

## Some Ternary Scandium Sulphides. Structure Refinement by Powder Neutron Diffraction

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**Abstract.**  $\text{CaSc}_2\text{S}_4$ ,  $a = 11.5014$  (5),  $b = 13.4695$  (6),  $c = 3.7284$  (1) Å,  $R_{\text{weight}} = 0.0610$  for 177 reflexions;  $\text{SrSc}_2\text{S}_4$ ,  $a = 11.6352$  (4),  $b = 13.6523$  (4),  $c = 3.7799$  (1) Å,  $R_{\text{weight}} = 0.0514$  for 172 reflexions;  $\text{PbSc}_2\text{S}_4$ ,  $a = 11.6595$  (5),  $b = 13.6933$  (5),  $c = 3.7531$  (1) Å,  $R_{\text{weight}} = 0.0591$  for 176 reflexions; all  $Pnam$ ,  $Z = 4$ . Structure refinement based on neutron diffraction powder diagrams establish the  $\text{CaFe}_2\text{O}_4$  structure of the compounds.

**Introduction.** Interest in the feature of chemical twinning (Bakker & Hyde, 1978) led to the study of the crystal structures of  $A\text{Sc}_2\text{S}_4$  with  $A = \text{Ca}, \text{Sr}$  and  $\text{Pb}$ . Flahaut (1968) reported the existence of the compounds, but their structures were not given. We prepared  $\text{PbS}$  from the elements in a quartz tube at 1100 K and  $\text{Sc}_2\text{S}_3$  from the commercially available  $\text{Sc}_2\text{O}_3$  (99.9%) in a carbon crucible under hydrogen sulphide atmosphere in an induction furnace. The alkaline-earth ternary sulphides were prepared from an appropriate mixture of the carbonates and  $\text{Sc}_2\text{S}_3$  in hydrogen sulphide atmosphere at about 1600 K for one day. The products were annealed at 1200 K for another day.  $\text{PbSc}_2\text{S}_4$  was prepared by heating the binary sulphides in a quartz tube at 1100 K for a week.

The X-ray patterns, taken with a Philips PW1040 diffractometer, could be indexed with orthorhombic cells; the absent reflections led to the space group  $Pnam$  or  $Pna2_1$ .

The lattice parameters and space group suggest the compounds have the  $\text{CaFe}_2\text{O}_4$  structure (Decker & Kasper, 1957). No single crystals were available, so we decided to use the neutron powder profile refinement technique (Rietveld, 1969) in order to obtain precise structural information. The neutron data were collected at 300 K on the powder diffractometer at the Petten High Flux Reactor as earlier described (van Laar, Rietveld & IJdo, 1971). A wavelength of 2.5867 (5) Å was used.

The complete range of data obtained ( $5.4 < 2\theta < 162^\circ$ ; in steps of  $0.144^\circ$ ) was used in the refinement except some parts of the diagrams where lines from the sample holder were present. Absorption and extinction effects were small and no corrections were made. The

background points were estimated at regions of the diffraction diagram where peaks were known to be absent.

We used the structure of  $\text{CaSc}_2\text{O}_4$  (Müller-Buschbaum & Schnering, 1965) as the trial model, space group  $Pnam$  with all atoms in the position  $4(c): x, y, \frac{1}{4}$ . The variables in the refinement procedure were: a scale factor, three half-width parameters defining the Gaussian line shape, the counter zero error, the unit-cell parameters, the atomic position parameters, isotropic temperature factors, a preferred orientation parameter and, below  $2\theta = 37.4^\circ$ , an asymmetry parameter. The coherent scattering lengths (fm) assumed were: Ca 4.7, Sr 6.9, Pb 9.4, Sc 11.8 and S 2.8 (Bacon, 1972).

The Rietveld program minimizes the function  $\chi^2 = \sum_i w_i [y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2$ ;  $y(\text{obs})$  and  $y(\text{calc})$  represent observed and calculated profile data points,  $w$  is the statistical weight allotted to each data point and  $c$  the scale factor. The following  $R$  factor is calculated:

