Crystal structure of erbium sesquiselenide, Er_2Se_3

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Abstract

Er_2Se_3 with Sc_2S_3-type structure is orthorhombic, space group $Fddd$, $a = 8.085(1)$ Å, $b = 11.346(1)$ Å, $c = 24.140(2)$ Å, $V = 2214.4(4)$ Å^3, $Z = 16$. Refinement proceeded to $R_F = 0.068$ for 1035 observed reflections with $I > 2.5\sigma(I)$. There are two types of crystallographically independent Er atoms both at 16(g) and two kinds of crystallographically independent Se atoms at 16(e) and 32(h). Both types of Er atoms are in slightly distorted octahedral coordination by Se; Se atoms are coordinated by erbium atoms at four of the six vertices of a slightly distorted octahedron, vacancies are in *cis* positions.

Keywords: Erbium sesquiselenide; Crystal structure

1. Introduction

At ambient conditions the erbium selenides known in the literature are ErSe with a homogeneity ranging from $ErSe_{0.75}$ to $ErSe_{1.10}$ with sodium chloride type structure [1], a compound Er_2Se_3 with a homogeneity ranging from $ErSe_{1.50}$ to $ErSe_{1.43}$ with Sc_2S_3-type structure [2,3], and a compound Er_4Se_7 [4–6]. There is a compound $ErSe_2$ stable above 890 °C with UTe_2-type structure [1,4]. A phase Er_3Se_4 stable at high pressure and high temperature with defect Th_3P_4-type structure extends from $ErSe_{1.33}$ to $ErSe_{1.50}$ [7]. Some sesquiselenides and sesquitellurides (M_2X_3, M = Sc, Y and the late rare earth metal Gd to Lu, X = Se and Te) have the Sc_2S_3-type structure with structural data known only from powder diffraction [8,9]. Here a single-crystal study is presented for erbium sesquiselenide Er_2Se_3 with Sc_2S_3-type structure as an extension of our work on erbium sesquisulphides [10].

2. Experimental details

Yellow-coloured crystals were obtained in a crystal growing experiment by vapour transport. The starting material for vapour transport was Er_2Se_3 prepared by high temperature reaction of the elements at 1273 K for 10 days. The transport agent was chlorine and the gradient was 1273–1073 K. Crystals grow at the low temperature side of the quartz tube.

3. X-ray diffraction

The first two selected crystals for data collection were found to be twins; the relation was found by the program DIRAX [11]. The twins have a common axis [103] with rotation angle 180.04°. A yellow-coloured crystal of dimensions 0.12 mm×0.15 mm×0.075 mm was cut from a larger crystal and mounted on a fibre glass tip onto a goniometer head. Single-crystal diffraction data were collected on an Enraf–Nonius CAD-4F diffractometer, with the use of graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), interfaced to a VAX-11/730 computer. The unit cell parameters were determined by using the setting angles of 22 randomly distributed intense reflections having $11.45° < \theta < 20.00°$. Unit cell parameters and orientation matrix were determined from a least-squares treatment of the SET4 [12] setting angles. The space group was derived from the extinct reflections. The unit cell was identified as orthorhombic, space group $Fddd$. The unit cell was checked for the presence of higher lattice symmetry [13]. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements [14,15]. The experimental stability was checked by three standard reflections which were measured every 3 h of X-ray exposure time; there was no indication of crystal decomposition. A 360° ψ scan for a reflection close to axial (511) revealed a variation in intensity of 31% about the mean value. Intensity data were corrected for Lorentz and polarization effects, the scale variation and for absorption (gaussian inte-

Table 1
Crystal data

Crystal data and details of the structure determination	
Chemical formula	Er_2Se_3
Formula mass (g mol^{-1})	571.40
Crystal system	Orthorhombic
Space group [19]	*Fddd* (origin choice 2)
a (Å)	8.085(1)
b (Å)	11.346(1)
c (Å)	24.140(2)
V (Å^3)	2214.4(4)
Z	16
D_{calc} (g cm^{-3})	6.855
$F(000)$, electrons	3808
μ(Mo Kα) (cm^{-1})	499.0
Approximate crystal dimensions (mm × mm × mm)	0.12 × 0.15 × 0.075
Data collection	
Radiation	Mo Kα
Wavelength (Å)	0.71073
Monochromator	Graphite
Temperature (K)	295
θ range (deg)	1.00–40.0
ω–2θ scan (deg)	$\Delta\omega = 0.80 + 0.34 \tan \theta$
Data set	h, 0 to 14; k, 0 to 20; l, -1 to 43
Crystal-to-receiving-aperture distance (mm)	173
Horizontal and vertical apertures (mm)	$3.2 + \tan \theta$, 4.0
Reference reflections and	$11\bar{1}$, 0.6
r.m.s. deviation (%)	$1\bar{1}1$, 0.7
Instability constant P	0.0163
Drift correction	1.000–1.027
Minimum and maximum absorption correction factor	7.76, 40.69
X-ray exposure time (h)	36.4
Total data	1958
Unique data	1720
Observed data ($I \geqslant 2.5\sigma(i)$)	1035
$R_1 = \Sigma(I - \bar{I})/\Sigma I$	0.057
$R_2 = \Sigma\sigma/\Sigma I$	0.045
Number of equivalent reflections	118
Refinement	
Number of reflections	1035
Number of refined parameters	12
Isotropic secondary extinction coefficient g	0.036(1) × 10^{-4}
Final agreement factors	
$R_F = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.068
$w_R = [\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma w\|F_o\|^2]^{1/2}$	0.075
Weighting scheme	$1/\sigma^2(F)$
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$ (m, number of observations; n, number of variables)	4.387
Residual electron densities in final difference Fourier map (e Å^{-3})	-15.2, 18.2
Maximum shift/σ, final cycle	0.705 × 10^{-2}
Average shift/σ, final cycle	0.195 × 10^{-3}

