*Acta Cryst.* (1982). B**38**, 2442–2444

# Zinc Rare-Earth Sulphides with the Olivine Structure

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(*Received* 2 *November* 1981; *accepted* 30 *March* 1982)

**Abstract.** $ZnLu_2S_4$, orthorhombic, *Pnma*, $a$ = 13·2180 (9), $b$ = 7·6848 (5), $c$ = 6·2606 (4) Å, $Z$ = 4, has been refined by profile analysis of powder neutron diffraction data at room temperature ($R_{nuclear}$ = 5·55, $R_{profile}$ = 10·00, $R_{weight}$ = 9·94% for 159 observed reflections). $ZnLu_2S_4$, $ZnYb_2S_4$, $ZnTm_2S_4$ and $ZnEr_2S_4$ have been found to have the olivine structure.

**Introduction.** The investigation of the crystal structure of $ZnLu_2S_4$ forms part of a research programme on the structural relations among compounds $AB_2S_4$, where $A$ represents a transition metal and $B$ a trivalent cation. $ZnLu_2S_4$ and $ZnTm_2S_4$ were reported by Yim, Fan & Stofko (1973). By comparison of their lattice parameters and those of $ZnNa_2Cl_4$, reported by van Loon & Visser (1977), we concluded that the structure was probably that of olivine (Table 1). The neutron powder-refinement technique (Rietveld, 1969) was used in order to obtain precise structural information for $ZnLu_2S_4$ and we also tried to extend the series by $ZnEr_2S_4$, $ZnHo_2S_4$ *etc.*

We prepared the compounds by firing an equimolar mixture of the binary sulphides in a stream of hydrogen sulphide at 1323 K for the first three members of the series; the ZnS + $Er_2S_3$ mixture required a higher temperature: 1473 K. $ZnHo_2S_4$ could not be prepared. The heating experiment took a few hours in an induction furnace with carbon crucibles. The $ZnLu_2S_4$ compound was annealed at 1223 K for another day.

Table 1. *Lattice parameters* (Å)

| | *a* | *b* | *c* | Reference |
|---|---|---|---|---|
| $ZnLu_2S_4$* | 13·183 | 7·658 | 6·246 | (1) |
| $ZnTm_2S_4$* | 13·227 | 7·734 | 6·263 | |
| $ZnNa_2Cl_4$* | 13·695 (1) | 8·0528 (7) | 6·4017 (8) | (2) |
| Present work: | | | | |
| $ZnLu_2S_4$ | 13·2180 (9) | 7·6848 (5) | 6·2606 (4) | Neutron |
| $ZnYb_2S_4$ | 13·261 (4) | 7·718 (2) | 6·278 (2) | X-ray |
| $ZnTm_2S_4$ | 13·301 (4) | 7·747 (2) | 6·281 (1) | |
| $ZnEr_2S_4$ | 13·344 (4) | 7·786 (2) | 6·299 (1) | |

References: (1) Yim *et al.* (1973); (2) van Loon & Visser (1977).

Standard errors in the lattice parameters do not include errors in the neutron wavelength.

* *b* and *c* axes interchanged.

The neutron diffraction diagrams were collected at 300 K on the powder diffractometer at the Petten High-Flux Reactor as described by van Laar, Rietveld & IJdo (1971). A wavelength of 2·5912 (4) Å from the (111) planes of a Cu monochromator was used. The complete range of data obtained (5·4° < 2$\theta$ < 141·2°, in steps of 0·144°) was used in the refinement except for regions where a slight impurity of ZnS was present. All data were corrected for absorption [$ZnLu_2S_4$, $\mu R$ = 0·2753 at 300 K, $\lambda$ = 2·5912 (4) Å] (Weber, 1967).