Table 1. Atomic parameters

		$x$	$y$	$B$ (Å <sup>2</sup> )
Ca	4(c)	0.7602 (5)	0.6658 (4)	0.36 (13)
Sc(1)	4(c)	0.4149 (2)	0.0972 (2)	0.71 (7)
Sc(2)	4(c)	0.4413 (2)	0.6110 (2)	0.61 (7)
S(1)	4(c)	0.2021 (8)	0.1657 (8)	0.2 (2)
S(2)	4(c)	0.1281 (7)	0.4673 (9)	0.1 (3)
S(3)	4(c)	0.5308 (9)	0.7864 (8)	0.6 (3)
S(4)	4(c)	0.4065 (7)	0.4263 (7)	0.1 (2)
Sr	4(c)	0.7609 (3)	0.6655 (2)	0.21 (7)
Sc(1)	4(c)	0.4185 (2)	0.0988 (1)	0.76 (5)
Sc(2)	4(c)	0.4394 (1)	0.6093 (1)	0.60 (6)
S(1)	4(c)	0.2037 (6)	0.1583 (7)	0.04 (18)
S(2)	4(c)	0.1255 (6)	0.4727 (7)	0.1 (2)
S(3)	4(c)	0.5262 (7)	0.7868 (6)	0.4 (3)
S(4)	4(c)	0.4118 (6)	0.4272 (5)	0.02 (19)
Pb	4(c)	0.7605 (3)	0.6696 (2)	1.20 (7)
Sc(1)	4(c)	0.4178 (2)	0.0973 (2)	1.06 (16)
Sc(2)	4(c)	0.4412 (2)	0.6103 (2)	0.91 (7)
S(1)	4(c)	0.2029 (7)	0.1572 (7)	0.1 (2)
S(2)	4(c)	0.1245 (7)	0.4694 (8)	0.5 (3)
S(3)	4(c)	0.5285 (9)	0.7859 (7)	0.9 (3)
S(4)	4(c)	0.4097 (8)	0.4268 (6)	0.4 (2)

$$R_{\text{weight}} = \left\{ \frac{\sum w|y(\text{obs}) - \frac{1}{c}y(\text{calc})|^2}{\sum w|y(\text{obs})|^2} \right\}^{1/2},$$

where  $w$ ,  $y$  and  $c$  have the meanings defined above.

The atomic parameters are given in Table 1, the agreement between observed and calculated profiles is

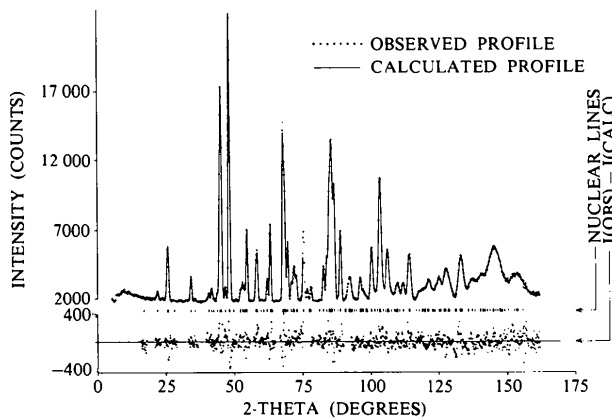


Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile for  $\text{CaSc}_2\text{S}_4$ .

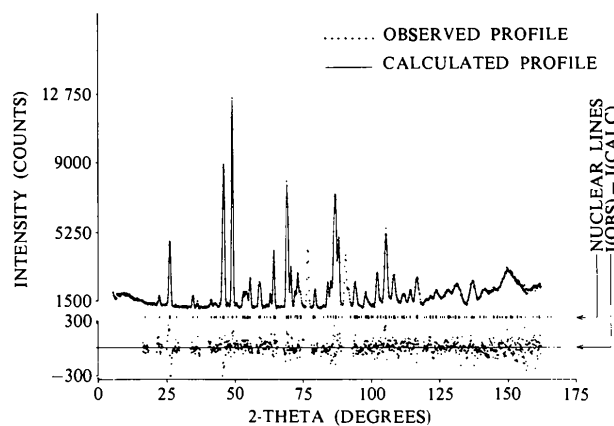


Fig. 2. Observed (dots) and calculated (full line) neutron diffraction profile for  $\text{SrSc}_2\text{S}_4$ .

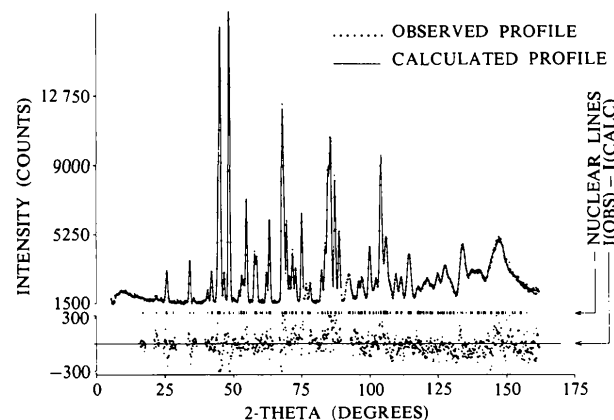


Fig. 3. Observed (dots) and calculated (full line) neutron diffraction profile for  $\text{PbSc}_2\text{S}_4$ .

