Crystal structure of bismuth selenite, $Bi_2(SeO_3)_3$

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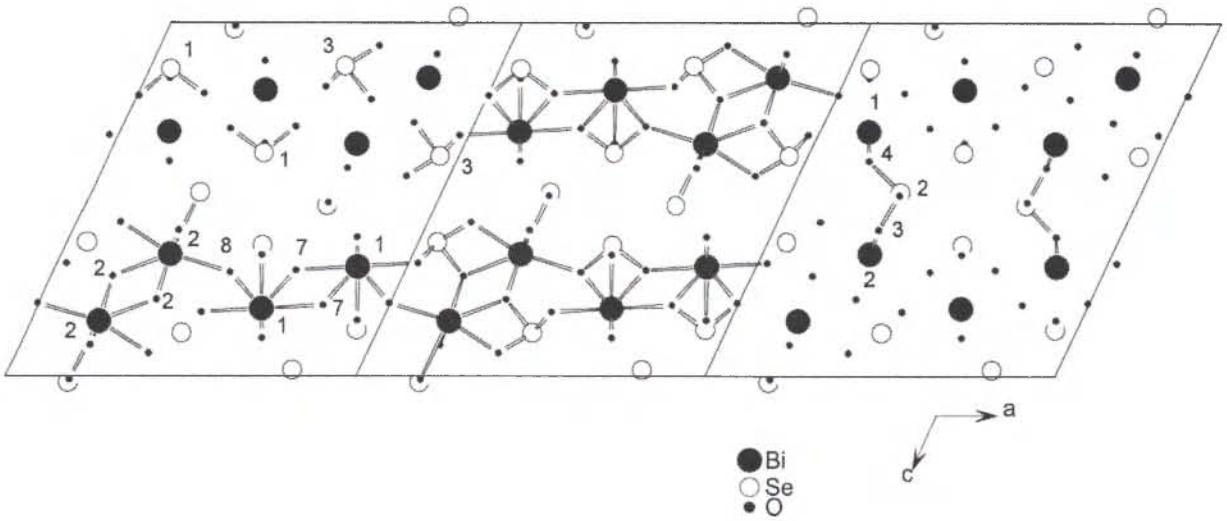

Abstract

$Bi_2O_9Se_3$, monoclinic, $P12_1/n1$ (No. 14), a = 13.491(1) Å, b = 4.675 Å, c = 14.961(1) Å, β = 115.164(4)°, V = 854.1 Å^3, Z = 4, $R(F)$ = 0.039, $wR_{ref}(F^2)$ = 0.095, T = 293 K.

Source of material

The title compound is one of six at room temperature thermodynamically stable phases on the quasibinary line Bi_2O_3-SeO_2. The thermical decomposition gives solid Bi_2SeO_5 and gaseous SeO_2 in the measureable region from 623 K to 773 K [1]. $Bi_2Se_3O_9$ decomposes peritectical in solid Bi_2SeO_5 and SeO_2-rich melt at 853 K ± 5 K. The decomposition pressure arises at this point 3 atm. $Bi_2Se_3O_9$ coexist in the O-poorer region with $Bi_2SeO_{5,s}$ + Se_l at the one side and $Bi_2Se_4O_{11,s}$ and Se_l on the other side [2-4]. Phase pure $Bi_2Se_3O_9$ were obtained by sintering of stoichiometric mixtures of Bi_2O_3 and SeO_2 at 623 K. Single crystals are prepared by chemical transport reaction with $BiBr_3$ or Br_2. Phase pure $Bi_2Se_3O_9$ was closed in evacuated quarz tubes with some mg $BiBr_3$ or Br_2 and transported in a temperature gradient from 773 K to 673 K. The transport rate in ampouls of 15 cm length and 1.5 cm diameter arises 0.1 mg/h. The crystals are clear prisms of 1-2 mm length. We understud the transport simultanously to the above thermal decomposition via:

$Bi_2Se_3O_{9,s} + Br_{2,g} = 2BiSeO_3Br_g + SeO_{2,g} + 1/2O_{2,g}$ (1)

and

$Bi_2Se_3O_{9,s} + BiBr_{3,g} = 3BiSeO_3Br_g$. (2)

For the existence of gaseous $BiSeO_3Br$ see [5].

