angles are slightly distorted compared with idealized SiO_4 tetrahedra (deviations from mean values $8{\cdot}67 \times 10^{-4}$, $9{\cdot}07 \times 10^{-2}$, $7{\cdot}75 \times 10^{-2}$ and $9{\cdot}55 \times 10^{-2}$°, respectively) (Liebau, 1985). The K—O polyhedra are irregular in shape and bondings are ionic. Thus, these polyhedra compensate for all the strains derived from the framework constructed by the rigid, rather covalent sp^3 configuration of SiO_4 and ZnO_4. This is consistent with the fact that compounds containing $A_xZn_ySi_pO_q$ (A = alkali metal) are more abundant than those containing only $Zn_xSi_pO_q$.

The rather large values of the standard deviations of the oxygen positional parameters in Table 2 may be attributed to both the small size of the crystal specimen and crystallogenetic problems. The syntheses of better single crystals for more precise structure analyses are still difficult by currently used hydrothermal methods.

The sum of electrostatic charges calculated with the parameters of Brown & Wu (1976) is satisfactory, ranging from 1·86 to 2·11 for O, 2·057 for Zn, from 0·804 to 0·805 for K and from 4·009 to 4·095 valence units for Si atoms.

The intensity measurements were carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University. The authors thank the staff at the Research Center for their kind help with the manipulation of the four-circle diffractometer.

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Room-Temperature Structure of $La_2O_2S_2$

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Abstract. Lanthanum oxide sulfide $La_2O_2S_2$, $M_r = 373{\cdot}947$, orthorhombic, $Cmca$, $a = 13{\cdot}215\,(2)$, $b = 5{\cdot}943\,(1)$, $c = 5{\cdot}938\,(1)$ Å, $V = 466{\cdot}3\,(2)$ Å^3, $Z = 4$, $D_x = 5{\cdot}32$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 18{\cdot}87$ mm^{-1}, $F(000) = 648$, $R = 0{\cdot}017$, 582 unique observed reflections, flux growth, data corrected for twinning of the crystal. The structure is built from infinitive layers of LaO_4S_4 square antiprisms connected by edges; these layers share either oxygen or disulfide common planes. Short S—S distances [$d = 2{\cdot}103\,(2)$ Å] correspond to S_2^{2-} entities.

Introduction. The rare-earth oxysulfides Ln_2O_2S form an important class of luminescent materials with numerous applications as phosphors (Klaassen, Van Leuken & Maessen, 1988) or as high-gain laser materials (Alves, Buchanan, Wickersheim & Yates, 1971). During the crystal growth by flux method of dilanthanum dioxide sulfide, formation of small yellow crystals occurs at low temperature (Ostoréro, Fadly & Makram, 1976). They were identified as dilanthanum dioxide disulfide. The crystal structure of these compounds does not seem to be precisely

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established (Khodadad, Tat Tek, Flahaut & Domange, 1965; Ballestracci, 1967; Dugué, 1978; Wichelhaus, 1978; Borodulenko, Eliseev, Kuz'micheva, Perepelkin & Ponomarev, 1984) and the true space group remains an open question. Due to the pseudo quadratic character of the cell, twinning can easily occur. This fact explains the discrepancy observed between the different results in the literature. Thus we have undertaken a new structure determination of $La_2O_2S_2$.

Experimental. Flux growth from S, K_2S and La_2O_3 at $T = 923$ K under 1·5 MPa argon pressure with slow cooling at 1·5 K h^{-1} in Al_2O_3 crucible. Yellow rectangular platelet 0·04 × 0·08 × 0·18 mm limited by (100), (01$\bar{1}$) and (011) faces respectively. Data collected on a Siemens AED2 four-circle diffractometer; ω–2θ step-scan mode in N steps of 0·035°, $37 \leq N \leq 45$; time per step: min. 1 s, max. 4 s; aperture D = 3·5 mm; lattice constants based on 34 reflections measured in double step-scan mode at $\pm(2\theta \simeq 30°)$; absorption correction by the Gauss method, A_{max} = 0·447, A_{min} = 0·184. h 0→22, k 0→10, l 0→10. Intensity measurement to $2\theta \leq 80°$ of one unique set; standard reflections 202, 2$\bar{4}$0, 20$\bar{2}$, intensity variation 0·7%; 846 reflections measured, 582 unique observed reflections used for refinements [$|F| > 6\sigma(|F|)$]; structure solved by direct methods with *TANG* option of *SHELX76* program (Sheldrick, 1976). F magnitudes used in least-squares refinements: 18 parameters refined; max. Δ/σ = 0·03; secondary-extinction factor: $x = 2{\cdot}45\,(6) \times 10^{-7}$; atomic scattering factors for La, O, S from *International Tables for X-ray Crystallography* (1974); calculations with *SHELX76* program (Sheldrick, 1976) on a MicroVAX II computer.

Data collection in a primitive cell indicates the presence of very few weak reflections incompatible with a C centering of the cell (Dugué, 1978). This fact was observed by Wichelhaus and led this author to refine the structure of $La_2O_2S_2$ in the space group *Pcam*. Most of the weak observed reflections agree with those calculated by using the space group *Pcam* with the exception of 411_P which is zero in our work. It must be noted also that supplementary conditions to *Pcam* affect the existence of reflections. Moreover, all the weak reflections can be derived from strong reflections of a C lattice by applying a symmetry plane at 45° to the quasi-equal b and c axes; their relative intensity also depends on the crystal. This can be readily explained by the existence of a (01$\bar{1}$) twin crystal B with interchanged b and c axes. The volume ratio $r = 20$ for crystals A and B was then estimated from the unique reflections of A and B (Fig. 1). Intensities corresponding to the larger crystal A were calculated by using the relation $I(hkl)_A = [I_1 - (1/r)I_2][r^2/(r^2-1)]$ with $I_1 = I(hkl)_A + I(hlk)_B$ and $I_2 = I(hlk)_A + I(hkl)_B$ (Leblanc, Ferey, De Pape & Teillet, 1984). The space group *Cmca* was then derived from this set of corrected data and used for the structure determination.

