$Ce_3Mg_{0.5}GeS_7$ from single-crystal data

L. D. Gulay,[a] M. Daszkiewicz,[b]* M. R. Huch[c] and A. Pietraszko[b]

[a]Department of Ecology and Protection of the Environment, Volyn State University, Voli Avenue 13, 43009 Lutsk, Ukraine, [b]W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna Street 2, PO Box 1410, 50-950 Wrocław, Poland, and [c]Department of General and Inorganic Chemistry, Volyn State University, Voli Avenue 13, 43009 Lutsk, Ukraine

Correspondence e-mail: m.daszkiewicz@int.pan.wroc.pl

Single crystals of tricerium hemimagnesium germanium heptasulfide were obtained by sintering a Ce_2S_3–MgS–GeS_2 mixture. The compound crystallizes in the space group $P6_3$ and is isotypic with other $Ln_3T_{0.5}XS_7$ phases (Ln = lanthanide, T = divalent transition metal, and X = Si or Ge). The slightly distorted trigonal $[MgS_6]$ antiprism has 3 symmetry, with the Mg position half-occupied. The latter position correlates well with the disordered Ag2 positions in the $Ln_3Ag_{1-\delta}SnS_7$ (Ln = La, Ce; δ = 0.18–0.19) and $Ln_3Ag_{1-\delta}SiS_7$ (Ln = La–Nd, Sm; δ = 0.10–0.23) structures. The present single-crystal study confirms the previous refinement from powder data, but with all displacement parameters refined anisotropically.

Related literature

For investigations of the phase relations in the quasi-ternary Ce_2S_3–MgS–GeS_2 system and a previous structure refinement of the title compound from powder data, see Huch *et al.* (2006). For studies of $Ln_3Ag_{1-\delta}SnS_7$ (Ln = La, Ce; δ = 0.18–0.19) and $Ln_3Ag_{1-\delta}SiS_7$ (Ln = La–Nd, Sm; δ = 0.10–0.23) compounds, see Daszkiewicz *et al.* (2007*a,b*), respectively.

Experimental

Crystal data

$Ce_3Mg_{0.50}GeS_7$	$Z = 2$
$M_r = 729.53$	Mo $K\alpha$ radiation
Hexagonal, $P6_3$	$\mu = 16.91$ mm^{-1}
$a = 10.2626$ (15) Å	$T = 293$ (2) K
$c = 5.7679$ (12) Å	$0.13 \times 0.11 \times 0.08$ mm
$V = 526.09$ (15) Å^3	

Data collection

Kuma KM-4 diffractometer with CCD area detector	7638 measured reflections
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006)	945 independent reflections
	919 reflections with $I > 2\sigma(I)$
$T_{min} = 0.175$, $T_{max} = 0.367$	$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.013$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
$wR(F^2) = 0.022$	$\Delta\rho_{min} = -0.56$ e Å^{-3}
$S = 1.01$	Absolute structure: Flack (1983), 409 Friedel pairs
945 reflections	Flack parameter: -0.017 (12)
38 parameters	
1 restraint	

Table 1
Selected bond lengths (Å).

Ce—S2^i	2.8567 (7)	Ce—S1	3.0465 (7)
Ce—S2	2.8589 (7)	Ce—S2^{vi}	3.1298 (12)
Ce—S3^{ii}	2.8972 (8)	Ge1—S1	2.1671 (14)
Ce—S2^{iii}	2.9720 (12)	Ge1—S3	2.2216 (8)
Ce—S3^{iv}	2.9941 (8)	Mg1—S2	2.655 (3)
Ce—S3^v	3.0351 (8)	Mg1—S2^{iii}	2.650 (3)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2007).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2149).

References

Brandenburg, K. (2005). *DIAMOND*. Release 3.0e. Crystal Impact GbR, Bonn, Germany.

Daszkiewicz, M., Gulay, L. D., Pietraszko, A. & Shemet, V. Ya. (2007*a*). *J. Solid State Chem.* **180**, 2053–2060.

