg. Chem.* **2012**, *51*, 4588–4596.
8. Lissner, F.; Hartenbach, I.; Schleid, Th. $K_3Er_7S_{12}$ und $Rb_3Er_7S_{12}$: Zwei Ternäre Erbium(III)-Sulfide mit Kanalstruktur. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1552.
9. Yao, J.; Deng, B.; Ellis, D. E.; Ibers, J. A. Syntheses and Structures of $CsHo_3Te_5$ and $Cs_3Tm_{11}Te_{18}$ and the Electronic Structure of $CsHo_3Te_5$. *J. Solid State Chem.* **2005**, *178*, 41–46.
10. Buyer, C.; Zimmermann, D. D.; Schleid, Th. $CsSc_3S_5$. The First Ternary Sulfide with $CsEr_3Se_5$-type Structure. *Z. Kristallogr.* **2018**, *S38*, 100.
11. Kim, S.-J.; Park, S.-J.; Yun, H.; Do, J. Syntheses and Crystal Structures of New Ternary Selenides: $Rb_3Yb_7Se_{12}$ and $CsEr_3Se_5$. *Inorg. Chem.* **1996**, *35*, 5283–5289.
12. Folchnandt, M.; Schleid, Th. Neue Ternäre Selenide Dreiwertiger Lanthanoide mit Cäsium: $CsNd_5Se_8$, $Cs_3Gd_7Se_{12}$, $CeEr_3Se_5$. *Z. Kristallogr.* **1997**, *S12*, 125.
13. Konczyk, J.; Demchenko, P.; Bodak, O.; Demchenko, G.; Marciniak, B.; Prochwicz, W.; Muratova, L. Crystal Structure of δ-Tm_2S_3. *Chem. Met. Alloys* **2008**, *1*, 38–42.
14. Böttcher, P. Synthesis and Crystal Structure of the Dirubidiumpentachalcogenides Rb_2S_5 and Rb_2Se_5. *Z. Kristallogr. – Cryst. Mater.* **1979**, *150*, 65–74.