

Fig. 1. Projection of one $c/8$ thickness slice of the structure, down the c axis, showing the interconnections of the PO_4 tetrahedra and $(\text{Na,Zr})\text{O}_6$ octahedra. For clarity, P and (Na,Zr) sites are omitted.

$(\text{Na,Zr})\text{O}_6$ octahedra. Each octahedron is connected to five P_2O_7 anions: three of them in the slice, through atoms O(1) and O(3), and the other two in adjacent slices through atoms O(1) and O(2). In consecutive slices related by twofold axes, chains of octahedra in directions $[110]$ and $[1\bar{1}0]$ share edges defining a distorted tetrahedron formed by O(1) atoms around the empty $8(a)$ Wyckoff position with symmetry 222 (Fig. 2). The angle between $[110]$ and adjacent $[1\bar{1}0]$ chains of octahedra is near 60° . The blocks (thickness $c/4$) formed by two such slices are connected through O(2) atoms.

We thank Dr Benjamin Martínez from the Instituto de Ciència dels Materials de Barcelona (CSIC)

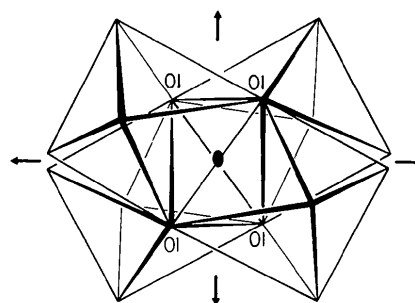


Fig. 2. Detail of the intersection of $(\text{Na,Zr})\text{O}_6$ octahedra chains in directions $[110]$ and $[1\bar{1}0]$ around the 222 empty Wyckoff position. The orientation is the same as in Fig. 1.

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Synthesis and Crystal Structures of Two Novel Selenites, $\text{NaY}(\text{SeO}_3)_2$ and $\text{NaLa}(\text{SeO}_3)_2$

BY R. E. MORRIS, J. A. HRILJAC AND A. K. CHEETHAM

Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, England

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Abstract. Sodium yttrium diselenite, $M_r = 365.8$, orthorhombic, $P2_1cn$, $a = 5.397(2)$, $b = 8.525(2)$, $c = 12.765(2)$ Å, $V = 587.3$ Å³, $Z = 4$, $D_x = 4.132$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 237.2$ cm⁻¹, $F(000) = 664$, room temperature, $R = 0.027$ for 805 observed reflections with $I > 3\sigma(I)$. Lanthanum sodium diselenite, $M_r = 415.8$, monoclinic, $P2_1/n$, $a = 6.696(4)$, $b = 6.761(4)$, $c =$

$13.199(5)$ Å, $\beta = 101.51(3)^\circ$, $V = 585.5$ Å³, $Z = 4$, $D_x = 4.716$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 196.75$ cm⁻¹, $F(000) = 736$, room temperature, $R = 0.056$ for 1312 observed reflections with $I > 3\sigma(I)$. Both compounds were prepared hydrothermally at 532 K. Both structures contain discrete SeO_3 groups and pentacoordinate sodium. The yttrium atom in $\text{NaY}(\text{SeO}_3)_2$ is coordinated by seven oxygens in a

distorted capped trigonal prism while the lanthanum atom in NaLa(SeO₃)₂ adopts ten coordination based on a distorted bicapped square antiprism.

