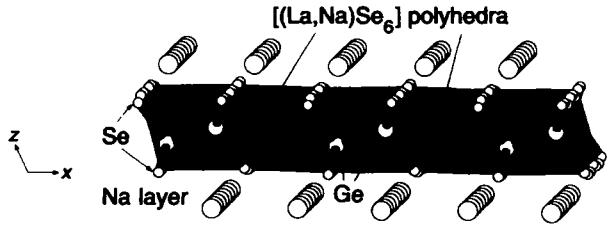
Crystal structure of nonasodium lanthanum(III) bis[hexaselenodigermanate], $Na_9La[Ge_2Se_6]_2$

B. R. Martin[I], J. M. Knaust[II] and P. K. Dorhout*,[II]

[I] Texas State University - San Marcos, Department of Chemistry and Biochemistry, 601 University Drive, San Marcos, TX 78666, USA
[II] Colorado State University, Department of Chemistry, Fort Collins, CO 80523, USA

Received April 15, 2005, accepted and available on-line May 31, 2005; CSD no. 409826



Abstract

$Ge_4LaNa_9Se_{12}$, monoclinic, $C12/m1$ (no. 12),
$a = 7.974(1)$ Å, $b = 12.337(2)$ Å, $c = 7.114(1)$ Å,
$\beta = 107.101(3)°$, $V = 669.0$ Å^3, $Z = 1$,
$R_{gt(F)} = 0.027$, $wR_{ref(F^2)} = 0.053$, $T = 173$ K.

Source of material

Crystals of $Na_9La[Ge_2Se_6]_2$ were formed from a molten chalcogenide flux reaction of 19.2 mg La, 39.5 mg Ge, 110.2 mg Se, and 57.2 mg Na_2Se_2. These reactants were combined, loaded into a carbon crucible and then placed in a fused silica ampoule in an inert atmosphere glovebox. The ampoule was sealed under vacuum and heated to 725 °C at a rate of 35 K/h. After 150 hours of heating, the ampoule was cooled at 4 K/h to RT. Platy crystals were obtained after the product was washed with dimethylformamide to dissolve any remaining flux.

Experimental details

The structure of $Na_9La[Ge_2Se_6]_2$ was modeled with occupational disorder at the La1/Na1 site. When the atoms were allowed to refine freely, the occupancies of La1 and Na1 gave 0.246(2)/0.754, yielding a charge balanced structure of 0.25/0.75.

Discussion

$Na_9La[Ge_2Se_6]_2$ belongs to a family of compounds with the general formula $Na_{12-m-y}Ln^{m+}{}_y[M_2Q_6]_2$ (M = Si or Ge; Q = Se or Te). The title compound is isostructural to the previously reported quaternary samarium compound, $Na_9Sm[Ge_2Se_6]_2$, but is not isostructural to the contemporary reported quaternary europium compound $Na_8Eu_2[Si_2Se_6]_2$ [1]. The structure contains ethane-like hexaselenodigermanate(III) anions, $[Ge_2Se_6]^{6-}$, and La1 is coordinated in a distorted octahedral fashion to six selenium atoms from three different $[Ge_2Se_6]^{6-}$ anions. $Na_9La[Ge_2Se_6]_2$ is a two-dimensional structure with $^2_\infty\{(La,Na_3)[Ge_2Se_6]_2^{6-}\}$ layers separated by sodium cations. In this structure the Ge–Ge bond in $[Ge_2Se_6]^{6-}$ has an angle of 19.2° relative to the layer plane; whereas in the similar compound $Na_8Eu_2[Si_2Se_6]_2$ [1], the Si–Si bond is in a perpendicular orientation with respect to the layers.

Table 1. Data collection and handling.

Crystal:	orange plate, size 0.05 × 0.40 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	157.58 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, φ/ω
$2\theta_{max}$:	46.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2025, 960
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 914
$N(param)_{refined}$:	65
Programs:	SHELXS-97 [3], SHELXL-97 [4], X-Seed-A [5]

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}
La(1)	4*h*	0.25	½	0.67785(7)	½	0.0199(6)	0.0203(4)	0.0217(5)	0	0.0076(5)	0
Na(1)	4*h*	0.75	½	0.67785	½	0.0199	0.0203	0.0217	0	0.0076	0
Na(2)	4*g*		0	0.6543(2)	0	0.038(2)	0.039(2)	0.040(2)	0	0.020(2)	0
Na(3)	2*a*		½	½	0	0.031(2)	0.035(2)	0.035(2)	0	–0.003(2)	0
Ge(1)	4*i*		0.15881(8)	½	0.55861(9)	0.0128(3)	0.0179(3)	0.0133(3)	0	0.0035(3)	0
Se(1)	8*j*		0.24966(6)	0.34334(3)	0.75270(6)	0.0218(3)	0.0171(2)	0.0190(2)	0.0017(2)	0.0051(2)	0.0033(2)
Se(2)	4*i*		0.25655(8)	½	0.27763(9)	0.0207(4)	0.0265(3)	0.0157(3)	0	0.0083(3)	0

Acknowledgment. This research was funded by NSF-DMR-0343412.

References

1. Martin, B. R.; Polyakova, L. A.; Dorhout, P. K.: Synthesis and characterization of a family of two related quaternary selenides: $Na_8Eu_2(Si_2Se_6)_2$ and $Na_9Sm(Ge_2Se_6)_2$. J. Alloys Compd. (2005) in press.
2. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
3. Sheldrick, G. M.: SHELXS-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
4. Barbour, L. J.: X-Seed-A. Software tool for supramolecular crystallography. J. Supramol. Chem. 1 (2001) 189-191.

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