

## Refinement of pucherite, $\text{BiVO}_4$

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**Abstract.** Pucherite,  $\text{BiVO}_4$ , from Schneeberg, Saxony, is orthorhombic, space group *Pnca*, with  $a = 5.328(2)$ ,  $b = 5.052(2)$ ,  $c = 12.003(3)$  Å at 291 K,  $Z = 4$ ,  $D_x = 6.69$  g cm<sup>-3</sup>. The crystal structure of pucherite has been refined from single-crystal X-ray diffraction data to  $R_w = 0.020$  for 221 unique reflections measured with  $\text{AgK}\alpha$  radiation. The structure consists of  $\text{VO}_4$  tetrahedra and  $\text{BiO}_8$  triangulated dodecahedra. Each dodecahedron shares one edge with a tetrahedron and two edges with neighbouring dodecahedra.

### Introduction

The structure of pucherite was determined by Qurashi and Barnes (1952, 1953), using visually estimated intensities for the three principal zones and Buerger precession photographs for data collection. In their attempts to synthesize pucherite Roth and Waring (1963) obtained a single phase which proved to be a monoclinic form of  $\text{BiVO}_4$ , isostructural with fergusonite. At 528 K this fergusonite type structure undergoes a ferroelastic phase transition to a tetragonal structure of the scheelite type. In contrast to pucherite both these structures (ferroelastic and paraelastic) have been refined from precise diffraction data (David et al., 1979; Sleight et al., 1979).

It has been suggested (Roth and Waring, 1963) that perhaps pucherite is not a stable phase in the system  $\text{Bi}_2\text{O}_3 - \text{V}_2\text{O}_5$ . In order to compare pucherite with the fergusonite type structure of  $\text{BiVO}_4$  and to throw some light on the formation of pucherite, a more accurate structure refinement of pucherite is of considerable interest: the results of such a study are reported herein.

### Experimental

A natural specimen of pucherite, from the original locality of Pucher Shaft, Wolfgang Mine, Schneeberg, Saxony, was obtained from Dr. M. Hänisch

of the Mineralogical Museum, Hamburg. A single-crystal was prepared and mounted along the  $b$ -axis. The crystal selected is a fragment  $0.046 \times 0.083 \times 0.056$  mm in size. Weissenberg photographs were taken with Ni-filtered  $\text{CuK}\alpha$  radiation. The results of the Weissenberg study showed no evidence of twinning or polycrystalline intergrowth. Space group  $Pnca$  was confirmed.

1301 intensity data were measured by the  $\omega$ - $2\theta$  technique. In the range  $4^\circ < 2\theta < 42^\circ$  all reflections in one hemisphere of reciprocal space ( $-6 \leq h \leq 6$ ,  $0 \leq k \leq 6$ ,  $-14 \leq l \leq 14$ ) were collected using a Enraf-Nonius CAD-4 diffractometer with graphite-monochromated  $\text{AgK}\alpha$  radiation ( $0.5608 \text{ \AA}$ ). Lorentz, polarization and absorption corrections [ $\mu(\text{AgK}\alpha) = 309.5 \text{ cm}^{-1}$ ] were applied, and equivalent reflections averaged to give 221 independent values with  $I > 3\sigma(I)$  which were used for all calculations. Cell parameters were determined by a least-squares calculation on 25 reflections in the range  $15^\circ < 2\theta < 39^\circ$  that were individually centered.

A microprobe analysis showed that the specimen consists of  $\text{BiVO}_4$  with a small amount of As. Moreover, the distribution of As indicates a zoning of the crystal. Unfortunately we could not quantify the fraction of As.