Introduction. The structural chemistry of compounds containing selenite groups, (SeO₃)²⁻, are characterized by the stereochemically active lone-pair of electrons on the selenium atom. Up to the present day, research has centred on simple metal selenites, especially those of the first transition series. Kohn, Inone, Horie & Akimoto (1976) used high pressure methods to synthesize the series of phases $M^{2+}SeO_3$ ($M = Mg, Co, Ni, Cu, Zn$) and a series of hydrated selenites, $M^{2+}SeO_3 \cdot 2H_2O$ ($M = Mg, Co, Ni, Cu, Zn, Mn$), have also been reported (Lieder & Gattow, 1967). Selenites of the heavier metals, such as the lanthanides, have been less extensively studied. The structures of Ce(SeO₃)₂ (Delage, Carpy, H'Naifi & Goursolle, 1986), Ce(SeO₃)(SeO₃H) (Harrison, McManus & Cheetham, 1990) and La(SeO₃)(SeO₃H) (Harrison *et al.*, 1990) have been determined using single-crystal X-ray data, but there are very few other examples. Similarly there have been very few reported attempts to prepare and characterize mixed metal phases, although Effenberger has described a number of copper selenites such as BaCu(SeO₃)₂ and SrCu(SeO₃)₂ (Effenberger, 1987), Sr₂Cu(SeO₃)₃ (Effenberger, 1988*a*) and PbCu₂(SeO₃)₃ (Effenberger, 1988*b*).

The present paper reports the synthesis and structural characterization of two new phases, NaY(SeO₃)₂ and NaLa(SeO₃)₂. The only other phase containing Na, Se^{IV} and O so far characterized is NaCo₂(SeO₃)₂OH (Harrison *et al.*, 1990).

Experimental.

Synthesis. Both compounds described here were prepared hydrothermally. A mixture of Y(NO₃)₃·5H₂O (1 g) and Na₂SeO₃·5H₂O (3 g) in 15 ml of water was heated to 523 K in a teflon-lined steel autoclave for a period of 48 h. The solution was then cooled at about 10 K h⁻¹ and the products retrieved by suction filtration, washed with water and dried in air. There were three different phases present, one of which consisted of colourless needle-shaped crystals of NaY(SeO₃)₂. The NaLa(SeO₃)₂ crystals were made and recovered in a similar fashion, with a starting mixture of La(NO₃)₃·6H₂O (1 g) and Na₂SeO₃·5H₂O (3 g). The crystals produced were colourless and hexagonal in shape.

Structure determination. The title compounds were characterized and their structures determined by single-crystal X-ray diffraction using an Enraf-Nonius CAD-4F diffractometer and Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$). Automatic peak search, indexing and centring routines were used to obtain the unit cells and orientation matrices. The final cells

Table 1. *Details of data collection and structure analyses*

	NaY(SeO ₃) ₂	NaLa(SeO ₃) ₂
Crystal size (mm)	0.4 × 0.1 × 0.1	0.25 × 0.25 × 0.075
θ min., max. (°)	1, 30	1, 30
ω -scan width parameters	0.6, 0.35	1.2, 0.35
A, B (°) ($A + B \tan \theta$)		
Horizontal aperture parameters	2.5, 0.00	2.0, 0.00
A, B (mm) ($A + B \tan \theta$)		
Scan speed min., max. (° min ⁻¹)	0.7, 6.7	1.5, 6.7
Total data	1455	2301
Total unique data	938	1709
Observed data	805	1312
$[I > n\sigma(I)], n$	3	3
Absorption correction	1.00, 2.13	2.33, 5.88
min., max.		
Range of h, k, l	-1, -1, -1 to 7, 12, 17	-9, -1, -1 to 9, 9, 18
Solved by	Direct methods	Direct methods
No. of parameters	92	92
Weighting scheme	Chebyshev 3-term	Chebyshev 4-term
Weights	2.7264, -0.7492, 0.9228	7.809, 0.569, 5.589, 0.946
Extinction parameter	9.7 (7)	—
Final shift/e.s.d.	0.00	0.02
Final R	0.027	0.056
Final wR	0.028	0.066
4σ max., min. (e \AA^{-3})	2.5, -3.1	3.4, -4.4

were determined by centring 24 high angle reflections (θ ranges 14.3 to 18.1 and 13.8 to 15.3° respectively). All data were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction was applied. In both cases, three standard reflections showed no significant intensity variations.

The heavy-atom positions for both structures were found using the computer program *SHELXS86* (Sheldrick, 1986). The remaining oxygen atoms were located from successive electron density difference syntheses. The structures were then refined (on F) using full-matrix least-squares methods. The computer programs *RC85* (Baird, 1987) and *CRYSTALS* (Watkin, Carruthers & Betteridge, 1989) were used throughout. Complex, neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All figures were plotted using the program *Chem-X* (Chemical Design Ltd, 1986).