gration [16]). Variance $\sigma^2(I)$ calculated on the basis of counting statistics plus the term $(PI)^2$, where $P = 0.016$ is the instability constant [17] as derived from the excess variance in the reference reflections. Equivalent reflections were averaged and stated as observed if satisfying the $I \geqslant 2.5\sigma(I)$ criterion of observability.

The structure was solved by Patterson methods [18] and the positional and anisotropic thermal displacement parameters were refined on F_o with full-matrix least-squares procedures (CRYLSQ [19]) minimizing the function $Q = \Sigma_h [w(\|F_o\| - k\|F_c\|)^2]$. On going to anisotropic refinement, the thermal displacement parameters for three atoms went to non-positive definite values. Ultimately isotropic displacement parameters were used in the final refinements. The crystal exhibited some secondary extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter [20]. Scattering factors from Cromer

Table 2

Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters with estimated standard deviations in parentheses

	x	y	z	U_{iso} (Å) [a]
Er(1)	0.12500(–)	0.12500(–)	0.04105(5)	0.0017(2)
Er(2)	0.37500(–)	0.37500(–)	0.12771(5)	0.0019(2)
Se(1)	0.3698(5)	0.12500(–)	0.12500(–)	0.0026(3)
Se(2)	0.6323(4)	0.3768(1)	0.20653(7)	0.0023(3)

[a] $F(h) = F_o(h) \exp\{-8\pi^2 U_{iso}[\sin(\theta)/\lambda]^2\}$.

and Mann [21] and anomalous-dispersion factors from Cromer and Liberman [22] were used. All calculations were carried out on the CDC-Cyber 962-31 computer at the university of Groningen with the program packages XTAL [23] and PLATON [24]. Crystal data are summarized in Table 1. Table 2 lists the final fractional atomic coordinates and isotropic thermal displacement parameters of Er_2Se_3.

4. Crystal structure

The structure of Er_2Se_3 proposed by Flahaut and co-workers [2,3] is confirmed. The structure is a

superstructure of a sodium chloride type structure due to ordering of vacancies: $a = 8.085(1)$ Å $\approx a_0\sqrt{2}$, $b = 11.346(1)$ Å $\approx 2a_0$, $c = 24.140(2)$ Å $\approx 3a_0\sqrt{2}$ ($a_0 = 5.69$ Å of the NaCl subcell); space group, $Fddd$. Er_2Se_3 is isostructural with Sc_2S_3 [25]. The 32 erbium atoms are located at two sets 16(g), 48 selenium atoms are at 16(e) and 32(h). Table 3 lists the important bond distances and angles. Both types of crystallographically different erbium atoms are in slightly distorted octahedral coordination (site symmetry 2). The deviations of the Er(1)–Se and Er(2)–Se distances from their average value are less than 0.01 Å, whereas the bond angles deviate on the average less than 1.7° from 90° or 180°. The same is found for Sc_2S_3 [25]. The average Er–Se distances (2.827 Å for Er(1) and 2.828 Å for Er(2)) are almost equal to the Er–Se distance (2.828 Å) in ErSe with sodium chloride structure ($a_0 = 5.656$ Å [1]). Both types of selenium atoms are coordinated to erbium atoms on four of the six vertices of an octahedron, the vacant sites being in cis position, as shown in Fig. 1. The vacancies are arranged in pairs parallel to the c axis. Parallel to the b axis there are two kinds of Er–Se chains: one continuous, –Se(1)–Er(2)–Se(1)–Er(2)–, and the other discontinuous, –Se(2)–Er(1)–Se(2)–V–Se(2)–. A photograph of a ball and stick model is given in the paper by Dismukes and White [8].