## Refinement

The structure of pucherite was refined by full-matrix least-squares calculations using the computer program ORFLS3. The atomic positional parameters of Qurashi and Barnes (1953) were used as starting parameters for the initial cycle. Refinement with anisotropic temperature factors gave  $R = 0.016$  and  $R_w = 0.020$ . Arsenic was allowed to substitute for vanadium. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where weights  $w = 1/\sigma^2(F_o)$  were from counting statistics. Scattering curves for  $\text{Bi}^{3+}$ ,  $\text{V}^{5+}$  and  $\text{As}^{5+}$ , and anomalous dispersion terms, were taken from International Tables for X-ray Crystallography (Ibers and Hamilton, 1974). The scattering curve for  $\text{O}^{2-}$  was obtained from Tokonami (1965). After several cycles the refinement converged. A final difference map was calculated with the program SHELX-76. Maximum and minimum height of difference electron density is  $1 \text{ e\AA}^{-3}$  and  $-1 \text{ e\AA}^{-3}$ , respectively. These large values can be attributed to truncation errors and inaccurate absorption corrections. The former are due to the limit of  $0.64 \text{ \AA}^{-1}$  for  $\sin\theta/\lambda$  whereas the latter result from the margins of error connected with the determination of the crystal shape. Final atomic coordinates and anisotropic temperature factors are presented in Table 1<sup>1</sup>.

<sup>1</sup> Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 50753, the names of the authors and the title of the paper

**Table 1.** Fractional coordinates and anisotropic temperature factors ( $\beta \times 100 \text{ \AA}^2$ ) defined as  $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2kl\beta_{23})]$  with e.s.d.'s in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Bi	1/4	0	0.10960(3)	0.89(2)	0.70(2)	0.150(3)	-0.09(6)	—	—
V	1/4	0	0.3938(1)	0.91(8)	0.58(9)	0.14(1)	0.1(3)	—	—
O(1)	0.083(1)	0.258(1)	0.4664(6)	0.6(2)	1.0(2)	0.27(4)	0.4(2)	-0.13(9)	-0.3(1)
O(2)	0.458(1)	0.143(1)	0.3077(5)	1.0(2)	1.3(3)	0.16(4)	0.0(2)	0.09(7)	0.0(1)

### Discussion

The structure of pucherite shows  $\text{VO}_4$  tetrahedra and  $\text{BiO}_8$  dodecahedra with triangular faces. These polyhedra both exhibit point symmetry 2.

The  $\text{VO}_4$  tetrahedron is slightly distorted with two pairs of bond lengths: 1.679(6) and 1.803(7) Å. These values are in good agreement with the distances of 1.670, 1.792 and 1.69, 1.77 Å reported by David et al. (1979) and Sleight et al. (1979), respectively, for the fergusonite type structure of  $\text{BiVO}_4$ . However, the angle between the long pair bonds amounts to the value of 122.2(5) which considerably exceeds the corresponding value of 114.8° for the fergusonite type structure.

The ideal triangulated dodecahedron shows point symmetry  $\bar{4}2m$ . According to the Hoard and Silverton (1963) the vertices of this dodecahedron can be labelled A and B. At vertex A four edges intersect, whereas vertex B has five intersecting edges. Despite its lowered symmetry the  $\text{BiO}_8$  dodecahedron in pucherite exhibits vertices A and B. Atoms O(1) and O(2) both occupy two of the sites A and B. The arrangement of the oxygens is shown in Figure 1, together with the oxygen – oxygen distances. In Table 2 the oxygen bond lengths are compared with those of fergusonite and scheelite type  $\text{BiVO}_4$ . The agreement between corresponding values is fairly good.

Peculiar to pucherite is that the  $\text{VO}_4$  tetrahedron shares one edge with the  $\text{BiO}_8$  triangulated dodecahedron. The lengths of the common edge is

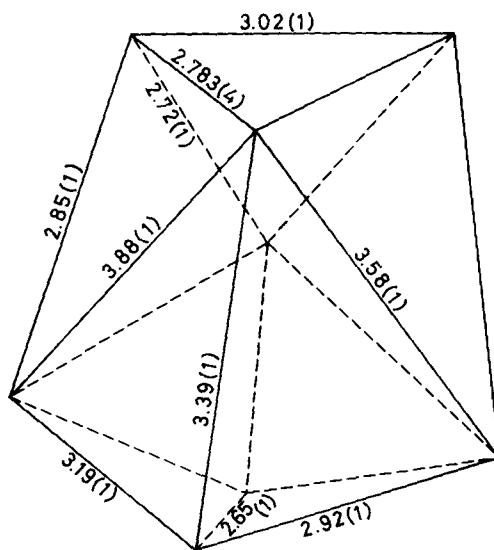


Fig. 1. The coordination of  $\text{Bi}^{3+}$  with oxygen – oxygen distances in Å and e.s.d.'s. The four atoms O(1) are situated on the vertices in the upper half whereas the four atoms O(2) are in the lower half