For NaY(SeO₃)₂, the systematic absences were consistent with the space groups *Pmcn* and *P2₁cn*. No model could be refined successfully in the centrosymmetric space group, so *P2₁cn* was chosen. This is a polar space group, the polar axis being a , along which the origin is not defined. The origin was fixed to be at the centroid of the structure (Waser, 1974). The final electron density synthesis showed only random fluctuations about the heavy atoms, and none of the isolated small peaks could be refined as additional oxygen atoms.

In the case of NaLa(SeO₃)₂ the systematic absences indicated the space group *P2₁/n* and the starting model refined with reasonable success. However, the anisotropic temperature factors remained at physically unreasonable values. The empirical absorption correction, *DIFABS* (Walker & Stuart,

Table 2. Atomic coordinates with *e.s.d.*'s and U_{eq} values for $\text{NaY}(\text{SeO}_3)_2$

$$U_{eq} = (U_1 U_2 U_3)^{1/3}.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Y(1)	0.2498 (3)	0.17579 (7)	0.08508 (4)	0.0069
Se(1)	-0.2531 (3)	-0.03055 (8)	0.20358 (4)	0.0084
Se(2)	0.2016 (3)	0.76504 (8)	0.08056 (5)	0.0079
Na(1)	0.2149 (8)	0.0069 (4)	0.3806 (3)	0.0194
O(1)	-0.0202 (11)	0.2837 (8)	-0.0253 (5)	0.0148
O(2)	-0.0346 (10)	0.5486 (8)	0.2858 (5)	0.0134
O(3)	0.6240 (10)	0.4354 (6)	0.4832 (4)	0.0108
O(4)	0.2986 (11)	0.4061 (6)	0.1732 (4)	0.0116
O(5)	0.9439 (10)	0.1254 (7)	0.2018 (5)	0.0103
O(6)	0.5068 (10)	0.1504 (7)	0.4850 (5)	0.0117

Table 3. Selected bond distances (\AA) and angles ($^\circ$), with *e.s.d.*'s, for $\text{NaY}(\text{SeO}_3)_2$

Y(1)—O(1)	2.226 (6)	Y(1)—O(2)	2.291 (6)
Y(1)—O(3)	2.582 (5)	Y(1)—O(3)	2.328 (5)
Y(1)—O(4)	2.278 (5)	Y(1)—O(5)	2.265 (6)
Y(1)—O(6)	2.398 (6)	Se(1)—O(2)	1.668 (6)
Se(1)—O(4)	1.687 (5)	Se(1)—O(5)	1.702 (6)
Se(2)—O(1)	1.710 (6)	Se(2)—O(3)	1.717 (5)
Se(2)—O(6)	1.662 (6)	Na(1)—O(1)	2.498 (7)
Na(1)—O(2)	2.542 (7)	Na(1)—O(4)	2.502 (8)
Na(1)—O(6)	2.399 (7)	Na(1)—O(6)	2.450 (7)
O(2)—Y(1)—O(1)	169.6 (2)	O(3)—Y(1)—O(1)	110.2 (2)
O(3)—Y(1)—O(2)	78.0 (2)	O(3)—Y(1)—O(1)	86.3 (2)
O(3)—Y(1)—O(2)	90.1 (2)	O(3)—Y(1)—O(3)	73.5 (1)
O(4)—Y(1)—O(1)	91.8 (2)	O(4)—Y(1)—O(2)	89.6 (2)
O(4)—Y(1)—O(3)	118.3 (2)	O(4)—Y(1)—O(3)	167.8 (2)
O(5)—Y(1)—O(1)	91.0 (2)	O(5)—Y(1)—O(2)	78.9 (2)
O(5)—Y(1)—O(3)	146.3 (2)	O(5)—Y(1)—O(3)	82.3 (2)
O(5)—Y(1)—O(4)	85.6 (2)	O(6)—Y(1)—O(1)	77.6 (2)
O(6)—Y(1)—O(2)	112.5 (2)	O(6)—Y(1)—O(3)	60.4 (2)
O(6)—Y(1)—O(3)	120.9 (2)	O(6)—Y(1)—O(4)	70.3 (2)
O(6)—Y(1)—O(5)	152.8 (2)	O(5)—Se(1)—O(2)	104.7 (3)
O(4)—Se(1)—O(2)	101.8 (3)	O(6)—Se(2)—O(1)	101.8 (3)
O(5)—Se(1)—O(4)	99.2 (3)	O(4)—Na(1)—O(1)	85.5 (2)
O(3)—Se(2)—O(1)	103.0 (3)	O(6)—Na(1)—O(1)	72.7 (2)
O(6)—Se(2)—O(3)	96.0 (3)	O(6)—Na(1)—O(4)	156.6 (3)
O(2)—Na(1)—O(1)	124.9 (2)	O(6)—Na(1)—O(2)	154.8 (2)
O(4)—Na(1)—O(2)	107.2 (2)	O(6)—Na(1)—O(6)	101.0 (2)
O(6)—Na(1)—O(2)	92.5 (2)		
O(6)—Na(1)—O(1)	79.7 (3)		
O(6)—Na(1)—O(4)	65.9 (2)		