Daszkiewicz, M., Gulay, L. D., Pietraszko, A. & Shemet, V. Ya. (2007*b*). *J. Alloys Compd.* In the press.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Huch, M. R., Gulay, L. D. & Olekseyuk, I. D. (2006). *J. Alloys Compd.* **424**, 114–118.

Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32.6. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Westrip, S. P. (2007). *publCIF*. In preparation.

supplementary materials

$Ce_3Mg_{0.5}GeS_7$ from single-crystal data

L. D. Gulay, M. Daszkiewicz, M. R. Huch and A. Pietraszko

Comment

The formation of the quaternary compound $Ce_3Mg_{0.5}GeS_7$ has been investigated very recently during phase formation studies in the quasi-ternary Ce_2S_3—MgS-GeS_2 system at 870 K, and its crystal structure was originally refined from X-ray powder diffraction data (Huch *et al.*, 2006). To obtain more accurate results we have now re-investigated the structure from single-crystal data.

The unit cell and coordination polyhedra of the Ce, Mg and Ge atoms in the structure of the title compound are shown in Fig. 1. The Ce atoms are surrounded by 8 S atoms which form distorted bi-capped trigonal prisms. The magnesium position is half-occupied and is in the centre of a trigonal antiprism which has 3 symmetry. This position correlates well with the disordered Ag2 position in the structures of $Ln_3Ag_{1-\delta}SnS_7$ (Ln = La, Ce; δ = 0.18–0.19) (Daszkiewicz *et al.*, 2007*a*) and $Ln_3Ag_{1-\delta}SiS_7$ (Ln = La—Nd, Sm; δ = 0.10–0.23) (Daszkiewicz *et al.*, 2007*b*). The Ge atom is situated on a position with 3 symmetry, and is surrounded tetrahedrally by four S atoms with one short and three longer Ge—S bonds.

Experimental

Single crystals of the title compound were grown by fusion of the elemental constituents (Alfa Aesar; purity > 99.9%$_{wt}$) in the stoichiometric ratio of Ce:Ge:Mg:*S* = 3:1:0.5:7 in evacuated silica ampoules. In order to avoid reaction of magnesium with SiO_2, the ampoule was covered with graphite. The ampoule was heated in a tube furnace with a heating rate of 30 K/h to 1420 K and were kept at this temperature for 3 h. It was then cooled down slowly (10 K/h) to 870 K and annealed at this temperature for further 240 h and finally quenched in cold water. The obtained red crystals had a prismatic habit with a maximal length of 0.3 mm.

Refinement

The site occupancy factor for Mg atom was constrained (s.o.f.=0.5) during refinement in order to satisfy the charge balance requirement. Results of single-crystal reinvestigation of $Ce_3Mg_{0.5}GeS_7$ agree well with those reported on the basis of the powder diffraction study (lattice parameters: a = 10.262 (2), c = 7.7849 (7) Å; Huch *et al.*, 2006), but with improved precision on atomic coordinates and interatomic distances.
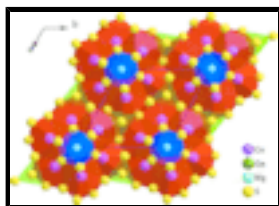
Figures

Fig. 1. The structure of $Ce_3Mg_{0.5}GeS_7$ viewed along the *c* axis.

supplementary materials

tricerium hemimagnesium germanium heptasulfide

Crystal data

$Ce_3Mg_{0.50}GeS_7$	$Z = 2$
$M_r = 729.53$	$F_{000} = 648$
Hexagonal, $P6_3$	$D_x = 4.605$ Mg m^{-3}
Hall symbol: P 6c	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 10.2626$ (15) Å	Cell parameters from 919 reflections
$b = 10.2626$ (15) Å	$\theta = 4.2–29.6º$
$c = 5.7679$ (12) Å	$\mu = 16.91$ mm^{-1}
$\alpha = 90º$	$T = 293$ (2) K
$\beta = 90º$	Prism, red
$\gamma = 120º$	$0.13 \times 0.11 \times 0.08$ mm
$V = 526.09$ (15) Å^3	