We used the structure of $ZnNa_2Cl_4$ as the trial model: space group *Pnma* with atomic positional parameters as follows: Zn in 4(*c*): $x,\frac{1}{4},z$; Lu(1) in 4(*a*): 0,0,0; Lu(2) in 4(*c*); S(1) in 4(*c*); S(2) in 4(*c*) and S(3) in 8(*d*): $x,y,z$. The variables in the refinement were: a scale factor, three half-width parameters defining the Gaussian line shape, the counter zero error, the unit-cell parameters, the atomic positional parameters, an asymmetry parameter below 2$\theta$ = 40°, five isotropic temperature factors and a preferred orientation (001) parameter. The coherent scattering lengths assumed were: Zn 5·7, Lu 7·3, S 2·8 fm (Bacon, 1972). The Rietveld program minimizes the function

$$\chi^2 = \sum_i w_i [y_i(\text{obs.}) - (1/c)\, y_i(\text{calc.})]^2,$$

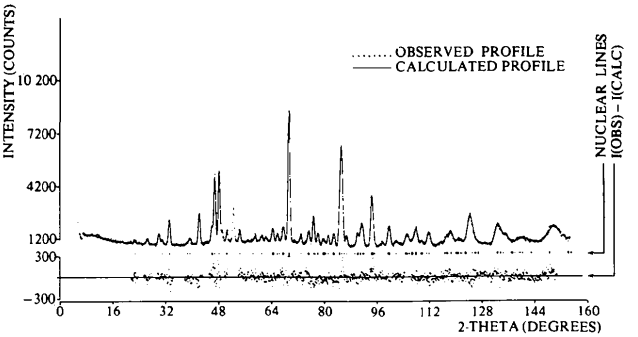


Fig. 1. Observed (dots) and calculated (full line) neutron intensity profile for $ZnLu_2S_4$. The positions of the 159 Bragg reflections are indicated.

0567-7408/82/092442-03$01.00 

Table 2. *Atomic parameters for* $ZnLu_2S_4$

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Zn | 0·0955 (4) | 0·25 | 0·4196 (7) | 0·90 (12) |
| Lu(1) | 0 | 0 | 0 | 0·70 (6) |
| Lu(2) | 0·2656 (3) | 0·25 | 0·9966 (10) | 0·70 (6) |
| S(1) | 0·0908 (13) | 0·25 | 0·7790 (14) | 0·48 (41) |
| S(2) | 0·4235 (12) | 0·25 | 0·2451 (14) | 0·50 (43) |
| S(3) | 0·1660 (9) | 0·0082 (13) | 0·2386 (11) | 0·12 (27) |

where $y$(obs.) and $y$(calc.) are the observed and calculated profile data points, $w$ is the statistical weight allotted to each data point and $c$ is the scale factor. The following $R$ factors were calculated:

$$R_{\text{nuclear}} = 100\sum |I(\text{obs.}) - (1/c)I(\text{calc.})|/\sum I(\text{obs.}) = 5{\cdot}55,$$

$$R_{\text{profile}} = 100\sum |y(\text{obs.}) - (1/c)y(\text{calc.})|/\sum y(\text{obs.}) = 10{\cdot}00,$$

$$R_{\text{weight}} = 100\,[\sum w|y(\text{obs.}) - (1/c)y(\text{calc.})|^2/\sum w|y(\text{obs.})|^2]^{1/2} = 9{\cdot}94,$$

and

$$R_{\text{expected}} = 6{\cdot}28\%$$

where $I$(obs.) and $I$(calc.) are the observed and calculated integrated intensities of each reflection.

Atomic positional parameters are given in Table 2, and the agreement between the observed and calculated profiles is shown in Fig. 1.* From the similarity in the lattice parameters and the X-ray patterns of the remaining compounds in Table 1, it is concluded that they are isostructural with $ZnLu_2S_4$.