Table 2. Distances (Å) in  $A\text{Sc}_2\text{S}_4$

Primed atoms have  $z = \frac{3}{4}$  or  $z = -\frac{1}{4}$ , unprimed atoms have  $z = \frac{1}{4}$ . The second column in each grouping indicates the bond multiplicity.

		$\text{CaSc}_2\text{S}_4$	$\text{SrSc}_2\text{S}_4$	$\text{PbSc}_2\text{S}_4$
Within the $A$ polyhedron				
$A-S(2')$	2	2.888 (9)	2.980 (7)	2.990 (8)
$A-S(4')$	2	2.947 (8)	3.036 (6)	3.033 (7)
$A-S(1')$	2	2.969 (9)	3.087 (8)	3.055 (8)
$A-S(3)$	1	3.098 (12)	3.194 (9)	3.139 (10)
$A-S(3)$	1	3.179 (12)	3.154 (9)	3.184 (11)
$S(1')-S(2')$	*	4.150 (16)	4.389 (13)	4.372 (14)
$S(1')-S(4')$	*	4.225 (13)	4.398 (11)	4.409 (13)
$S(2')-S(4')$	*	3.248 (12)	3.389 (10)	3.375 (12)
$S-S$	†	3.7284 (1)	3.7799 (1)	3.7531 (1)
Within the Sc octahedra				
$\text{Sc}(1)-S(1)$	1	2.615 (9)	2.627 (8)	2.636 (8)
$\text{Sc}(1)-S(2)$	1	2.603 (9)	2.599 (8)	2.678 (9)
$\text{Sc}(1)-S(2')$	2	2.604 (8)	2.607 (6)	2.614 (7)
$\text{Sc}(1)-S(3')$	2	2.514 (7)	2.536 (6)	2.544 (7)
$\text{Sc}(2)-S(1')$	2	2.595 (7)	2.606 (5)	2.600 (6)
$\text{Sc}(2)-S(3)$	1	2.578 (11)	2.625 (8)	2.611 (10)
$\text{Sc}(2)-S(4)$	1	2.519 (9)	2.506 (8)	2.539 (8)
$\text{Sc}(2)-S(4')$	2	2.607 (6)	2.611 (5)	2.608 (6)

\* These distances form the triangular face of the prism.

† These distances form the three parallel edges of the prism.

shown in Figs. 1–3, and metal–sulphur distances are given in Table 2.\*

**Discussion.** The compounds  $A\text{Sc}_2\text{S}_4$ , with  $A = \text{Ca}$ ,  $\text{Sr}$  and  $\text{Pb}$  have the  $\text{CaFe}_2\text{O}_4$  structure. The atomic parameters are in agreement with those of  $\text{CaFe}_2\text{O}_4$  (Decker & Kasper, 1957) and with those of  $\text{CaSc}_2\text{O}_4$  (Müller-Buschbaum & Schnering, 1965). Detailed structural studies for sulphides with the  $\text{CaFe}_2\text{O}_4$  structure are not known. In the structure studied each  $\text{ScS}_6$  octahedron shares four edges with neighbouring octahedra to form infinite double chains along the  $c$  axis. Each double chain shares corners with four other double chains. In this way channels are formed parallel to the  $c$  axis. In the channels the  $A$  atoms are situated, each surrounded by eight sulphur atoms forming a bicapped trigonal prism. One rectangular face, the uncapped side, is narrower than the other two, giving a rather short  $S(2')-S(4')$  distance in the prism (Table 2). No indication is found for an asymmetric position of  $\text{Pb}$  in the prism as was found for  $\text{PbZrS}_3$  (Lielieveld & IJdo, 1978). The octahedra are slightly distorted. The structure type is quite common as the low-temperature

\* The numerical intensity of each measured point on the profile, as a function of angle, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36609 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

phase for  $ALn_2S_4$  ( $A = Sr, Ba$  and  $Pb$  and  $Ln =$  lanthanide) with large radius of  $A$ , but for  $CaLn_2S_4$  ( $Ln = Ho \rightarrow Lu, Y$ ), with smaller radius of  $A$  at low temperature, the  $Yb_3S_4$  structure type with seven coordination of  $Ca$  is formed (Flahaut, 1968; Rodier & Tien, 1977).

