Crystal structures of octasodium dieuropium(II) bis[hexatellurodisilicate], $Na_8Eu_2[Si_2Te_6]_2$, octasodium dieuropium(II) bis[hexaselenodigermanate], $Na_8Eu_2[Ge_2Se_6]_2$, and nonasodium samarium(III) bis[hexaselenodisilicate], $Na_9Sm[Si_2Se_6]_2$

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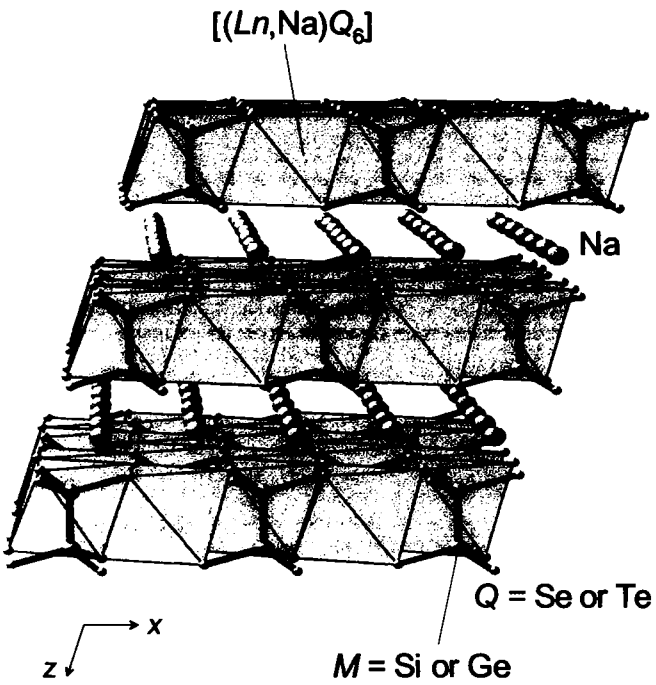

Abstract

$Eu_2Na_8Si_4Te_{12}$, monoclinic, $C12/m1$ (no. 12), $a = 7.648(1)$ Å, $b = 13.223(2)$ Å, $c = 8.439(1)$ Å, $\beta = 107.667(3)°$, $V = 813.1$ Å^3, $Z = 1$, $R_{gt}(F) = 0.029$, $wR_{ref}(F^2) = 0.059$, $T = 298$ K.

$Eu_2Ge_4Na_8Se_{12}$, monoclinic, $C12/m1$ (no. 12), $a = 7.137(2)$ Å, $b = 12.330(4)$ Å, $c = 8.019(3)$ Å, $\beta = 107.279(5)°$, $V = 673.8$ Å^3, $Z = 1$, $R_{gt}(F) = 0.034$, $wR_{ref}(F^2) = 0.087$, $T = 298$ K.

$Na_9Se_{12}Si_4Sm$, monoclinic, $C12/m1$ (no. 12), $a = 7.011(1)$ Å, $b = 12.098(2)$ Å, $c = 7.916(2)$ Å, $\beta = 107.178(3)°$, $V = 641.5$ Å^3, $Z = 1$, $R_{gt}(F) = 0.051$, $wR_{ref}(F^2) = 0.119$, $T = 173$ K.

Source of materials

Crystals of the title compounds were formed from molten chalcogenide flux reactions of 37.5 mg Eu, 17.6 mg Si, 149.8 mg Te, and 86.0 mg Na_2Te (for $Na_8Eu_2[Si_2Te_6]_2$); of 40.7 mg Eu, 49.0 mg Ge, 58.5 mg Se, and 109.8 mg Na_2Se_2 (for $Na_8Eu_2[Ge_2Se_6]_2$); as well as of 29.9 mg Sm, 33.6 mg Si, 62.6 mg Se, and 201.0 mg Na_2Se_2 (for $Na_9Sm[Si_2Se_6]_2$). The reactants were placed in fused silica ampoules in an inert atmosphere glovebox. The ampoules were sealed under vacuum, and heated to 750 °C (725 °C for $Na_9Sm[Si_2Se_6]_2$) at a rate of 35 K/h. After 150 hours of annealing, the ampoules were cooled at 3 K/h to room temperature (4 K/h for $Na_8Eu_2[Si_2Te_6]_2$). Crystals were obtained after the products were washed with dimethylformamide to dissolve remaining flux.