1983), was then applied and chemically sensible values obtained.

Details of both refinements are given in Table 1. Atomic coordinates and selected bond distances and angles are given for $\text{NaY}(\text{SeO}_3)_2$ in Tables 2 and 3, and for $\text{NaLa}(\text{SeO}_3)_2$ in Tables 4 and 5.*

Discussion. Both compounds exhibit high coordination around the heavy atoms, the yttrium being coordinated by seven oxygens making a distorted monocapped trigonal prism (C_{2v}) (Fig. 1). The lan-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53052 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Atomic coordinates ($\times 10^4$) with *e.s.d.*'s and U_{eq} for $\text{NaLa}(\text{SeO}_3)_2$

$$U_{eq} = (U_1 U_2 U_3)^{1/3} \times 10^4.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
La(1)	6560.3 (7)	1194.7 (8)	1637.6 (4)	50
Se(1)	6044 (1)	1649 (1)	6388.1 (8)	68
Se(2)	8097 (1)	1478 (1)	4312.3 (7)	64
Na(1)	8094 (7)	1692 (8)	8835 (4)	160
O(1)	1457 (11)	2195 (10)	8403 (6)	89
O(2)	994 (13)	132 (11)	6455 (7)	101
O(3)	4968 (12)	1813 (11)	9662 (6)	89
O(4)	4946 (11)	1694 (11)	7435 (6)	106
O(5)	9243 (12)	2063 (13)	580 (7)	138
O(6)	2906 (12)	1671 (12)	1705 (8)	142

Table 5. Selected bond distances (\AA) and angles ($^\circ$), with *e.s.d.*'s, for $\text{NaLa}(\text{SeO}_3)_2$

