Data collection

Rigaku AFC-7 diffractometer
ω–2θ scans
Absorption correction:
  empirical *via* ψ scans
  (Sheldrick, 1990)
  T_{min} = 0.42, T_{max} = 0.84
1152 measured reflections
620 independent reflections

559 reflections with
  $F > 4\sigma(F)$
R_{int} = 0.027
θ_{max} = 27.50°
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 19$
$l = -4 \rightarrow 4$
3 standard reflections
  every 100 reflections
  intensity decay: 0.2%

Refinement

Refinement on F
R = 0.026
wR = 0.052
S = 1.69
559 reflections
57 parameters
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = -1.06 e Å^{-3}
Extinction correction:
  Larson (1970)
Extinction coefficient:
  0.00028 (5)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Nb(1)—O(1)	1.714 (5)	Nb(3)—O(4''')	1.990 (2)
Nb(1)—O(1')	2.115 (5)	Nb(3)—O(5'')	2.286 (5)
Nb(1)—O(2)	2.012 (5)	Nb(3)—O(6)	1.770 (5)
Nb(2)—O(2)	1.816 (5)	Nb(3)—O(7)	2.015 (5)
Nb(2)—O(3)	1.843 (5)	Nb(1)—Nb(2)	3.818 (5)
Nb(2)—O(4)	2.253 (5)	Nb(2)—Nb(3')	3.387 (5)
Nb(2)—O(5)	1.987 (1)	Nb(2)—Nb(3'')	3.804 (5)
Nb(2)—O(6)	2.132 (5)	As—O(7)	1.705 (4)
Nb(3)—O(3'')	1.970 (5)		
O(1)—Nb(1)—O(1')	180.0 (1)	O(5)—Nb(2)—O(5''')	149.0 (3)
O(1)—Nb(1)—O(2)	95.7 (1)	O(6)—Nb(2)—O(5)	84.2 (1)
O(2)—Nb(1)—O(1')	84.3 (1)	O(3'')—Nb(3)—O(4''')	89.0 (2)
O(2)—Nb(1)—O(2'')	89.4 (1)	O(3'')—Nb(3)—O(5'')	86.0 (2)
O(2''')—Nb(1)—O(2'')	89.4 (1)	O(4'')—Nb(3)—O(4''')	148.3 (3)
O(2)—Nb(1)—O(2''')	168.5 (3)	O(5'')—Nb(3)—O(4'')	74.2 (1)
O(2)—Nb(2)—O(3)	98.4 (2)	O(6)—Nb(3)—O(3'')	94.8 (2)
O(2)—Nb(2)—O(4)	170.6 (2)	O(6)—Nb(3)—O(4''')	105.8 (1)
O(2)—Nb(2)—O(5)	104.2 (1)	O(6)—Nb(3)—O(5'')	179.2 (1)
O(2)—Nb(2)—O(6)	88.6 (2)	O(6)—Nb(3)—O(7)	95.3 (2)
O(3)—Nb(2)—O(4)	91.0 (2)	O(7)—Nb(3)—O(3'')	169.9 (2)
O(3)—Nb(2)—O(5)	94.0 (1)	O(7)—Nb(3)—O(4''')	88.2 (2)
O(3)—Nb(2)—O(6)	173.0 (2)	O(7)—Nb(3)—O(5'')	83.9 (2)
O(4)—Nb(2)—O(5)	75.0 (1)	O(7)—As—O(7'')	108.4 (1)
O(4)—Nb(2)—O(6)	82.1 (2)	O(7)—As—O(7')	111.7 (2)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-y, x, z$; (iii) $y - \frac{1}{4}, \frac{1}{4} - x, \frac{1}{4} - z$; (iv) $y - \frac{1}{4}, \frac{1}{4} - x, -\frac{1}{4} - z$; (v) $\frac{1}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$; (vi) $y, -x, -z$; (vii) $-x, -y, -z$; (viii) $x, y, 1 + z$; (ix) $\frac{1}{4} - y, \frac{1}{4} + x, z - \frac{1}{4}$; (x) $-x, 1 - y, -z$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All atoms were refined with anisotropic displacement parameters. The maximum and minimum residual electron-density peaks were located near O(3).

Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*.