Experimental details

All three structures were modeled with occupational disorder at the $Ln1$/Na1 site (Ln = Eu or Sm). When the atoms were allowed to refine freely, the occupancies of $Ln1$ and Na1 gave 0.480(5)/0.520 for $Na_8Eu_2[Si_2Te_6]_2$, 0.487(4)/0.513 for $Na_8Eu_2[Ge_2Se_6]_2$, and 0.254(3)/0.746 for $Na_9Sm[Si_2Se_6]_2$. The occupancies were then set to 0.50/0.50 and 0.25/0.75, respectively, yielding charge balanced compounds.

Discussion

$Na_8Eu_2[Si_2Te_6]_2$, $Na_8Eu_2[Ge_2Se_6]_2$, and $Na_9Sm[Si_2Se_6]_2$ belong to a family of chemical compounds with the general formula $Na_{12-m\cdot x}Ln^{m+}{}_x[M_2Q_6]_2$ (M = Si or Ge; Q = Se or Te). The three compounds are isostructural to the previously reported quaternary compound $Na_8Eu_2[Si_2Se_6]_2$ [1] and to $Na_8M'_2[M_2Q_6]_2$ (M' = Pb or Sn; M = Si or Ge; Q = S or Se) [2]. They are similar, but not isostructural to the previously reported quaternary samarium compound $Na_9Sm[Ge_2Se_6]_2$ [1]. The different formulas of the europium and samarium compounds described herein are accounted for by a change in the occupancies of the lanthanide and sodium cations that reside on a shared site. (The excitation and emission spectra of the Eu(II) compounds were consistent with those of $Na_8Eu_2[Si_2Se_6]_2$ [1].)

In both $Na_8Eu_2[Si_2Te_6]_2$ and $Na_8Eu_2[Ge_2Se_6]_2$, the shared site consists of Eu^{2+} and Na^+ each with site occupancy factors at 0.5, while in $Na_9Sm[Si_2Se_6]_2$, the shared site consists of Sm^{3+} and Na^+ with site occupancies of 0.25 and 0.75. The structures contain ethane-like hexatellurodisilicate(III), hexaselenodigermanate(III) or hexaselenodisilicate(III) anions, and in all three compounds the lanthanide cation is coordinated in a distorted octahedral fashion to six chalcogen atoms from three different $[M_2Q_6]^{6-}$ anions. $Na_8Eu_2[Si_2Te_6]_2$, $Na_8Eu_2[Ge_2Se_6]_2$, and $Na_9Sm[Si_2Se_6]_2$ are two-dimensional structures with $^2_\infty\{(Ln^{m+}{}_x, Na_{6-m\cdot x})[M_2Q_6]_2^{6-}\}$ layers separated by sodium cations. In these three structures the M–M bond in $[M_2Q_6]^{6-}$ lies in a perpendicular orientation relative to these layers; whereas in the similar compounds $Na_9Sm[Ge_2Se_6]_2$ [1] and $Na_9La[Ge_2Se_6]_2$ [3], the Ge–Ge bond is in a rather horizontal orientation with respect to the layers.

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1. Octasodium dieuropium(II) bis[hexatellurodisilicate(III)], $Na_8Eu_2[Si_2Te_6]_2$

Table 1. Data collection and handling.