**Discussion.** Lattice parameters of $ZnLu_2S_4$, $ZnYb_2S_4$, $ZnTm_2S_4$ and $ZnEr_2S_4$ are given in Table 1, and atomic parameters of $ZnLu_2S_4$ in Table 2. Interatomic distances and angles of $ZnLu_2S_4$ are collected in Table 3. From comparison of the lattice and atomic parameters of $ZnLu_2S_4$ with those of $ZnNa_2Cl_4$ it is concluded that the same structure, the olivine structure, has been found. This structure is based on a hexagonal close packing of S atoms with Lu in octahedral interstices and Zn in tetrahedral ones. The octahedra of Lu(1) and Lu(2) are different. The Lu(1) octahedra share edges with one another to form ribbons parallel to [010], alternate ribbons lying at heights $z = 0$ and $z = \frac{1}{2}$. The ribbons are linked to one another by Lu(2) octahedra sharing edges with them. The Zn atoms fit into tetrahedral interstices in such a way that each S atom has one Zn and three Lu neighbours (Megaw, 1973).

Table 3. *Interatomic distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Lu(1)–S(1)* | 2·654 (9) | S(1)–S(2) | 3·710 (17) |
| –S(2)* | 2·695 (8) | | 3·957 (16) |
| –S(3)* | 2·655 (11) | * | 3·853 (1) |
| Lu(2)–S(1) | 2·682 (16) | S(1)–S(3)* | 3·567 (12) |
| –S(2) | 2·603 (15) | * | 3·986 (12) |
| –S(3)* | 2·735 (10) | * | 3·933 (19) |
| –S(3)* | 2·714 (10) | * | 3·786 (19) |
| Zn–S(1) | 2·251 (9) | S(2)–S(3)* | 3·878 (18) |
| –S(2) | 2·496 (16) | * | 3·706 (18) |
| –S(3)* | 2·368 (10) | * | 3·923 (12) |
| | | * | 3·858 (12) |
| | | S(3)–S(3)* | 3·840 (14) |
| | | | 3·968 (20) |
| | | | 3·716 (20) |

| | | | |
|---|---|---|---|
| S(1)–Lu(1)–S(2) | 87·8 (3) | S(3)–Lu(2)–S(3) | 94·0 (4) |
| S(1)–Lu(1)–S(3) | 84·4 (4) | | 170·7 (2) |
| S(2)–Lu(1)–S(3) | 87·7 (4) | | 85·6 (4) |
| | | | 89·6 (2) |
| S(1)–Lu(2)–S(2) | 173·8 (4) | | |
| S(1)–Lu(2)–S(3) | 82·3 (3) | S(1)–Zn–S(2) | 112·8 (5) |
| | 89·1 (3) | S(1)–Zn–S(3) | 119·3 (3) |
| S(2)–Lu(2)–S(3) | 93·1 (3) | S(2)–Zn–S(3) | 99·2 (3) |
| | 95·1 (3) | S(3)–Zn–S(3) | 103·4 (5) |

* Distances marked with an asterisk occur in pairs.

From Table 3 it is seen that the S–S nearest-neighbour distance is not the same throughout the structure. The mean value is 3·84 (1) Å which is half the $b$ parameter, and the value that deviates most is 3·57 (1) Å for S(1)–S(3) which is a common edge between two different octahedra. This deviation is in accordance with the rules of Pauling (1929). Furthermore, we learn that octahedron (1) is more regular than octahedron (2), judged by the deviations from the mean Lu–S distance: 2·67 (1) Å for octahedron (1) and 2·70 (1) Å for octahedron (2). These values, however, are in good agreement with those found in $Lu_2S_3$ (corundum, $R\bar{3}c$): Lu–S = 2·642 (3) and 2·730 (4) Å (Range & Leeb, 1975). The mean Zn–S distance 2·37 (1) Å is a little more than the average value 2·342 (1) reported in the literature.