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#### References

BACON, G. E. (1972). *Acta Cryst.* **A28**, 357–358.

- BAKKER, M. & HYDE, B. G. (1978). *Philos. Mag.* **38**, 6, 615–628.  
 DECKER, B. F. & KASPER, J. S. (1957). *Acta Cryst.* **10**, 332–337.  
 FLAHAUT, J. (1968). *Progress in the Science and Technology of the Rare Earths*, Vol. 3, pp. 209–283 (219). Oxford: Pergamon Press.  
 LAAR, B. VAN, RIETVELD, H. M. & IJDO, D. J. W. (1971). *J. Solid State Chem.* **3**, 154–160.  
 LELIEVELD, R. & IJDO, D. J. W. (1978). *Acta Cryst.* **B34**, 3348–3349.  
 MÜLLER-BUSCHBAUM, H. & SCHNERING, H. G. (1965). *Z. Anorg. Allg. Chem.* **336**, 295–305.  
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.  
 RODIER, N. & TIEN, V. (1977). *C. R. Acad. Sci. Ser. C*, **284**, 909–911.

*Acta Cryst.* (1982). **B38**, 1551–1554

## A Neutron Diffraction Study of the Ferroelectric State of Deuterated Lithium Trihydrogenselenite, $LiD_3(SeO_3)_2$

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**Abstract.**  $LiD_3(SeO_3)_2$ , monoclinic,  $Pn$ ,  $a = 6.2473$  (4),  $b = 7.9030$  (7),  $c = 5.4471$  (3) Å,  $\beta = 104.995$  (5)°,  $V = 259.78$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $d_x = 3.412$  Mg m<sup>-3</sup>,  $\mu_{obs} = 0.0691$  (1) mm<sup>-1</sup>,  $\lambda = 1.210$  Å. Large single crystals were grown by the slow evaporation at room temperature of a solution made up from  $Li_2CO_3$  and  $SeO_2$  in  $D_2O$  (0.02%  $H_2O$ ). The data were collected with a voltage of 540 V mm<sup>-1</sup> applied in the  $c^*$  direction. The crystal structure is built up of  $Li^+$  and  $DSeO_3^-$  ions and of  $D_2SeO_3$  molecules. The isotope effect in the hydrogen bonds shows the general trend as expected for hydrogen bonds in the range 2.5–2.6 Å, *i.e.* a lengthening of the O...O distances and a shortening of the O–D distances. [The final  $R$  values were  $R(F^2) = 0.034$ ,  $R_w(F^2) = 0.044$ , and  $R(F) = 0.021$  for 818 unique reflexions.]

**Introduction.** Ferroelectric  $LiH_3(SeO_3)_2$  (henceforth LHS or LDS for the deuterated compound) has been the subject of several diffraction studies. Two complete neutron diffraction studies have been published (Tellgren & Liminga, 1972; Chomnilpan, Liminga & Tellgren, 1979). An as-grown crystal, *i.e.* most probably multidomain, was used in the first case. The crystal was prepared from chemicals containing a naturally occurring mixture of Li isotopes (about 92%

<sup>7</sup>Li and 8% <sup>6</sup>Li). The anomalous-dispersion effects for neutrons, originating from <sup>6</sup>Li, were thus negligible, and although the crystal was multidomain, the results were not affected (Chomnilpan *et al.*, 1979). The latter study was made using a single-domain crystal of <sup>6</sup>LiH<sub>3</sub>(SeO<sub>3</sub>). The absolute atomic arrangement was determined using the anomalous-scattering contribution from <sup>6</sup>Li for neutrons.

The structure of LHS consists of  $H_2SeO_3$  molecules and  $HSeO_3^-$  ions, hydrogen bonded to ring-formed dimers. A third hydrogen bond, originating from the  $HSeO_3^-$  ion, interlinks the dimers to form chains (Fig. 1 and figures in Tellgren & Liminga, 1972). In the two previous studies mentioned above, it was observed that one of the H atoms, H(2), had a rather elongated 'thermal' ellipsoid along the bond direction. The O–H distance, about 1.14 Å, was also much larger than expected for a 2.52 Å O...O hydrogen bond. No anomalous features were observed for the rest of the atoms.

This effect having been observed in two independent studies, based on a multi- and a single-domain crystal, respectively, there are reasons to believe that it is genuine. The most probable explanation is that the 'anomalous' H atom is situated in a shallow skew potential well. Information about the potential well in a