Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

$Cs_2Bi_2ZnSe_5$

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Received 19 July 2004
Accepted 28 July 2004
Online 7 August 2004

Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(Se–Zn) = 0.001 Å
R factor = 0.025
wR factor = 0.066
Data-to-parameter ratio = 29.9

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

Dicaesium dibismuth zinc pentaselenide, $Cs_2Bi_2ZnSe_5$, crystallizes in the orthorhombic space group *Pnma* and is isostructural with $Cs_2Bi_2ZnS_5$. The structure consists of two-dimensional $[Bi_2ZnSe_5]$ layers built from $BiSe_6$ octahedra and ZnS_4 tetrahedra. The layers are separated by Cs atoms.

Comment

A number of quaternary bismuth transition-metal chalcogenides have been prepared by the reactive flux method (Sunshine *et al.*, 1987). Examples include ABi_2CuS_4 (A = K and Cs; Yang *et al.*, 2000; Huang *et al.*, 2001), $RbBi_{2.66}CuSe_5$ (Huang *et al.*, 2001), $A_3Bi_5Cu_2S_{10}$ (A = Rb and Cs; Yang *et al.*, 2000; Huang *et al.*, 2001), $CsBiAg_2S_3$ (Huang *et al.*, 2001) and $Cs_2Bi_2MS_5$ (M = Zn, Cd and Mn; Huang *et al.*, 2003). These compounds crystallize in a variety of structure types that include two-dimensional layered structures and three-dimensional tunnel structures. We report here the structure of $Cs_2Bi_2ZnSe_5$, a new member of the bismuth transition-metal chalcogenide family.

$Cs_2Bi_2ZnSe_5$, which has the $Cs_2Bi_2ZnS_5$ structure type (Huang *et al.*, 2003), crystallizes in space group *Pnma* of the orthorhombic system. The atoms in the asymmetric unit (Fig. 1) are all on sites of symmetry *m*. The structure of $Cs_2Bi_2ZnSe_5$ (Fig. 2) comprises two-dimensional $[Bi_2ZnSe_5]$ layers separated by Cs atoms. Each Cs1 atom is coordinated by an octahedron of six Se atoms, whereas each Cs2 atom is coordinated by a monocapped trigonal prism of seven Se atoms. The Cs—Se separations range from 3.5060 (9) to 3.6777 (8) Å, comparable with those of 3.586 (1)–3.8387 (9) Å in $CsYbZnSe_3$ (Mitchell *et al.*, 2002). Each Bi1 atom is coordinated by a slightly distorted octahedron of six Se atoms, with Bi1—Se bond distances ranging from 2.8523 (8) to 3.0488 (9) Å. Each Bi2 atom is coordinated by a more severely distorted octahedron of six Se atoms, with Bi2—Se bond lengths ranging from 2.7418 (8) to 3.3416 (9) Å. Similar

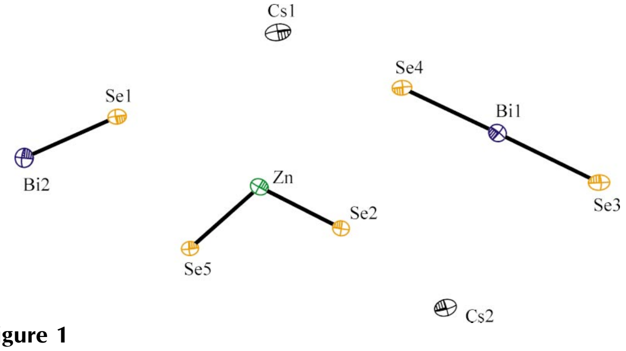

Figure 1
A view of the asymmetric unit of $Cs_2Bi_2ZnSe_5$, with displacement ellipsoids drawn at the 90% probability level.