Discussion

The structure of $Bi_2Se_3O_9$ include two distorted, slightly different octahedra $[Bi(1)O_6]^{9-}$ and $[Bi(2)O_6]^{9-}$ (bond lengths 2.247Å to 2.516 Å and 2.257 Å to 2.563 Å, respectively) as well as the trigonal-pyramidal units $[Se(1)O_3]^{2-}$, $[Se(2)O_3]^{2-}$ and $[Se(3)O_3]^{2-}$. Oxygen atoms linked by eddgesthe $[Bi(1)O_6]^{9-}$ polyhedra (O(7)) and the $[Bi(2)O_6]^{9-}$ polyhedra (O(2)) to chains along b-axis direction. Both chains are corner-linked over O(8) in direction of a-axis and form Bi-O double layers $[Bi_2O_9]^{12-}$ along the a-b plane (see figure, left part, down). These layers include the both polyhedra $[Se(1)O_3]^{2-}$ and $[Se(3)O_3]^{2-}$ (figure, left part, up) and generated the $^2_\infty[Bi_2Se_2O_9]^{4-}$ layers as the characteristical layer unit of the $Bi_2(SeO_3)_3$ structure (see figure, middle part). Between these $^2_\infty[Bi_2Se_2O_9]^{4-}$ layers enclosed a week $[Se(2)O_3]^{2-}$ layer, bonded to the main layers over Bi(1)-O(4)-Se(2)-O(3)-Bi(2) (right part in the figure).

Table 1. Data collection and handling.

Crystal:	colourless, clear prism, size 0.04 × 0.07 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	521.81 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω/2θ
$2\theta_{max}$:	55.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4266, 2057
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1763
$N(param)_{refined}$:	128
Programs:	SHELXS-97 [6], SHELXL-97 [7], DIAMOND [8]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	4*e*	0.64092(3)	0.13774(8)	0.80963(3)	0.0116(2)	0.0161(2)	0.0231(2)	0.0004(1)	0.0082(2)	0.0001(1)
Bi(2)	4*e*	0.80771(3)	0.13518(7)	0.15550(3)	0.0122(2)	0.0156(2)	0.0212(2)	0.0002(1)	0.0096(2)	0.0003(1)
Se(1)	4*e*	0.93979(8)	0.0942(2)	0.86907(7)	0.0111(5)	0.0156(4)	0.0202(4)	0.0008(4)	0.0074(4)	0.0003(3)
Se(2)	4*e*	0.68934(8)	0.1173(2)	0.51830(7)	0.0127(5)	0.0159(5)	0.0207(4)	0.0012(4)	0.0085(4)	0.0001(3)
Se(3)	4*e*	0.55426(8)	0.2142(2)	0.12201(7)	0.0107(5)	0.0199(5)	0.0246(5)	0.0003(4)	0.0101(4)	0.0002(4)
O(1)	4*e*	0.4295(7)	0.052(2)	0.3426(5)	0.021(4)	0.019(3)	0.026(3)	–0.002(3)	0.008(3)	–0.002(3)
O(2)	4*e*	0.1728(6)	0.153(2)	0.7170(5)	0.013(4)	0.027(4)	0.025(3)	0.003(3)	0.010(3)	0.006(3)
O(3)	4*e*	0.6991(7)	0.197(2)	0.4119(5)	0.024(4)	0.021(4)	0.027(3)	0.000(3)	0.012(3)	0.002(3)
O(4)	4*e*	0.8188(6)	0.169(2)	0.6072(6)	0.013(4)	0.023(4)	0.030(4)	0.001(3)	0.004(3)	0.000(3)
O(5)	4*e*	0.4739(7)	0.059(2)	0.8193(6)	0.026(4)	0.029(4)	0.032(4)	0.000(4)	0.019(3)	0.004(3)
O(6)	4*e*	0.6232(6)	0.051(2)	0.0652(5)	0.014(4)	0.040(4)	0.023(3)	–0.007(3)	0.012(3)	–0.012(3)
O(7)	4*e*	0.1883(6)	0.035(2)	0.2001(5)	0.010(3)	0.018(3)	0.028(3)	0.002(3)	0.011(3)	–0.002(3)
O(8)	4*e*	0.0041(6)	0.031(2)	0.2064(5)	0.010(3)	0.026(4)	0.031(3)	0.001(3)	0.011(3)	–0.004(3)
O(9)	4*e*	0.3110(6)	0.246(2)	0.4903(5)	0.023(4)	0.016(3)	0.022(3)	0.000(3)	0.009(3)	0.003(3)

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