Crystal:	orange prism, size 0.03 × 0.06 × 0.09 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	146.21 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2591, 1038
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 814
$N(param)_{refined}$:	36
Programs:	SHELXS-97 [4], SHELXL-97 [5], X-Seed-A [6]

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu(1)	4*h*	0.5	0	0.16648(6)	½	0.0215(4)	0.0225(5)	0.0253(5)	0	0.0063(4)	0
Na(1)	4*h*	0.5	0	0.16648	½	0.0215	0.0225	0.0253	0	0.0063	0
Na(2)	4*g*		0	0.3313(3)	0	0.040(2)	0.035(2)	0.027(2)	0	0.015(2)	0
Na(3)	2*a*		½	½	0	0.032(3)	0.043(3)	0.031(3)	0	0.002(2)	0
Si(1)	4*i*		0.0474(3)	½	0.6455(3)	0.013(1)	0.015(1)	0.021(1)	0	0.005(1)	0
Te(1)	8*j*		0.23635(5)	0.34403(3)	0.74377(5)	0.0221(2)	0.0176(2)	0.0204(2)	0.0044(2)	0.0043(2)	0.0016(2)
Te(2)	4*i*		–0.23154(7)	½	0.74178(7)	0.0165(3)	0.0268(3)	0.0208(3)	0	0.0071(2)	0

2. Octasodium dieuropium(II) bis[hexaselenodigermanate(III)], $Na_8Eu_2[Ge_2Se_6]_2$

Table 3. Data collection and handling.

Crystal:	orange-brown prism, size 0.02 × 0.03 × 0.09 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	253.16 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, φ/ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2143, 869
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 725
$N(param)_{refined}$:	37
Programs:	SHELXS-97 [4], SHELXL-97 [5], X-Seed-A [6]

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu(1)	4*h*	0.5	0	0.16602(5)	½	0.0177(3)	0.0184(5)	0.0174(4)	0	0.0044(3)	0
Na(1)	4*h*	0.5	0	0.16602	½	0.0177	0.0184	0.0174	0	0.0044	0
Na(2)	4*g*		0	0.3262(2)	0	0.028(2)	0.020(2)	0.017(2)	0	0.008(1)	0
Na(3)	2*a*		½	½	0	0.025(2)	0.021(3)	0.022(2)	0	–0.003(2)	0
Ge(1)	4*i*		0.05104(9)	½	0.65755(8)	0.0103(3)	0.0129(5)	0.0091(3)	0	0.0016(2)	0
Se(1)	8*j*		0.23990(7)	0.34229(4)	0.74989(6)	0.0163(3)	0.0135(4)	0.0150(3)	0.0035(2)	0.0030(2)	0.0011(2)
Se(2)	4*i*		–0.23165(9)	½	0.75013(8)	0.0125(3)	0.0201(5)	0.0159(4)	0	0.0056(3)	0

3. Nonasodium samarium(II) bis[hexaselenodisilicate(III)], $Na_9Sm[Si_2Se_6]_2$

Table 5. Data collection and handling.

Crystal:	yellow thick plate, size 0.1 × 0.1 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	196.43 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, φ/ω
$2\theta_{max}$:	56.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1985, 808
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 725
$N(param)_{refined}$:	36
Programs:	SHELXS-97 [4], SHELXL-97 [5], X-Seed-A [6]

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	4*h*	0.25	0	0.16575(9)	½	0.0176(6)	0.0154(6)	0.0170(7)	0	0.0038(5)	0
Na(1)	4*h*	0.75	0	0.16575	½	0.0176	0.0154	0.0170	0	0.0038	0
Na(2)	4*g*		0	0.3249(3)	0	0.033(2)	0.028(2)	0.034(2)	0	0.012(2)	0
Na(3)	2*a*		½	½	0	0.035(3)	0.025(3)	0.037(3)	0	−0.004(2)	0
Si(1)	4*i*		0.0493(3)	½	0.6526(2)	0.0120(8)	0.0120(9)	0.0121(9)	0	0.0019(7)	0
Se(1)	8*j*		0.23520(8)	0.34450(5)	0.74231(7)	0.0200(4)	0.0150(4)	0.0189(4)	0.0052(2)	0.0014(3)	0.0027(2)
Se(2)	4*i*		−0.2292(1)	½	0.7431(1)	0.0166(4)	0.0243(5)	0.0206(5)	0	0.0067(3)	0

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