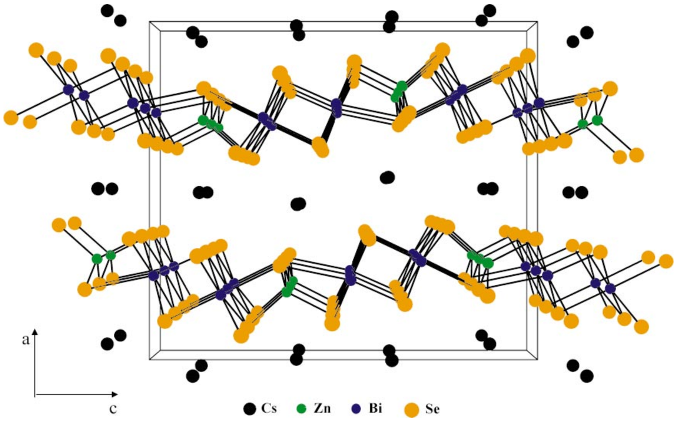

Figure 2
The structure of $Cs_2Bi_2ZnSe_5$, viewed down [010].

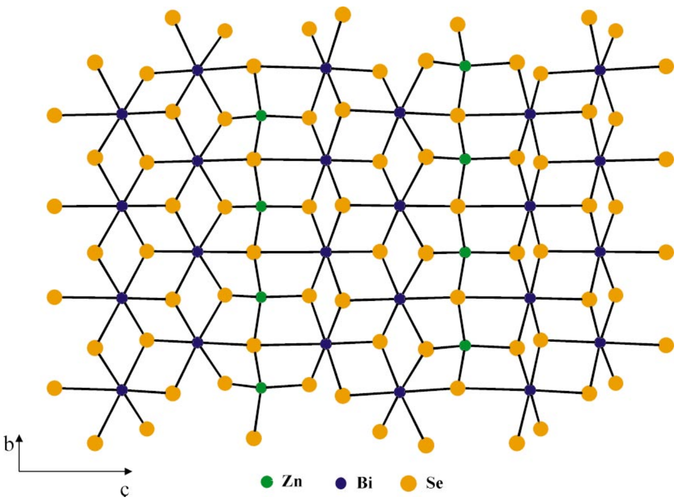

Figure 3
The structure of the two-dimensional $[Bi_2ZnSe_5]$ layer in $Cs_2Bi_2ZnSe_5$.

coordination geometries, which result from the stereochemical activity of the $6s^2$ lone pair of electrons of Bi^{3+}, have often been observed in bismuth chalcogenides, for example in $BaBi_2Se_4$ (Iordanidis *et al.*, 2001) and $CsBi_3Se_5$ (Iordanidis *et al.*, 2003). Each Zn atom is coordinated by a tetrahedron of four Se atoms, with Zn—Se distances ranging from 2.471 (1) to 2.5254 (6) Å, similar to those of 2.434 (1)–2.529 (1) Å in $CsYbZnSe_3$ (Mitchell *et al.*, 2002).

The two-dimensional $[Bi_2ZnSe_5]$ layer is constructed from $BiSe_6$ octahedra and $ZnSe_4$ tetrahedra (Fig. 3). The octahedra share corners and vertices to form a two-dimensional $[Bi_2Se_5]$ layer. These layers of octahedra are slightly buckled, giving rise to tetrahedral sites that are occupied by Zn atoms. Each $ZnSe_4$ tetrahedron links with four $BiSe_6$ octahedra by edge-sharing to form the two-dimensional $[Bi_2ZnSe_5]$ layer.

Experimental

$Cs_2Bi_2ZnSe_5$ was obtained as black needles from a solid-state reaction of Cs_2Se_3 (0.6 mmol), Bi (Johnson Matthey, 99.99%, 1.0 mmol), Zn (Johnson Matthey, 99.99%, 0.5 mmol) and Se (Aldrich, 99.5%, 1.0 mmol). The Cs_2Se_3 reactive flux was prepared by the stoichiometric reaction of Cs (Aldrich, 99.5%) and Se in liquid NH_3. The reactants were loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was sealed under a 10^{-4} Torr atmosphere (1 Torr = 133.322 Pa) and then placed in a computer-controlled furnace. The sample was heated to 973 K over a period of 25 h, kept at 973 K for 84 h, slowly cooled at 6 K h^{-1} to 373 K and then cooled rapidly to room temperature.