Data collection

Kuma KM-4 diffractometer with CCD area detector	945 independent reflections
Radiation source: fine-focus sealed tube	919 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.032$
Detector resolution: 1024x1024 with blocks 2x2, 33.133pixel/mm pixels mm^{-1}	$\theta_{max} = 29.6º$
$T = 293(2)$ K	$\theta_{min} = 4.2º$
ω scans	$h = -14 \rightarrow 13$
Absorption correction: numerical (CrysAlis; Oxford Diffraction, 2006)	$k = -13 \rightarrow 14$
$T_{min} = 0.175$, $T_{max} = 0.367$	$l = -7 \rightarrow 8$
7638 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0105P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.013$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.022$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
$S = 1.01$	$\Delta\rho_{min} = -0.56$ e Å^{-3}
945 reflections	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
38 parameters	Extinction coefficient: 0.0111 (3)
1 restraint	Absolute structure: Flack (1983), 409 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.017 (12)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\mathrm{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Ce	0.357264 (14)	0.231380 (14)	0.23296 (6)	0.00788 (5)	
Ge1	0.6667	0.3333	0.81575 (8)	0.00757 (11)	
Mg1	0.0000	0.0000	0.4694 (10)	0.0089 (6)	0.50
S1	0.6667	0.3333	0.4400 (2)	0.0098 (3)	
S2	0.08688 (7)	0.24688 (7)	0.21849 (17)	0.01013 (12)	
S3	0.52030 (8)	0.10633 (8)	0.96601 (13)	0.00851 (14)	

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce	0.00658 (7)	0.00734 (7)	0.00894 (7)	0.00289 (5)	0.00076 (9)	−0.00015 (10)
Ge1	0.00819 (15)	0.00819 (15)	0.0063 (2)	0.00409 (8)	0.000	0.000
Mg1	0.0063 (7)	0.0063 (7)	0.0141 (16)	0.0031 (4)	0.000	0.000
S1	0.0115 (4)	0.0115 (4)	0.0064 (6)	0.00574 (18)	0.000	0.000
S2	0.0080 (3)	0.0102 (3)	0.0123 (3)	0.0046 (2)	−0.0012 (4)	0.0000 (4)
S3	0.0067 (3)	0.0077 (3)	0.0099 (3)	0.0026 (3)	−0.0008 (3)	0.0004 (3)

Geometric parameters (Å, °)

Ce—S2[i]	2.8567 (7)	Ge1—S3[ix]	2.2216 (8)
Ce—S2	2.8589 (7)	Mg1—S2[x]	2.655 (3)
Ce—S3[ii]	2.8972 (8)	Mg1—S2	2.655 (3)
Ce—S2[iii]	2.9720 (12)	Mg1—S2[i]	2.655 (3)
Ce—S3[iv]	2.9941 (8)	Mg1—S2[iii]	2.650 (3)
Ce—S3[v]	3.0351 (8)	Mg1—S2[xi]	2.650 (3)
Ce—S1	3.0465 (7)	Mg1—S2[xii]	2.650 (3)
Ce—S2[vi]	3.1298 (12)	Mg1—Mg1[xi]	2.8839 (6)
Ce—Mg1	3.498 (2)	Mg1—Mg1[vii]	2.8840 (6)
Ce—Mg1[vii]	3.562 (3)	Mg1—Ce[i]	3.498 (2)
Ge1—S1	2.1671 (14)	Mg1—Ce[x]	3.498 (2)