Table 1. *Coordinates and equivalent isotropic temperature factors* (Å^2) *in* $La_2O_2S_2$ (*e.s.d.'s in parentheses*)

$$B_{eq} = (4/3)\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
La	0·3392 (1)	0	0	0·40 (1)
S	0	0·3750 (2)	0·3747 (2)	0·73 (2)
O	1/4	0·2446 (4)	1/4	0·55 (7)

Table 2. *Selected bond lengths* (Å) *in* $La_2O_2S_2$ (*e.s.d.'s in parentheses*)

2 × La—O	2·389 (2)	2 × O—S	3·473 (1)
2 × La—O	2·428 (2)	2 × O—S	4·036 (2)
2 × La—S	3·165 (1)	2 × O—S	4·048 (1)
2 × La—S	3·168 (1)	2 × S—S	3·320 (2)
		2 × S—S	3·320 (2)
2 × O—O	2·970 (1)	S—S	2·103 (3)
2 × O—O	2·971 (1)		

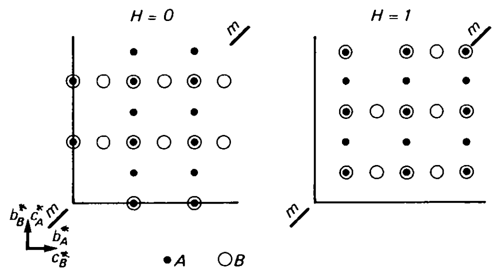

Fig. 1. Projection of a part of 0*kl* and 1*kl* reciprocal layers of a twin crystal of $La_2O_2S_2$. Weak reflections due to parasitic crystal B are shown by empty circles.

A solution with the La atom in special position 8(*d*) was found with the multisolution tangent direct method of *SHELX76*. Successive refinements and difference Fourier maps located the S and O atoms. Refinement of anisotropic thermal motion parameters led to $R = 0{\cdot}017$, $wR = 0{\cdot}018$; $w = 1{\cdot}0/[\sigma^2(|F_o|) + 0{\cdot}00005F_o^2]$. Max. and min. heights in final difference map: +2·5 and −2·9 e Å^{-3}.

Discussion. Final atomic parameters are listed in Table 1 and selected interatomic distances in Table 2.* The (100) projection of the structure is given in Fig. 2. The atomic position parameters, though more

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52816 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

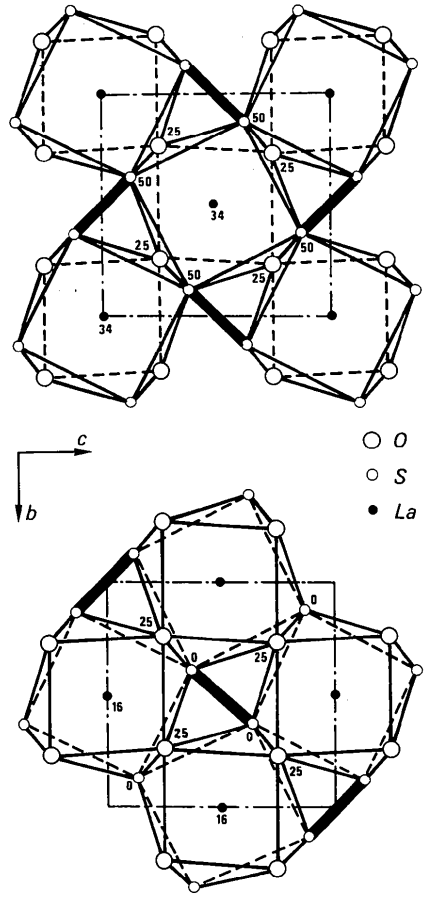

Fig. 2. [100] projection of layers of LaO_4S_4 square antiprisms lying at $x = 0{\cdot}16$ and $x = 0{\cdot}34$. Thick lines correspond to short S—S distances.

precise, do not differ significantly from those of Dugué (1978); however, the anisotropic thermal parameters are more consistent with the structure. Thermal motion is now almost isotropic in the *bc* plane while a large discrepancy between U_{22} and U_{33} values was reported by Dugué (1978).

The structure can be described as built up of slightly distorted LaS_4O_4 square antiprisms. These polyhedra share edges in the *bc* plane and along **a**. They build infinite (100) layers connected together either by oxygen or disulfide common planes. Short S—S distances [$d = 2{\cdot}103$ (2) Å] are consistent with the presence of expected disulfide S_2^{2-} groups.

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Structure de $Cu(HPO_3H)_2$

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Abstract. Copper bis(hydrogenphosphonate), $Cu(HPO_3H)_2$, $M_r = 225{\cdot}5$, monoclinic, $P2_1/a$, $a = 7{\cdot}4748$ (6), $b = 9{\cdot}9406$ (7), $c = 7{\cdot}5175$ (5) Å, $\beta = 99{\cdot}722$ (4)°, $V = 550{\cdot}55$ (8) Å^3, $Z = 4$, $D_m = 2{\cdot}81$ (1) (by pycnometry), $D_x = 2{\cdot}722$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 4{\cdot}323$ mm^{-1}, $F(000) = 444$, room

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