Crystal data

$Cs_2Bi_2ZnSe_5$
$M_r = 1143.95$
Orthorhombic, *Pnma*
$a = 16.374$ (2) Å
$b = 4.2382$ (5) Å
$c = 18.780$ (2) Å
$V = 1303.2$ (3) $Å^3$
$Z = 4$
$D_x = 5.830$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5155 reflections
$\theta = 1.7$–28.9°
$\mu = 48.18$ mm^{-1}
$T = 153$ (2) K
Needle, black
0.42 × 0.050 × 0.026 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: numerical face indexed (*SHELXTL*; Sheldrick, 2003)
$T_{min} = 0.022$, $T_{max} = 0.298$
15 257 measured reflections
1853 independent reflections
1729 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 28.9°$
$h = -21 \rightarrow 21$
$k = -5 \rightarrow 5$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.066$
$S = 1.15$
1853 reflections
62 parameters
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.93$ e $Å^{-3}$
$\Delta\rho_{min} = -2.38$ e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00038 (5)

Table 1
Selected geometric parameters (Å, °).

Bi1—Se4	2.8523 (8)	$Bi2—Se4^{ii}$	3.0129 (6)
$Bi1—Se5^{i}$	2.9189 (6)	$Bi2—Se3^{iii}$	3.3416 (9)
$Bi1—Se1^{i}$	2.9614 (6)	Zn—Se2	2.4710 (12)
Bi1—Se3	3.0488 (9)	Zn—Se5	2.5035 (12)
Bi2—Se1	2.7418 (8)	$Zn—Se3^{ii}$	2.5254 (6)
$Bi2—Se2^{ii}$	2.9114 (6)		
$Se4—Bi1—Se5^{i}$	95.323 (19)	$Se1—Bi2—Se4^{ii}$	91.44 (2)
$Se5^{i}—Bi1—Se5^{iv}$	93.10 (2)	$Se2^{ii}—Bi2—Se4^{ii}$	88.554 (17)
$Se4—Bi1—Se1^{i}$	90.36 (2)	$Se2^{v}—Bi2—Se4^{ii}$	177.022 (19)
$Se5^{i}—Bi1—Se1^{i}$	87.472 (17)	$Se4^{v}—Bi2—Se4^{ii}$	89.39 (2)
$Se5^{iv}—Bi1—Se1^{i}$	174.21 (2)	$Se1—Bi2—Se3^{iii}$	167.58 (2)
$Se1^{iv}—Bi1—Se1^{i}$	91.38 (2)	$Se2^{ii}—Bi2—Se3^{iii}$	80.765 (18)
Se4—Bi1—Se3	179.34 (2)	$Se4^{ii}—Bi2—Se3^{iii}$	97.366 (18)
$Se5^{i}—Bi1—Se3$	85.129 (19)	Se2—Zn—Se5	111.37 (4)
$Se1^{i}—Bi1—Se3$	89.181 (19)	$Se2—Zn—Se3^{ii}$	108.87 (3)
$Se1—Bi2—Se2^{ii}$	90.77 (2)	$Se5—Zn—Se3^{ii}$	106.82 (3)
$Se2^{ii}—Bi2—Se2^{v}$	93.42 (2)	$Se3^{ii}—Zn—Se3^{v}$	114.10 (4)

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

The highest residual electron density is 0.02 Å from the Bi1 site. The deepest hole is 0.81 Å from this same site.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This research was supported by the MRSEC program of the US National Science Foundation (DMR00-76097) at the Materials Research Center of Northwestern University.

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