So far, two types of structure with composition $ZnB_2S_4$ have been reported: the spinel structure with $B$ as a small cation, such as $Cr^{3+}$ (Raccah, Bouchard & Wold, 1966), $Sc^{3+}$ (Tressler, Hummel & Stubican, 1968), and the olivine structure with $B$ as a somewhat larger cation: $Lu^{3+}$–$Er^{3+}$. Attempts to isolate crystals in which $Zn^{2+}$ is combined with large trivalent cations

* Numerical data corresponding to the difference profile of Fig. 1 and a complete list of distances <4 Å and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36933 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

($Ho^{3+}$, $Y^{3+}$, *etc.*) all failed. When $Zn^{2+}$ is replaced by the larger $Cd^{2+}$ the spinel structure has been found for $CdB_2S_4$ with $B$ as $Cr^{3+}$ (Raccah *et al.*, 1966), $Lu^{3+}$, $Yb^{3+}$, $Tm^{3+}$, $Er^{3+}$, $Y^{3+}$, $Ho^{3+}$ (Flahaut, 1968), though a transition has been observed in $CdHo_2S_4$ (Bakker, Vollebregt & Plug, 1981). For $CdDy_2S_4$, $CdTb_2S_4$, *etc.* the $Th_3P_4$ structure has been reported (Flahaut, 1968).

The authors are indebted to Mr J. F. Strang of the Energie-onderzoek Centrum Nederland, Petten, for collecting the neutron diffraction data.

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*Acta Cryst.* (1982). B**38**, 2444–2445

# Structure du Polysulfure de Thorium $Th_2S_5$

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(*Reçu le 4 janvier* 1982, *accepté le 1 avril* 1982)

**Abstract.** $Th_2S_5$, orthorhombic (pseudotetragonal), *Pcnb*, $a = 7{\cdot}623$ (4), $b = 7{\cdot}677$ (4), $c = 10{\cdot}141$ (5) Å, $Z = 4$, $D_c = 6{\cdot}99$ Mg m$^{-3}$, $\mu r = 3$, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The structure was solved by the heavy-atom method. $R = 0{\cdot}048$ for 608 reflections. Thorium is coordinated by ten sulfur atoms, and a short S=S distance equal to 2·117 (7) Å in each Th coordination polyhedron confirms that $Th_2S_5$ is a polysulfide.

**Introduction.** La littérature signale l'existence de cinq sulfures de thorium: ThS, $Th_2S_3$, $Th_7S_{12}$, $ThS_2$, $Th_2S_5$ (Graham & McTaggart, 1960), et seule la structure cristalline de $Th_2S_5$ restait inconnue. Les diagrammes de diffraction X de poudre de ce composé, et des chalcogénures d'actinides de même formulation ($Th_2Se_5$, $U_2S_5$, $Np_2S_5$) étaient indexés dans le système tétragonal (Marcon, 1967), mais nous avons montré que la symétrie est en fait orthorhombique (Noël, 1980).

Le monocristal utilisé pour la détermination structurale, obtenu par transport en phase gazeuse (Noël, 1980), a des dimensions homogènes et a été assimilé à une sphere de rayon moyen $r = 0{,}005$ cm. Les intensités de 624 réflexions ont été mesurées sur diffractomètre automatique Nonius CAD 4, suivant le mode $\omega$–$2\theta$, dans l'intervalle $2 < \theta < 30°$. 608 intensités telles que $I > 2\sigma(I)$ ont été corrigées des facteurs de Lorentz, de polarisation et de l'absorption.

La résolution de la fonction de Patterson tridimensionnelle nous a permis de positionner les huit atomes de thorium de la maille élémentaire en position générale 8(*d*) du groupe *Pcnb*. Les vingt atomes de soufre ont été ensuite localisés, par l'exploitation d'une synthèse de Fourier 'différence', en deux positions 8(*d*) et une position 4(*c*). Les affinements par moindres carrés et matrice totale (Frenz, 1978) portant sur les

Tableau 1. *Paramètres atomiques et facteurs d'agitation thermique isotrope*

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Th | 0,23171 (9) | 0,02183 (9) | 0,14600 (8) | 0,33 (1) |
| S(1) | 0,3615 (7) | 0,3876 (7) | 0,6077 (6) | 0,44 (9) |
| S(2) | 0,9028 (7) | 0,8484 (7) | 0,5996 (6) | 0,40 (9) |
| S(3) | 0 | 0,25 | 0,7528 (9) | 0,5 (1) |

0567-7408/82/092444-02$01.00 