

Europium thiosilicate at 100 K

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Key indicators

Single-crystal X-ray study

T = 100 K

Mean $\sigma(\text{S}-\text{Si}) = 0.003 \text{ \AA}$

R factor = 0.045

wR factor = 0.072

Data-to-parameter ratio = 25.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of Eu_2SiS_4 was determined from single-crystal data. The title compound crystallizes as a monoclinic Sr_2GeS_4 -type in the space group $P2_1/m$, both at room temperature and at 100 K. The main structural features are almost undistorted SiS_4^{4-} tetrahedra and Eu^{2+} in 6(+2) coordination by sulfur. The thiosilicate is isotypic with the paraelectric phase of Eu_2GeS_4 , stable above $T_C = 335 \text{ K}$. Unlike the thiogermanate, down to 100 K Eu_2SiS_4 shows no structural transition into a ferroelectric phase with space group $P2_1$.

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Comment

Recently, we reported on the structural phase transition of monoclinic europium thiogermanate (Tampier & Johrendt, 2001). Eu_2GeS_4 crystallizes in the space group $P2_1$ at room temperature ($\alpha\text{-Eu}_2\text{GeS}_4$), but above the Curie point $T_C = 335 \text{ K}$, the structure is centrosymmetric with the space group $P2_1/m$ ($\beta\text{-Eu}_2\text{GeS}_4$). The main contributions of the transition are an anti-distorsive tilt of the tetrahedral GeS_4^{4-} groups and small shifts of the Eu^{2+} ions, whose coordination numbers change from 7 to 6(+2). The mechanism is similar to what has been found for isostructural ferroelectric K_2ZnBr_4 (Bärnighausen, 1992). From the structural viewpoint, we concluded that Eu_2GeS_4 should be ferroelectric below $T_C = 335 \text{ K}$ and paraelectric above this temperature.

Europium thiosilicate, Eu_2SiS_4 , has already been mentioned in the literature (Olivier-Fourcade *et al.*, 1978), but up to now no detailed structural data have been published. From our results on Eu_2GeS_4 the question arises, whether or not the isostructural thiosilicate also undergoes a ferroelectric phase transition. In order to clarify this, we have first determined the room-temperature structure of Eu_2SiS_4 . This confirmed the monoclinic structure type in the space group $P2_1/m$. This structure did not differ significantly from the low temperature structure except that the displacement parameters U^{22} of the S1 and S2 on the mirror plane ($2e$) were 0.030 \AA^2 , in contrast to S3 on the general position ($4f$) with $U^{22} = 0.010 \text{ \AA}^2$. This indicated only a small degree of disorder, if at all, of the S atoms on the special position. In going to lower temperatures, a structural transition would manifest itself by an ordering of the S1 and S2 positions and small shifts of the Eu atoms away from $y = \frac{1}{4}$, tantamount to a change of the space group to the non-centrosymmetric $P2_1$.

The structure determination of Eu_2SiS_4 at 100 K resulted in different behaviour. Important interatomic distances are listed in Table 1. The displacement parameters U^{22} of the S atoms in question decrease to 0.016 \AA^2 . This means that the deviation

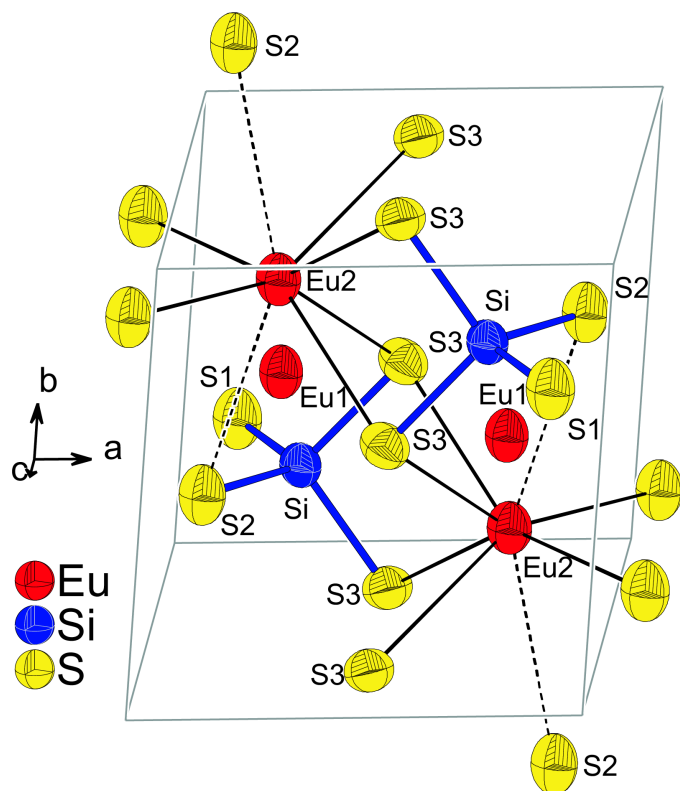


Figure 1
Unit cell of the crystal structure of Eu_2SiS_4 .

of the S1 and S2 atoms from their ideal position $y = \frac{1}{4}$ decreases with temperature and would probably vanish as $T \rightarrow 0$. Attempts to refine the structure with space group $P2_1$ were not successful. Thus, Eu_2SiS_4 is isotypic with $\beta\text{-Eu}_2\text{GeS}_4$, but shows no transition to the non-centrosymmetric α -phase; rather, it changes continuously towards the ideal Sr_2GeS_4 -type.