La(1)—O(1)	2.654 (7)	La(1)—O(1)	2.585 (8)
La(1)—O(2)	2.517 (8)	La(1)—O(3)	2.646 (8)
La(1)—O(3)	2.725 (8)	La(1)—O(4)	2.612 (7)
La(1)—O(4)	2.708 (7)	La(1)—O(5)	2.554 (8)
La(1)—O(6)	2.487 (8)	La(1)—O(2)	2.859 (9)
Se(1)—O(4)	1.690 (7)	Se(1)—O(6)	1.677 (8)
Se(1)—O(5)	1.684 (8)	Se(2)—O(2)	1.681 (8)
Se(2)—O(1)	1.711 (7)	Na(1)—O(1)	2.454 (8)
Se(2)—O(3)	1.699 (7)	Na(1)—O(4)	2.511 (9)
Na(1)—O(3)	2.55 (1)	Na(1)—O(6)	2.44 (1)
Na(1)—O(5)	2.29 (1)		
O(1)—La(1)—O(1)	119.0 (2)	O(2)—La(1)—O(1)	156.4 (2)
O(2)—La(1)—O(1)	68.9 (2)	O(3)—La(1)—O(1)	102.8 (2)
O(3)—La(1)—O(1)	138.0 (2)	O(3)—La(1)—O(2)	74.1 (3)
O(3)—La(1)—O(1)	58.0 (2)	O(3)—La(1)—O(1)	143.9 (2)
O(3)—La(1)—O(2)	130.2 (3)	O(3)—La(1)—O(3)	58.0 (3)
O(4)—La(1)—O(1)	66.8 (2)	O(4)—La(1)—O(1)	79.1 (2)
O(4)—La(1)—O(2)	135.9 (2)	O(4)—La(1)—O(3)	117.6 (2)
O(4)—La(1)—O(3)	66.8 (2)	O(4)—La(1)—O(1)	94.6 (2)
O(4)—La(1)—O(1)	66.3 (2)	O(4)—La(1)—O(2)	67.4 (3)
O(4)—La(1)—O(3)	116.2 (2)	O(4)—La(1)—O(3)	144.9 (2)
O(4)—La(1)—O(4)	125.7 (1)	O(5)—La(1)—O(1)	77.2 (3)
O(5)—La(1)—O(1)	123.0 (2)	O(5)—La(1)—O(2)	80.2 (3)
O(5)—La(1)—O(3)	67.3 (3)	O(5)—La(1)—O(3)	92.5 (3)
O(5)—La(1)—O(4)	143.9 (3)	O(6)—La(1)—O(1)	127.7 (2)
O(6)—La(1)—O(1)	73.1 (3)	O(6)—La(1)—O(2)	75.2 (3)
O(6)—La(1)—O(3)	79.0 (3)	O(6)—La(1)—O(3)	82.6 (3)
O(6)—La(1)—O(4)	66.8 (2)	O(5)—La(1)—O(4)	57.7 (2)
O(6)—La(1)—O(4)	132.2 (3)	O(6)—La(1)—O(5)	142.6 (3)
O(5)—Se(1)—O(4)	97.8 (4)	O(6)—Se(1)—O(4)	101.9 (4)
O(6)—Se(1)—O(5)	102.1 (4)	O(2)—Se(2)—O(1)	100.1 (4)
O(3)—Se(2)—O(1)	99.7 (4)	O(3)—Se(2)—O(2)	105.5 (4)
O(3)—Na(1)—O(1)	164.9 (3)	O(4)—Na(1)—O(1)	120.2 (3)
O(4)—Na(1)—O(3)	71.0 (3)	O(5)—Na(1)—O(1)	94.5 (3)
O(5)—Na(1)—O(3)	72.9 (3)	O(5)—Na(1)—O(4)	143.5 (4)
O(6)—Na(1)—O(1)	105.8 (3)	O(6)—Na(1)—O(3)	87.3 (3)
O(6)—Na(1)—O(4)	69.1 (3)	O(6)—Na(1)—O(5)	114.4 (4)

thanum atoms adopt a higher coordination number, as expected, with ten oxygens forming a distorted bicapped square antiprism (Fig. 2). This coordination seems to be novel for lanthanum; indeed there are very few examples of ten coordination for lanthanum, although $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ (Shinn & Eick, 1968) adopts ten coordination based on capping of a triangulated dodecahedron. Both compounds contain discrete, pyramidal SeO_3 groups with bond distances and angles that are similar to those quoted in the literature for related compounds (Kohn *et al.*,

1976; Lieder & Gattow, 1967). The sodium atoms are pentacoordinated in both compounds, but with differing geometries. In $\text{NaY}(\text{SeO}_3)_2$ they are coordinated as a distorted trigonal bipyramid, similar to that seen in $\text{NaCo}_2(\text{SeO}_3)_2\text{OH}$ (Harrison *et al.*, 1990) while in $\text{NaLa}(\text{SeO}_3)_2$ five oxygens form a distorted square pyramid around the sodium.

Both structures can be described in terms of either chains or layers which contain all of the heavy metals and also a proportion of the selenium atoms. These chains or layers are then linked together by sodium and the rest of the selenium atoms to form three-dimensional structures.