Table 3

Important interatomic distances (ångströms) and angles (degrees) in Er_2Se_3

Er(1)–Se(2)	2.817(1) (2×)	Er(2)–Se(2)	2.819(3) (2×)
Er(1)–Se(2)	2.831(3) (2×)	Er(2)–Se(2)	2.826(3) (2×)
Er(1)–Se(1)	2.833(3) (2×)	Er(2)–Se(1)	2.838(1) (2×)
Average	2.827	Average	2.828
Se(1)–Er(1)–Se(1)a	88.65(9)	Se(1)–Er(1)–Se(2)y	88.31(5)
Se(1)–Er(1)–Se(2)k	91.79(8)	Se(1)–Er(1)–Se(2)n	89.99(6)
Se(1)a–Er(1)–Se(2)k	179.39(7)	Se(2)j–Er(1)–Se(2)k	87.77(8)
Se(2)k–Er(1)–Se(2)n	92.10(6)	Se(2)j–Er(1)–Se(2)n	89.61(6)
Se(2)n–Er(1)–Se(2)y	177.62(7)		
Se(1)–Er(2)–Se(1)o	177.36(5)	Se(2)–Er(2)–Se(2)*	95.11(8)
Se(2)–Er(2)–Se(2)y	176.43(8)	Se(1)–Er(2)–Se(2)	91.94(7)
Se(1)–Er(2)–Se(2)x	90.06(7)	Se(2)–Er(2)–Se(1)o	89.85(7)
Se(1)–Er(2)–Se(2)y	88.04(7)	Se(2)–Er(2)–Se(2)x	88.47(7)
Se(2)x–Er(2)–Se(2)y	87.96(8)		
Er(1)–Se(1)–Er(2)	91.54(6)	Er(2)n–Se(1)–Er(1)p	91.54(6)
Er(1)–Se(1)–Er(2)n	89.65(6)	Er(2)–Se(1)–Er(1)p	89.65(6)
Er(1)–Se(1)–Er(1)p	91.35(12)	Er(2)–Se(1)–Er(2)n	178.30(16)
Er(1)c–Se(2)–Er(1)o	90.39(6)	Er(2)–Se(2)–Er(1)o	90.33(6)
Er(1)c–Se(2)–Er(2)x	92.14(10)	Er(1)o–Se(2)–Er(2)x	92.11(6)
Er(2)–Se(2)–Er(1)c	176.24(10)	Er(2)–Se(2)–Er(2)x	91.53(6)

Symmetry codes

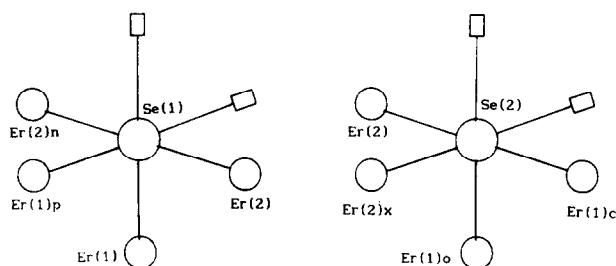| a	$1/4-x$, $1/4-y$, z	c	$-x$, $1/4+y$, $1/4+z$
j	$1/4+x$, $1/2-y$, $3/4+z$	k	$-x$, $3/4+y$, $3/4+z$
n	$3/4-x$, $1/2+y$, $1/4-z$	o	$3/4-x$, $1/2+y$, $1/4-z$
p	x, $1/4-y$, $1/4-z$	x	$1/4-x$, y, $1/4-z$
y	$1/2+x$, $3/4-y$, $1/4-z$	z	$1/2+x$, $3/4-y$, $1/4-z$
*	$3/4+x$, $1/2-y$, $1/4+z$		

Fig. 1. Coordination of Se(1) and Se(2) by Er(1) and Er(2) and vacancies (□).

The Sc₂S₃ structure is found for a number of compounds, i.e. Sc_2S_3 and the late rare earth sesquiselenides Ho_2Se_3, Er_2Se_3, Tm_2Se_3, Yb_2Se_3, Lu_2Se_3 and Y_2Se_3 (the ionic radius for Y^{3+} being close to that of Ho^{3+}), and tellurides (Ln_2Te_3, $Ln = Gd–Lu$, and Y, Sc) [9,26]. The ionic radii ratio $Z(M^{3+})/Z(X^{2-})$ for these compounds favours octahedral coordination of M^{3+}; polarization energy due to the asymmetric coordination of X^{2-} (vacancies in *cis* position) is important for stabilizing this structure. In the corund (α-Al_2O_3) structure one finds the Al^{3+} ions in distorted octahedral coordination by O^{2-}; the arrangement of four Al^{3+} ions around O^{2-} approximates tetrahedral coordination, and polarization energy is not important. It may be noted that for pure geometrical reasons an M_2X_3 structure with regular octahedral coordination of M and regular tetrahedral coordination of X by M is not possible [27].

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