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Crystal structures of potassium terbium(III) tetrasulfidogermanate, $KTbGeS_4$, and potassium praseodymium(III) tetraselenidogermanate, $KPrGeSe_4$

B. C. Chan and P. K. Dorhout*

Colorado State University, Department of Chemistry, Fort Collins, CO 80523, USA

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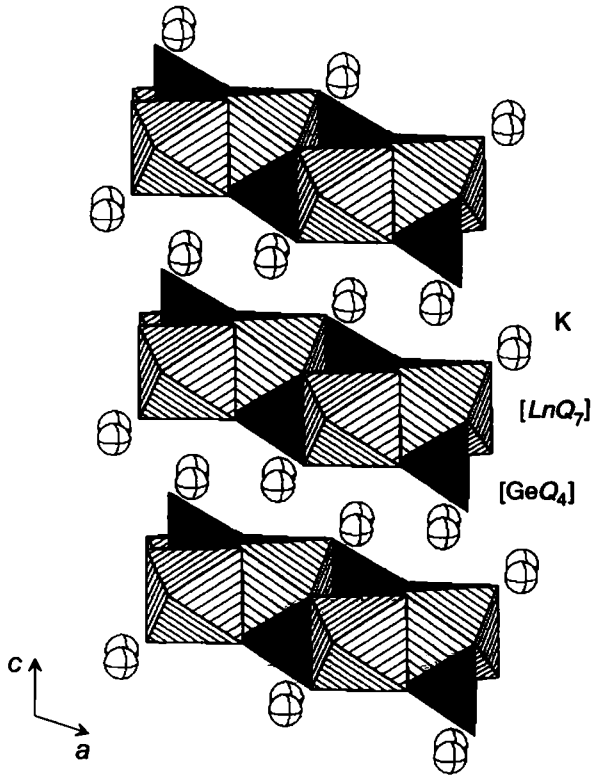

Abstract

GeKS4Tb, monoclinic, $P12_11$ (no. 4), a = 6.471(2) Å, b = 6.645(2) Å, c = 8.623(3) Å, β = 107.992(5)°, V = 352.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.086, T = 298 K.

GeKPrSe4, monoclinic, $P12_11$ (no. 4), a = 6.8280(8) Å, b = 7.0105(8) Å, c = 8.987(1) Å, β = 108.157(2)°, V = 408.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.090, T = 298 K.

Source of material

Crystals of $KTbGeS_4$ and $KPrGeSe_4$ were formed from a molten chalcogenide flux reaction of 51.5 mg Tb (Pr), 21.8 mg Ge, 94.0 mg S, and 40.6 mg K_2S_2 (K_2Se_2). The reactants were combined in a fused silica ampoule in an inert atmosphere glovebox, sealed under vacuum, and heated to 725 °C at a rate of 35 K/hour. After 150 hours of heating, the ampoule was cooled at 4 K/hour to room temperature. Dimethylformamide was added to dissolve remaining potassium sulfide flux, resulting in well-formed plates of $KTbGeS_4$ ($KPrGeSe_4$).

Discussion

Both compounds are isostructural to $KLnMQ_4$ (Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se) [1]. The structures consist of bicapped trigonal prisms of terbium sulfide (praseodymium selenide) interconnected by tetrahedra of GeS_4 ($GeSe_4$) to form anionic layers of $TbGeS_4$ ($PrGeSe_4$) separated by potassium cations. The Flack x parameters were 0.20(4) for $KTbGeS_4$ and 0.45(5) for $KPrGeSe_4$.

1. Potassium terbium(III) tetrasulfidogermanate, $KTbGeS_4$

Table 1. Data collection and handling.

Crystal:	transparent colorless platelet, size 0.01 × 0.15 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	158.56 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	46.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2239, 1018
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 973
$N(param)_{refined}$:	66
Program:	SHELXTL [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tb(1)	2a	0.2296(1)	0.13737(8)	0.55137(7)	0.0085(4)	0.0117(4)	0.0132(4)	0.0000(4)	0.0039(3)	0.0002(4)
Ge(1)	2a	0.2207(2)	−0.3976(3)	0.3227(2)	0.0083(7)	0.008(1)	0.0139(8)	−0.0001(7)	0.0039(6)	0.0007(7)
S(1)	2a	0.0145(7)	−0.1280(6)	0.2949(6)	0.014(2)	0.010(2)	0.015(3)	0.003(2)	0.003(2)	0.001(2)
S(2)	2a	0.0279(7)	−0.1367(6)	0.7226(6)	0.012(2)	0.009(2)	0.018(3)	0.003(2)	0.002(2)	0.002(2)
S(3)	2a	0.5793(6)	0.1010(7)	0.8377(4)	0.014(2)	0.025(3)	0.014(2)	0.002(2)	0.007(2)	0.003(2)
S(4)	2a	0.5685(6)	0.0412(6)	0.4259(5)	0.008(2)	0.019(2)	0.012(2)	0.001(2)	0.002(2)	−0.002(2)
K(1)	2a	0.2665(6)	0.1170(9)	0.0638(4)	0.033(2)	0.034(3)	0.021(2)	0.001(2)	0.009(2)	−0.004(2)

* Correspondence author (e-mail: pkd@lamar.colostate.edu)

2. Praseodymium(III) tetraselenidogermanate, $KPrGeSe_4$

Table 3. Data collection and handling.

Crystal:	orange platelet, size 0.01 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	277.77 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	46.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2578, 1178
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1153
$N(param)_{refined}$:	66
Program:	SHELXTL [2]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr(1)	2*a*	0.2317(1)	−0.0003(1)	0.55344(8)	0.0128(4)	0.0176(5)	0.0149(5)	0.0007(3)	0.0065(3)	−0.0003(4)
Se(1)	2*a*	0.0097(2)	0.2588(2)	0.2835(2)	0.0167(7)	0.0135(8)	0.019(1)	−0.0020(6)	0.0066(6)	−0.0005(7)
Se(2)	2*a*	0.0327(2)	0.2750(2)	0.7306(2)	0.0156(7)	0.0142(8)	0.0167(9)	−0.0020(7)	0.0051(6)	−0.0009(7)
Se(3)	2*a*	0.4148(2)	0.5346(3)	0.1513(2)	0.0179(7)	0.039(1)	0.0144(8)	0.0011(7)	0.0086(6)	0.0033(8)
Se(4)	2*a*	0.5771(2)	0.0852(2)	0.4223(2)	0.0146(7)	0.0261(9)	0.0143(8)	−0.0047(7)	0.0054(6)	0.0005(7)
Ge(1)	2*a*	0.2168(2)	0.5320(2)	0.3182(2)	0.0114(7)	0.0139(9)	0.0158(8)	−0.0003(7)	0.0061(6)	−0.0006(7)
K(1)	2*a*	0.2576(5)	0.0114(8)	0.0624(4)	0.040(2)	0.045(2)	0.021(2)	0.002(2)	0.013(2)	0.000(2)

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References

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