References

Benabbas, A., Borel, M. M., Grandin, A., Leclaire, A. & Raveau, B. (1991). *Acta Cryst.* C47, 849–850.
Chernorukov, N. G., Egorov, N. P. & Korshunova, I. A. (1979). *Inorg. Mater. (Engl. Transl.)*, 15, 1722–1724.
Chernorukov, N. G., Egorov, N. P., Shitova, E. V. & Chigirinskii, Yu. I. (1981). *Russ. J. Inorg. Chem. (Engl. Transl.)*, 26, 1454–1456.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
Levin, E. M. & Roth, R. S. (1970). *J. Solid State Chem.* 2, 250–261.
Roth, R. S., Wadsley, A. D. & Andersson, S. (1965). *Acta Cryst.* 18, 643–647.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.2. *Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Waring, J. L. & Roth, R. S. (1964). *Acta Cryst.* 17, 455–456.

Li3AsS3

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Abstract

The structure of lithium trithioarsenate(3−) consists of AsS_3 pyramids in which all S atoms are non-bridging. The Li atoms are involved in LiS_4 tetrahedra and LiS_{3+2} distorted trigonal bipyramids. The tetrahedra are linked together *via* corners. This structure appears to be a new member of the M_3AX_3 group of compounds.

Comment

Sulfide glasses with a high alkali content are studied because of their high ionic conductivities, *e.g.* 10^{-3} Ω^{-1} cm^{-1} at room temperature for thioborate-based glasses (Ménétrier *et al.*, 1991). Lithium arsenic sulfide based glasses, designated $x\mathrm{Li_2S}.(1-x)\mathrm{As_2S_3}$, have been synthesized recently, giving homogeneous glasses for $0.67 < x < 0.75$ (Shastry *et al.*, 1993). The elucidation of the structural evolution occurring on the

addition of Li_2S to As_2S_3 is an important factor in the understanding of the physical properties, especially the ionic conductivity. The hygroscopic character of these glasses makes them difficult to synthesize and to characterize.

When studying the relationship between the structure of a glassy compound and its ionic conductivity, it is very convenient to compare, when possible, a glass and a crystalline compound having the same composition. This work reports the preparation and structural determination of the crystalline phase c-Li_3AsS_3, corresponding to $x = 0.75$, which was investigated in connection with the structural study of the corresponding glass (v-Li_3AsS_3).

c-Li_3AsS_3 exhibits a new structure type. The As atoms are tricoordinated by S atoms to constitute trigonal AsS_3 pyramids. These pyramids are interconnected by Li ions: Li2 and Li3 form two LiS_4 distorted tetrahedra and Li1 is inside a distorted trigonal bipyramid, LiS_{3+2} (three S atoms at shorter distances from Li1 constituting a quasi-plane with Li1, and two other S atoms at longer distances on each side of this plane). All the $Li2S_4$ and $Li3S_4$ tetrahedra are linked together by their corners. The average As—S bond distance is 2.25 Å, which is similar to the values observed in orpiment (2.24 Å; Wyckoff, 1957), Ag_3AsS_3 (2.25 Å; Harker, 1936) and Tl_3AsS_3 (2.25 Å; Yang & Pertlik, 1994). The average Li1—S, Li2—S and Li3—S distances are 2.59, 2.45 and 2.51 Å, respectively, which are similar to the corresponding distances found in Li_2S and c-Li_3BS_3 (Vinatier *et al.*, 1994).

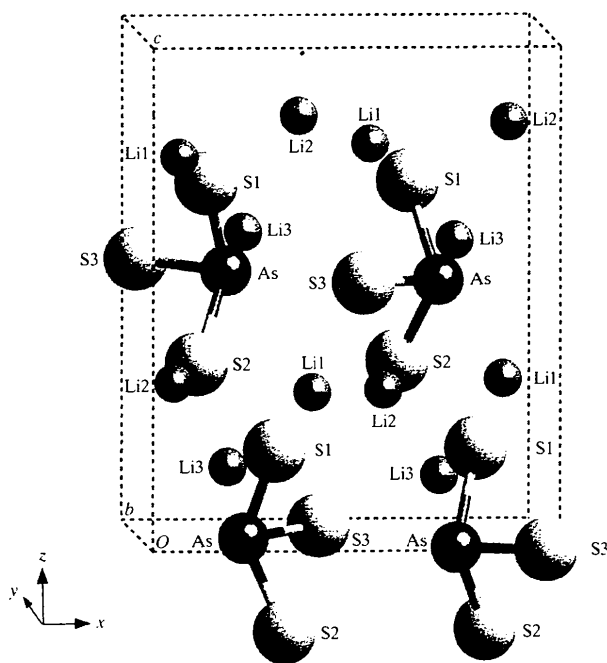A three-dimensional view of the Li_3AsS_3 atomic arrangement is shown in Fig. 1. The structure can be described as AsS_3 pyramids linked by two LiS_4 tetrahedra and one LiS_{3+2} bipyramid.

