Crystal structure of trirubidium dodekaselenoheptadysprosate(III), $\text{Rb}_3\text{Dy}_7\text{Se}_{12}$

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Dedicated to Professor Gerd Meyer (Universität Köln) on the occasion of his 50th birthday

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Abstract

$\text{Dy}_7\text{Rb}_3\text{Se}_{12}$, orthorhombic, $Pn\bar{m}$ (No. 58), $a = 12.590(1) \text{ \AA}$, $b = 26.183(2) \text{ \AA}$, $c = 4.1271(4) \text{ \AA}$, $V = 1360.5 \text{ \AA}^3$, $Z = 2$, $R_{\text{gt}}(F) = 0.054$, $wR(F^2) = 0.119$, $T = 293 \text{ K}$.

Source of material

Straw-yellow, lath-shaped, transparent single crystals of $\text{Rb}_3\text{Dy}_7\text{Se}_{12}$ were obtained from the elements dysprosium and selenium (about 1:2 molar ratios) in the presence of large amounts of RbCl as fluxing agent upon heating the mixture in a sealed evacuated silica vessel at 1123 K for seven days followed by subsequent cooling down to ambient temperature.

Discussion

The crystal structure of $\text{Rb}_3\text{Dy}_7\text{Se}_{12}$ belongs to the $\text{Cs}_3\text{Y}_7\text{Se}_{12}$ -type arrangement [1, 2], as is the case for some ternary tricesium heptalanthanoid dodekaselenides, $\text{Cs}_3\text{M}_7\text{Se}_{12}$ ($\text{M} = \text{Gd-Ho}$, [3–5]), and $\text{Rb}_3\text{Yb}_7\text{Se}_{12}$ [6]. The orthorhombic unit cell contains $[\text{DySe}_6]^{9-}$ octahedra which share common vertices and edges to form a three-dimensional anionic network according to ${}^3_2\{(\text{Dy}_7\text{Se}_{12})^{3-}\}$. The Dy—Se distances range from 280 pm to 298 pm with an average of 286.6 pm. This rigid frame exhibits one-dimensional channels along [001] apt to take up three Rb^+ cations per formula unit offering coordination numbers of six (trigonal prism for Rb2) and seven plus one (bicapped trigonal prism for Rb1). Since both sites for rubidium are fourfold (4g, see table 2) one of them, the Rb2 site namely, has to be half-occupied only with a refined occupation probability of 0.52(1). The Rb—Se distances are found in intervals between 347 pm and 371 pm (plus 447 pm) for Rb1 or between 340 pm and 391 pm for Rb2, respectively. A (001) projection of the crystal structure of $\text{Rb}_3\text{Dy}_7\text{Se}_{12}$ is given in the figure (Rb: large black and grey, Dy: small black, Se: large open circles) where the condensed $[\text{DySe}_6]^{9-}$ octahedra are depicted by linked Se—Se edges.

Table 1. Data collection and handling.

Crystal:	straw-yellow, transparent, lath-shaped needle, size $0.05 \times 0.08 \times 0.25 \text{ mm}$
Wavelength:	$\text{Mo } K_{\alpha}$ radiation ($0.71069 \text{ \AA}$)
μ :	403.42 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 200 exposures, $\Delta\phi = 1^\circ$
$2\theta_{\text{max}}$:	48.16°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6259, 1241
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 4 \sigma(I_{\text{obs}})$, 1092
$N(\text{param})_{\text{refined}}$:	72
Programs:	HABITUS [7], SHELXS-86 [8], SHELXL-93 [9]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Rb(1)	4g	0.52(1)	0.2879(2)	0.3661(1)	0	0.023(2)	0.037(2)	0.025(2)	0.004(1)	0	0
Rb(2)	4g		0.5612(5)	0.0297(3)	0	0.031(4)	0.038(5)	0.078(6)	0.013(3)	0	0
Dy(1)	2a		0	0	1/2	0.0149(9)	0.0133(9)	0.0092(9)	−0.0027(8)	0	0
Dy(2)	4g		0.2174(1)	0.08384(5)	0	0.0148(7)	0.0158(7)	0.0086(6)	−0.0038(5)	0	0
Dy(3)	4g		0.4091(1)	0.71186(5)	0	0.0134(7)	0.0148(7)	0.0090(6)	−0.0015(5)	0	0
Dy(4)	4g		0.0775(1)	0.68252(5)	0	0.0138(7)	0.0160(7)	0.0101(7)	0.0035(5)	0	0
Se(1)	4g		0.2540(2)	0.1962(1)	0	0.011(1)	0.017(1)	0.008(1)	−0.001(1)	0	0
Se(2)	4g		0.1289(2)	0.5776(1)	0	0.015(1)	0.018(1)	0.013(1)	0.003(1)	0	0
Se(3)	4g		0.4336(2)	0.6035(1)	0	0.012(1)	0.015(1)	0.010(1)	0.000(1)	0	0
Se(4)	4g		0.0593(2)	0.7891(1)	0	0.008(1)	0.013(1)	0.011(1)	−0.003(1)	0	0
Se(5)	4g		0.1531(2)	0.9805(1)	0	0.014(1)	0.016(1)	0.011(1)	0.001(1)	0	0
Se(6)	4g		0.4235(2)	0.8212(1)	0	0.015(1)	0.016(1)	0.011(1)	−0.000(1)	0	0

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