The structure of $\text{NaY}(\text{SeO}_3)_2$ consists of YO_7 polyhedra sharing corners to form zigzag chains which run parallel to the a axis (Fig. 3). 50% of the selenium atoms are also included in the chains, the SeO_3 units connecting two YO_7 polyhedra through

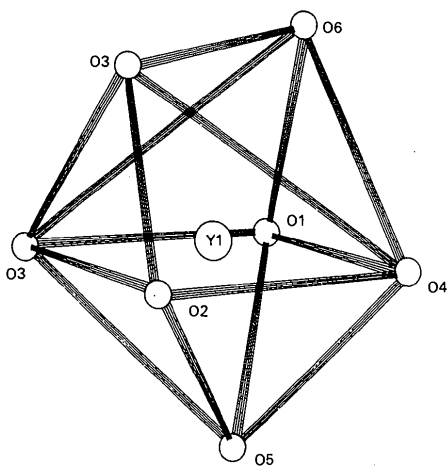


Fig. 1. Distorted capped trigonal prismatic coordination of oxygen around yttrium in $\text{NaY}(\text{SeO}_3)_2$.

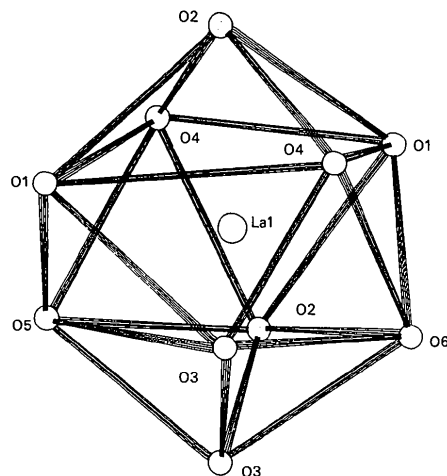


Fig. 2. Distorted bicapped square antiprismatic coordination of oxygen around lanthanum in $\text{NaLa}(\text{SeO}_3)_2$.

the sharing of an edge and a corner. These chains are interlinked by NaO_5 polyhedra, which share corners and edges with the YO_7 polyhedra in the chains and also corners with the rest of the SeO_3 groups. The interlinking SeO_3 units share only corners with the YO_7 polyhedra, two from the same chain and one from another.

In $\text{NaLa}(\text{SeO}_3)_2$, the LaO_{10} polyhedra share faces and edges to form infinite two-dimensional layers which also contain half of the selenium atoms (Fig. 4). The SeO_3 groups in the layers connect with the LaO_{10} groups *via* the sharing of edges and corners. The sodium and the remaining selenium atoms interlink the layers to form an infinite three-dimensional network.

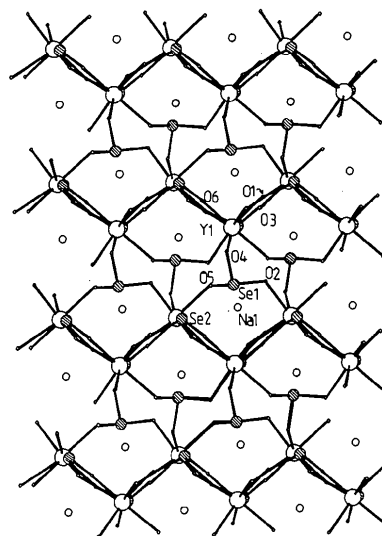


Fig. 3. Structure of $\text{NaY}(\text{SeO}_3)_2$, viewed down the b axis. The hatched circles are selenium atoms and the open circles are, in order of decreasing size, yttrium, sodium and oxygen.