Ge1—S3^{viii}	2.2216 (8)	Mg1—Ce^{xii}	3.562 (3)
Ge1—S3	2.2216 (8)		
S2^{i}—Ce—S2	84.84 (3)	S2^{xi}—Mg1—Ce^{i}	55.79 (3)
S2^{i}—Ce—S3^{ii}	142.14 (3)	S2^{xii}—Mg1—Ce^{i}	126.72 (3)
S2—Ce—S3^{ii}	108.53 (2)	S2^{x}—Mg1—Ce	124.03 (19)
S2^{i}—Ce—S2^{iii}	77.34 (2)	S2—Mg1—Ce	53.26 (5)
S2—Ce—S2^{iii}	77.31 (2)	S2^{i}—Mg1—Ce	53.21 (5)
S3^{ii}—Ce—S2^{iii}	139.37 (2)	S2^{iii}—Mg1—Ce	55.79 (3)
S2^{i}—Ce—S3^{iv}	73.94 (2)	S2^{xi}—Mg1—Ce	126.72 (3)
S2—Ce—S3^{iv}	140.79 (3)	S2^{xii}—Mg1—Ce	126.77 (3)
S3^{ii}—Ce—S3^{iv}	73.92 (3)	Ce^{i}—Mg1—Ce	105.79 (10)
S2^{iii}—Ce—S3^{iv}	127.211 (19)	S2^{x}—Mg1—Ce^{x}	53.26 (5)
S2^{i}—Ce—S3^{v}	144.09 (2)	S2—Mg1—Ce^{x}	53.21 (5)
S2—Ce—S3^{v}	71.09 (2)	S2^{i}—Mg1—Ce^{x}	124.03 (19)
S3^{ii}—Ce—S3^{v}	72.593 (16)	S2^{iii}—Mg1—Ce^{x}	126.72 (3)
S2^{iii}—Ce—S3^{v}	71.74 (2)	S2^{xi}—Mg1—Ce^{x}	126.77 (3)
S3^{iv}—Ce—S3^{v}	140.464 (19)	S2^{xii}—Mg1—Ce^{x}	55.79 (3)
S2^{i}—Ce—S1	115.164 (15)	Ce^{i}—Mg1—Ce^{x}	105.79 (10)
S2—Ce—S1	150.03 (2)	Ce—Mg1—Ce^{x}	105.79 (10)
S3^{ii}—Ce—S1	70.08 (2)	S2^{x}—Mg1—Ce^{xii}	127.74 (2)
S2^{iii}—Ce—S1	85.33 (3)	S2—Mg1—Ce^{xii}	58.29 (3)
S3^{iv}—Ce—S1	68.84 (2)	S2^{i}—Mg1—Ce^{xii}	127.69 (2)
S3^{v}—Ce—S1	80.388 (17)	S2^{iii}—Mg1—Ce^{xii}	52.29 (5)
S2^{i}—Ce—S2^{vi}	74.81 (2)	S2^{xi}—Mg1—Ce^{xii}	121.89 (19)
S2—Ce—S2^{vi}	74.78 (2)	S2^{xii}—Mg1—Ce^{xii}	52.33 (5)
S3^{ii}—Ce—S2^{vi}	75.01 (2)	Ce^{i}—Mg1—Ce^{xii}	177.67 (17)
S2^{iii}—Ce—S2^{vi}	141.90 (2)	Ce—Mg1—Ce^{xii}	75.523 (7)
S3^{iv}—Ce—S2^{vi}	68.07 (2)	Ce^{x}—Mg1—Ce^{xii}	75.523 (7)
S3^{v}—Ce—S2^{vi}	121.248 (19)	Ge1—S1—Ce^{viii}	113.08 (2)
S1—Ce—S2^{vi}	130.18 (3)	Ge1—S1—Ce^{ix}	113.08 (2)
Mg1—Ce—Mg1^{vii}	48.212 (11)	Ce^{viii}—S1—Ce^{ix}	105.63 (3)
S1—Ge1—S3^{viii}	112.96 (2)	Ge1—S1—Ce	113.08 (2)
S1—Ge1—S3	112.96 (2)	Ce^{viii}—S1—Ce	105.63 (3)
S3^{viii}—Ge1—S3	105.77 (3)	Ce^{ix}—S1—Ce	105.63 (3)
S1—Ge1—S3^{ix}	112.96 (2)	Mg1—S2—Mg1^{vii}	65.87 (2)
S3^{viii}—Ge1—S3^{ix}	105.77 (3)	Mg1—S2—Ce^{x}	78.69 (2)
S3—Ge1—S3^{ix}	105.77 (3)	Mg1^{vii}—S2—Ce^{x}	80.52 (2)
S2^{x}—Mg1—S2	93.12 (15)	Mg1—S2—Ce	78.65 (2)
S2^{x}—Mg1—S2^{i}	93.12 (15)	Mg1^{vii}—S2—Ce	80.48 (2)
S2—Mg1—S2^{i}	93.12 (15)	Ce^{x}—S2—Ce	154.89 (3)
S2^{x}—Mg1—S2^{iii}	179.8 (2)	Mg1—S2—Ce^{v}	142.58 (11)

