Refinement of the crystal structure of arsenolite, As_2O_3

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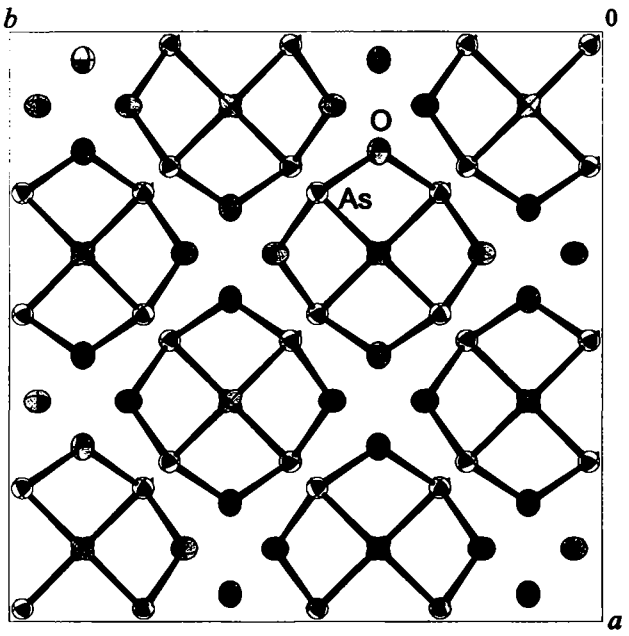

Abstract

As_2O_3, cubic, $Fd\bar{3}m$ (No. 227), $a = 11.07343(5)$ Å, $V = 1357.8$ Å^3, $Z = 16$, $R(P) = 0.056$, $wR(P) = 0.073$, $R(I) = 0.068$, $T = 295$ K.

Source of material

A white powder of the title compound was obtained by oxidation of realgar (As_4S_4). A crystal of realgar from M.te Sughereto, Latium, Italy has been crushed into an agate mortar. An open quartz-glass capillary was filled with the resulting red-ruby powder and inserted into an electric oven at 568 K. The sample was kept at this temperature for a week.

Experimental details

The capillary was mounted on a goniometer head and fitted in a Siemens D5005 automatic powder diffractometer operating in transmission geometry. The instrument has Goebel mirrors along the incident beam providing a X-ray parallel beam.

Starting positional parameters were those of [1] after origin redefinition ($Fd\bar{3}m$, origin choice 2). Background was fitted with a Chebyshev polynomial, peak shape by a pseudo-Voigt modified to incorporate asymmetry [2]. Absorption was modelled by means of the empirical formula [3]. The presence of preferred orientation effects was checked [4].

Discussion

The structure of arsenolite, the cubic As_2O_3 polymorph ($Fd\bar{3}m$, a = 11.074 Å), has been determined by Bozorth [5] and subsequently confirmed in [1,6,7]. The best available structural data of arsenolite [1], however, report strongly negative displacement parameters of As.

The structure of arsenolite may be described by As_4O_6 cages built up by AsO_3 ψ-tetrahedra linked via bridging oxygens. The As—O bond distance is of 1.786(2) Å, the O–As–O and As–O–As bond angles are of 98.4(2)° and 128.7(3)°, respectively. These values compares favourably with reference data (1.787 Å, 98.3°, and 128.8° [1]). Anisotropic thermal parameters of both As and O are similar to those reported for senarmontite, Sb_2O_3 [8].

Table 1. Data collection and handling.

Powder:	white
Wavelength:	Cu K_α radiation (1.54059 Å)
μ:	229.82 cm^{-1}
Diffractometer, scan mode:	Siemens D5005, transmission
$2\theta_{max}$, stepwidth:	150°, 0.02°
$N(points)_{measured}$:	7000
$N(hkl)_{measured}$:	175
$N(param)_{refined}$:	59
Program:	GSAS [9]

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}
As	32*e*	0.77221(5)	x	x	0.0169(3)	U_{11}	U_{11}	0.0003(3)	U_{12}	U_{12}
O	48*f*	0.9524(4)	1/8	1/8	0.027(3)	0.020(2)	U_{22}	0	0	0.010(2)

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