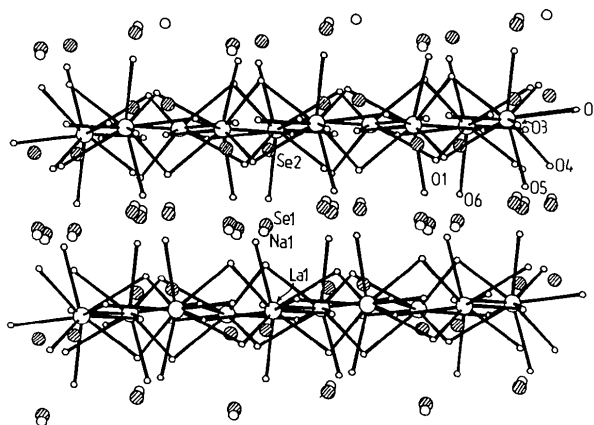


Fig. 4. Structure of $\text{NaLa}(\text{SeO}_3)_2$, viewed down the b axis showing the layered arrangement of LaO_{10} polyhedra. The hatched circles are selenium and the open circles are, in order of decreasing size, lanthanum, sodium and oxygen.

As demonstrated by this work, there is a rich structural chemistry of sodium lanthanide selenites which is readily accessible using hydrothermal synthetic techniques. The stereochemically active lone pair on the selenium atom, in conjunction with high, often irregular, coordination around lanthanide atoms, may be an excellent combination in the search for novel asymmetric structures. Such materials could have useful non-linear properties with potential applications in electro-optical devices.

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Structure of Lithium Gallium Sulfide, LiGaS₂

By J. LEAL-GONZALEZ,* S. S. MELIBARY† AND A. J. SMITH

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, England

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Abstract. LiGaS₂, $M_r = 140.787$, orthorhombic, $Pna2_1$, $a = 6.519$ (6), $b = 7.872$ (7), $c = 6.238$ (4) Å, $V = 320.1$ Å³, $Z = 4$, $D_m = 2.98$, $D_x = 2.92$ g cm⁻³, $F(000) = 264$, Mo $K\alpha$ ($\lambda = 0.71069$ Å), $\mu = 98.88$ cm⁻¹, room temperature, final $R = 0.049$ for 356 unique observed reflexions. The structure is based on a hexagonal closest-packed array of S atoms with the metal atoms in tetrahedral holes. It is derived from the zincite structure and related to the structure of enargite. The title compound is isostructural with NaFeO₂ and with LiGaO₂.

Introduction. LiGaS₂ was investigated by Ivanov-Emin & Rabovik (1947), who prepared a series of $MGaS_2$ compounds which they formulated as $M_2[Ga_2S_4]$, but they made no X-ray studies.

Experimental. The title compound was prepared (Melibary, 1967) by heating an equimolar mixture of gallium oxide and lithium carbonate in a stream of purified dry hydrogen sulfide gas for 2 h at 1073 K, and then 4 h at 1173 K. After slow cooling under the

gas stream the brown mass was broken up and yielded suitable crystals. Analysis: Found: S 45.78, Li 4.81; calculated for LiGaS₂: S 45.55, Li 4.93; S gravimetrically and Li by flame photometry.

The bulk product gave an X-ray powder pattern which was indexed on the basis of the unit cell above. The structure analysis was first carried out from visually measured photographic films (Melibary, 1967) with refinement converging at $R = 0.11$. We have now re-examined the same material using diffractometer data.

X-ray reflexion data from a small (approximately $0.13 \times 0.08 \times 0.15$ mm) brown-red crystal were collected on a Stoe Stadi-2 two-circle diffractometer operating in the $\theta/2\theta$ -scan mode and using Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0.71069$ Å). The unit-cell parameters were determined by least squares from the ω measurements of 43 well centred and well distributed reflexions. The measured density is that reported by Ivanov-Emin & Rabovik (1947). Reflexions in the range $6.5 < 2\theta < 60^\circ$ and having $0 \leq h \leq 9$, $0 \leq k \leq 11$ and $0 \leq l \leq 8$ were measured. A check reflexion was monitored every 50 reflexions and showed no evidence of decay. Measurements were made of 501 unique reflexions, of which 356 were accepted as observed [$I > 3\sigma(I)$]. The data were

* Present address: Real del Monte 2913, Col. Mitras Centro, Monterrey, N. L., Mexico.

† Present address: Modi Establishment, PO Box 12672, Jeddah, Saudi Arabia.