Experimental

Since Li_3AsS_3 is sensitive to moisture, all manipulations were carried out in a glove box filled with dry argon and containing less than 5 p.p.m. water. The synthesis of Li_3AsS_3 involves procedures employed for the preparation of the glasses (Shastry *et al.*, 1993). An Li_2S:As_2S_3 mixture of molar ratio 3:1 was introduced into a carbon crucible, itself placed in a silica tube sealed under vacuum. The tube was then heated to 923 K and held at that temperature for 20 h, allowing complete chemical reaction. The assembly was then cooled slowly to room temperature at a rate of 0.6 K h^{-1}. It was then annealed at 513 K for 7 d. The ampoule was opened inside a glove box and green crystals were recovered from within a block of polycrystalline material. Chemical analysis of the crystals gave S:As and Li:As ratios close to 3.

Crystal data

Li_3AsS_3	Mo $K\alpha$ radiation
$M_r = 191.94$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 25
$Pna2_1$	reflections
$a = 8.052\,(3)$ Å	$\theta = 6-17°$
$b = 6.632\,(5)$ Å	$\mu = 7.44 \text{ mm}^{-1}$
$c = 9.815\,(2)$ Å	$T = 293\,(2)$ K
$V = 524.1\,(5)$ Å^3	Irregular plate
$Z = 4$	$0.35 \times 0.10 \times 0.05$ mm
$D_x = 2.432 \text{ Mg m}^{-3}$	Green
D_m not measured	

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer	1069 independent reflections with $F^2 > 3\sigma(F^2)$
$\theta/2\theta$ scans	$R_{int} = 0.077$ (on F^2)
Absorption correction:	$\theta_{max} = 44.86°$
ψ scan (North *et al.*, 1968)	$h = -15 \rightarrow 15$
	$k = -13 \rightarrow 13$
$T_{min} = 0.38$, $T_{max} = 0.69$	$l = -18 \rightarrow 0$
6423 measured reflections	3 standard reflections
2470 reflections with	frequency: 360 min
$F^2 > 3\sigma(F^2)$	intensity decay: $< 7\%$

Refinement

Refinement on F^2	$\Delta\rho_{max} = 2.06$ e Å^{-3}
$R(F) = 0.051$	$\Delta\rho_{min} = -1.31$ e Å^{-3}
$wR(F^2) = 0.102$	Extinction correction: none
$S = 1.182$	Scattering factors from
1069 reflections	*International Tables for*
64 parameters	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	Absolute structure: Flack (1983)
$(\Delta/\sigma)_{max} = 0.001$	Flack parameter = 0.00 (3)

Fig. 1. A three-dimensional view of c-Li_3AsS_3.

Table 1. *Selected geometric parameters (Å, °)*

As—S3^i	2.236 (3)	Li2—S2	2.44 (2)
As—S2	2.255 (3)	Li2—S3^{ii}	2.44 (2)
As—S1^{ii}	2.266 (2)	Li2—S1	2.46 (2)
Li1—S3	2.46 (2)	Li2—S2^{iii}	2.48 (2)
Li1—S3^{iii}	2.48 (2)	Li3—S2^{vi}	2.39 (2)
Li1—S2^{iv}	2.56 (2)	Li3—S1	2.51 (2)
Li1—S1	2.70 (2)	Li3—S3	2.56 (2)
Li1—S1^v	2.76 (2)	Li3—S1^{vii}	2.58 (2)
S1^{ii}—As—S2	100.25 (9)	S3^{ii}—Li2—S1	122.2 (7)
S1^{viii}—As—S3^i	102.14 (9)	S3^{ii}—Li2—S2^{iii}	117.7 (7)
S2—As—S3^i	103.81 (8)	S3^{ii}—Li2—S2	100.0 (6)
S3—Li1—S3^{iii}	110.5 (7)	S2—Li2—S2^{iii}	110.6 (7)
S3—Li1—S1^v	109.1 (7)	S2—Li2—S1	105.1 (6)
S3—Li1—S1	99.3 (6)	S1—Li2—S2^{iii}	100.5 (5)
S3—Li1—S2^{iv}	96.5 (6)	S2^{vi}—Li3—S1	126.1 (7)
S3^{iii}—Li1—S2^{iv}	152.8 (8)	S2^{vi}—Li3—S1^{vii}	112.3 (7)
S3^{iii}—Li1—S1	89.7 (6)	S2^{vi}—Li3—S3	102.5 (6)
S3^{iii}—Li1—S1^v	83.6 (5)	S1—Li3—S1^{vii}	114.5 (6)
S2^{iv}—Li1—S1	82.5 (5)	S1—Li3—S3	102.0 (7)
S2^{iv}—Li1—S1^v	90.9 (6)	S3—Li3—S1^{vii}	90.8 (6)
S1—Li1—S1^v	151.4 (8)		