Fig. 1 shows the unit cell of Eu_2SiS_4 emphasizing the SiS_4 -tetrahedra and the coordination of europium. Six S atoms form a trigonal prism and two extra S atoms are located over the square faces (dashed bonds). Fig. 2 shows the connection of the EuS_6 polyhedra and the additional S atoms between them. The S1 and S2 atoms are slightly disordered in the space group $P2_1/m$ and move towards the mirror plane as the temperature decreases. If the $P2_1/m \rightarrow P2_1$ transition would occur, the dashed Eu—S bonds would have unequal lengths due to the ordering of S1 and S2 and the opposing shifts of europium. This would lead to a ferroelectric structure as is the case for europium thiogermanate, but not for the thiosilicate.

Experimental

Eu_2SiS_4 was prepared from the elements in two steps. First, europium metal and silicon powder were heated to 1173 K for 15 h in a quartz tube under an argon atmosphere. The resulting alloy was ground in an argon-filled glove-box and then oxidized by the stoichiometric amount of sulfur at 1123 K for 24 h, again homogenized and reheated to 1073 K for 50 h. This results in a dark-yellow powder containing small single crystals suitable for the X-ray experiments.

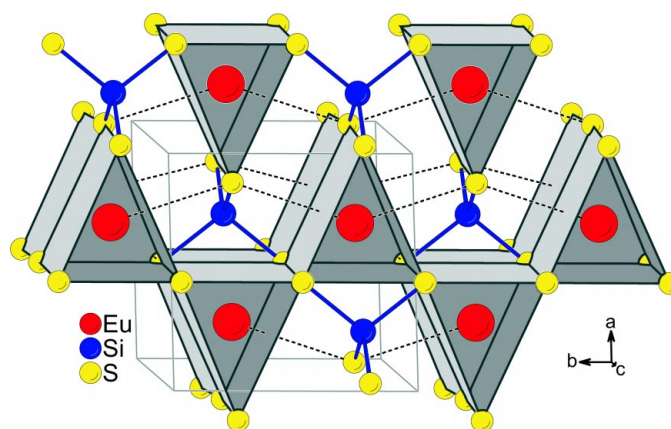


Figure 2
Crystal structure of Eu_2SiS_4 . The 6(+2)-coordination of the Eu atoms and the SiS_4 -tetrahedra are emphasized.

Crystal data

Eu_2SiS_4
 $M_r = 460.25$
 Monoclinic, $P2_1/m$
 $a = 6.524(1) \text{ \AA}$
 $b = 6.591(1) \text{ \AA}$
 $c = 8.205(2) \text{ \AA}$
 $\beta = 108.29(3)^\circ$
 $V = 334.99(11) \text{ \AA}^3$
 $Z = 2$

$D_x = 4.563 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 3437 reflections
 $\theta = 3\text{--}30^\circ$
 $\mu = 19.84 \text{ mm}^{-1}$
 $T = 100(2) \text{ K}$
 Irregular, dark yellow
 $0.09 \times 0.08 \times 0.07 \text{ mm}$

Data collection

Stoe IPDS diffractometer
 ω scans
 Absorption correction: Gaussian
 (*X-RED*; Stoe & Cie, 1998)
 $T_{\min} = 0.075$, $T_{\max} = 0.143$
 5587 measured reflections
 1062 independent reflections

890 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.106$
 $\theta_{\text{max}} = 30.4^\circ$
 $h = -9 \rightarrow 9$
 $k = -9 \rightarrow 9$
 $l = -11 \rightarrow 11$
 Intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.072$
 $S = 1.13$
 1062 reflections
 41 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0350P)^2 + 1.9742P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.82 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.55 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0051 (7)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Eu1—S2 ⁱ	2.940 (2)	Eu2—S3 ^{vii}	3.0247 (15)
Eu1—S3 ⁱⁱⁱ	2.9914 (16)	Eu2—S3	3.0958 (17)
Eu1—S3 ⁱⁱⁱ	2.9914 (16)	Eu2—S3 ^{iv}	3.0958 (17)
Eu1—S1 ⁱ	3.018 (2)	Eu2—S1 ^{viii}	3.104 (2)
Eu1—S3	3.0912 (16)	Eu2—S2 ^{ix}	3.4134 (7)
Eu1—S3 ^{iv}	3.0912 (16)	Eu2—S2 ^{vi}	3.4134 (7)
Eu1—S1 ^v	3.4683 (8)	Si1—S3 ^{iv}	2.121 (2)
Eu1—S1 ⁱⁱ	3.4683 (8)	Si1—S3	2.121 (2)
Eu2—S2 ⁱ	2.990 (2)	Si1—S2	2.123 (3)
Eu2—S3 ^{vi}	3.0247 (15)	Si1—S1	2.124 (3)
S3 ^{iv} —Si1—S3	102.51 (13)	S3 ^{iv} —Si1—S1	109.14 (9)
S3 ^{iv} —Si1—S2	109.74 (9)	S3—Si1—S1	109.14 (9)
S3—Si1—S2	109.74 (9)	S2—Si1—S1	115.75 (14)

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

The data collection was performed on a Stoe IPDS diffractometer, equipped with an Oxford Cryostream cooler. The measuring temperature was 100 ± 2 K. 118 exposures were taken in the φ -range of 0 – 284° with a crystal to detector distance of 50 mm and an exposure time of 3 min. Dynamic profiles (9–25 pixels) with no allowance for overlap were used for integration. 96.7% completeness of data has been achieved in the θ -range 2.6 – 30.35° . Absorption effects were corrected numerically using the experimental crystal description. The atomic coordinates of Eu_2GeS_4 were initially used and refined by least-squares cycles using *SHELXL97* (Sheldrick, 1997).

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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