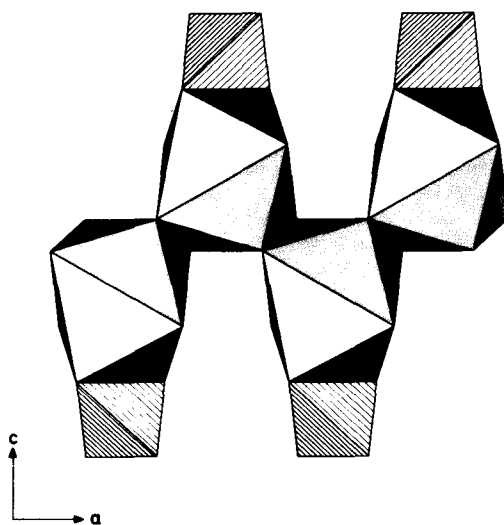
2.65(1) Å with Bi–O and V–O distances of 2.721(6) and 1.803(7) Å, respectively. In addition, the dodecahedron shares edges with two neighbouring dodecahedra forming infinite chains along [100], see Figure 2. Along these edges the O–O separation is 2.72(1) Å with Bi–O bond lengths of 2.289(6) and 2.340(6) Å. The  $\text{BiO}_8$  dodecahedra also share corners with tetrahedra and dodecahedra whereas there is no linkage between tetrahedra.

Comparison of the structure of pucherite with fergusonite and scheelite type  $\text{BiVO}_4$  shows that these structures are very similar in so far as all of them consist of  $\text{VO}_4$  tetrahedra and  $\text{BiO}_8$  dodecahedra. Regarding the connection between the polyhedra pucherite differs from the other types. Whereas the

**Table 2.** Comparison of bismuth–oxygen bond lengths between pucherite and fergusonite and scheelite type  $\text{BiVO}_4$

vertex oxygen	bond length (Å)					
	pucherite			scheelite type <sup>a</sup>		
B O(1)	2.340(6)	2.3789	2.372	}	2.448	2.453
B O(2)	2.580(6)	2.5020	2.516			
A O(1)	2.289(6)	2.3431	2.354	}	2.497	2.499
A O(2)	2.721(6)	2.6404	2.628			

<sup>a</sup> values from David et al. (left column) and Sleight et al. (right column)



**Fig. 2.** Chain of edge-sharing  $\text{BiO}_8$  triangulated dodecahedra and  $\text{VO}_4$  tetrahedra projected along [010]

dodecahedron in pucherite shares two edges with two other dodecahedra and one edge with a tetrahedron each dodecahedron in the fergusonite or scheelite structure shares four edges with neighbouring dodecahedra and no edges with any tetrahedron.

When heated in a high-temperature powder chamber pucherite converted to scheelite type  $\text{BiVO}_4$ . At 698 K the pattern showed the pucherite and scheelite structure plus a few unidentified lines. When after 4 hours at 698 K the temperature was raised to 773 K the pucherite structure was completely destroyed whereas increased intensities were observed for both the scheelite type structure and the unidentified lines. On cooling the tetragonal scheelite structure changed to the monoclinic fergusonite type.

However, for the transformation of pucherite to tetragonal  $\text{BiVO}_4$  a definite transition temperature could not be determined as different specimens of pucherite converted to scheelite type  $\text{BiVO}_4$  at various temperatures. This behaviour supports the suggestion of Roth and Waring (1963) that perhaps pucherite is stabilized in nature by the presence of minor amounts of impurities. The results of our microprobe analysis and structure refinement suggest that arsenic may be of great importance in the formation of pucherite. According to our structure refinement about 6 per cent of vanadium have been replaced by arsenic. This value is around 3 times the size of the standard deviation.

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