Symmetry codes: (i) $x, y, z - 1$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (v) $-x, -y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (viii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$.

Single-crystal analyses were performed using crystals loaded into glass capillaries in a glove box under a dry argon atmosphere. The symmetry and space group were determined by Weissenberg and Buerger photographs. Data collection covered half the reciprocal space (6423 reflections). As the single crystals were of poor quality and correcting for the absorption by the crystal and the capillary was difficult, we chose to consider only $\frac{3}{8}$ of the reciprocal space (removing reflections with $h < 0$ and $k < 0$, the great majority of which showed a systematic lowering of intensity). Empirical absorption corrections were carried out using ψ scans of nine reflections in the range $5.7 < \theta < 35.8°$. The structure was solved in the non-centrosymmetric space group $Pna2_1$ by Patterson function deconvolution and heavy-atom methods, using the 1069 independent reflections for which $I > 3\sigma(I)$. $\Delta\rho_{max}$ and $\Delta\rho_{min}$ were found near As atoms (at distances of 0.75 and 0.69 Å, respectively). This unusual approach to the structure determination seemed to us to be the best available after several trials with different single crystals. In spite of the preparation and handling difficulties, crystallochemical considerations and bond-valence calculations confirmed that the structural model is correct.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local programs. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *CERIUS* (Molecular Simulations, 1993). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1180). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.
Harker, D. (1936). *J. Chem. Phys.* 4, 381–390.

Ménétrier, M., Hojjaji, A., Estournès, C. & Levasseur, A. (1991). *Solid State Ion.* 48, 325–330.
Molecular Simulations (1993). *CERIUS*. Version 3.1. St Johns Innovation Centre, Cambridge, England.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.
Shastry, M. C. R., Ménétrier, M. & Levasseur, A. (1993). *Solid State Commun.* 85, 887–889.
Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Vinatier, P., Gravereau, P., Ménétrier, M., Trut, L. & Levasseur, A. (1994). *Acta Cryst.* C50, 1180–1183.
Wyckoff, R. G. (1957). *Crystal Structure.* Vol. 2. p. 26. New York: Wiley.
Yang, Z. M. & Pertlik, F. (1994). *J. Alloys Compd.* 216, 155–158.

Trirubidium Tetrathioniobate

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Abstract

The reaction of Rb$_2$S$_3$, NbO and S yields single crystals of trirubidium tetrathioniobate, Rb$_3$NbS$_4$. The crystal structure is based on discrete tetrahedral NbS$_4^{3-}$ anions, which are connected *via* Rb$^+$ cations. The compound crystallizes with the K$_3$VS$_4$ structure type and is isotypic with previously reported K and Cs analogues.

Comment

The title compound, (I), was obtained as a by-product during the synthesis of new oxo–chalcogenide compounds containing alkali and Group 5 metals.

(I)
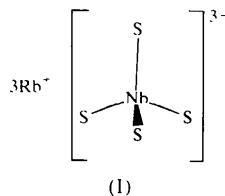
Chalcogenometallates of the alkali metals of composition A_3BX_4 (A = alkali metal; B = V, Nb, Ta; X = S, Se) crystallize with the K$_3$VS$_4$ structure type (van den Berg & de Vries, 1964). The following compounds of this type have been reported: the potassium salts K$_3$NbS$_4$,