S2—Mg1—S2^{iii}	86.754 (14)	Mg1^{vii}—S2—Ce^{v}	76.72 (11)
S2^{i}—Mg1—S2^{iii}	86.754 (14)	Ce^{x}—S2—Ce^{v}	95.74 (2)
S2^{x}—Mg1—S2^{xi}	86.754 (14)	Ce—S2—Ce^{v}	95.69 (2)
S2—Mg1—S2^{xi}	179.8 (2)	Mg1—S2—Ce^{xii}	75.51 (11)
S2^{i}—Mg1—S2^{xi}	86.754 (14)	Mg1^{vii}—S2—Ce^{xii}	141.38 (11)
S2^{iii}—Mg1—S2^{xi}	93.37 (15)	Ce^{x}—S2—Ce^{xii}	92.36 (2)
S2^{x}—Mg1—S2^{xii}	86.754 (14)	Ce—S2—Ce^{xii}	92.32 (2)
S2—Mg1—S2^{xii}	86.754 (14)	Ce^{v}—S2—Ce^{xii}	141.90 (2)
S2^{i}—Mg1—S2^{xii}	179.8 (2)	Ge1—S3—Ce^{xiii}	91.41 (3)
S2^{iii}—Mg1—S2^{xii}	93.37 (15)	Ge1—S3—Ce^{xiv}	88.90 (2)
S2^{xi}—Mg1—S2^{xii}	93.37 (15)	Ce^{xiii}—S3—Ce^{xiv}	110.96 (3)
S2^{x}—Mg1—Ce^{i}	53.21 (5)	Ge1—S3—Ce^{iii}	122.24 (3)
S2—Mg1—Ce^{i}	124.03 (19)	Ce^{xiii}—S3—Ce^{iii}	140.35 (3)
S2^{i}—Mg1—Ce^{i}	53.26 (5)	Ce^{xiv}—S3—Ce^{iii}	91.63 (2)
S2^{iii}—Mg1—Ce^{i}	126.77 (3)		

Symmetry codes: (i) −*x*+*y*, −*x*, *z*; (ii) −*x*+*y*+1, −*x*+1, *z*−1; (iii) *y*, −*x*+*y*, *z*+1/2; (iv) *x*, *y*, *z*−1; (v) *x*−*y*, *x*, *z*−1/2; (vi) *y*, −*x*+*y*, *z*−1/2; (vii) −*x*, −*y*, *z*−1/2; (viii) −*y*+1, *x*−*y*, *z*; (ix) −*x*+*y*+1, −*x*+1, *z*; (x) −*y*, *x*−*y*, *z*; (xi) −*x*, −*y*, *z*+1/2; (xii) *x*−*y*, *x*, *z*+1/2; (xiii) −*y*+1, *x*−*y*, *z*+1; (xiv) *x*, *y*, *z*+1.

Fig. 1