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Synthesis and Structure of $BiMnVO_5$ and $BiMnAsO_5$

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The isostructural compounds $BiMnVO_5$ and $BiMnAsO_5$ have been prepared for the first time. Their structures were determined from single-crystal X-ray diffraction data in space group $P\bar{1}$ with $Z = 2$. For the vanadate $a = 6.912(4)$ Å, $b = 6.991(2)$ Å, $c = 5.354(1)$ Å, $\alpha = 108.55(2)^\circ$, $\beta = 95.98(4)^\circ$ and $r = 109.73(4)^\circ$. For the arsenate $a = 6.868(1)$ Å, $b = 6.905(2)$ Å, $c = 5.360(1)$ Å, $\alpha = 109.47(2)^\circ$, $\beta = 95.91(2)^\circ$, and $\gamma = 109.32(2)^\circ$. The structures are based on MnO_6 octahedra sharing one edge to form Mn_2O_{10} groups, Bi_2O_8 groups, and MO_4 tetrahedra with $M =$ As or V. The same moieties are found in the $BiMnPO_5$ structure, which has monoclinic symmetry. However, the triclinic structures for $BiMnVO_5$ and $BiMnAsO_5$ cannot be regarded as distorted versions of the monoclinic $BiMnPO_5$ structure because the connectivity of the moieties is distinctly different. © 2002 Elsevier Science (USA)

Key Words: **bismuth manganese vanadate; bismuth manganese arsenate; crystal structures.**

INTRODUCTION

Oxides containing Bi(III) have been of interest as oxygen ion conductors, bright yellow pigments, selective oxidation, catalysts, ferroelectrics, ferroelastics, and superconductors. We have been expanding the number of oxides containing Bi(III) by exploring those that contain a divalent and pentavalent cation in addition to Bi(III). This has led to the discovery of $BiSr_2V_3O_{11}$, $BiMg_2VO_6$, $BiMg_2PO_6$, $BiMg_2AsO_6$, $BiCa_4V_3O_{23}$, $BiBa_2V_3O_{11}$, $BiBa_2V_2PO_{11}$, $BiCa_2VO_6$, $BiCu_2AsO_6$, $BiCu_2VO_6$, $BiCa_2AsO_6$, $BiCdVO_5$, $BiCd_2VO_6$, $Bi_2CaV_2O_9$, $Bi_3Ca_9V_{11}O_{41}$, $BiCa_9V_7O_{28}$, $BiMg_{2.5}V_{18.5}O_{38}$, and $Bi_{1-2x}A_{2x}VO_{4-x}$ where $A =$ Ca, Cd, or Sr (1–16). All of these compounds were prepared in air. Interesting properties such as a nonlinear optical response (13, 14, 16), ferroelectricity (6) and high oxygen ion conductivity (17) were found in some of these new compounds. Recently, we have reported the synthesis of $BiMn_2PO_6$, $BiMn_2VO_6$, $BiMn_2AsO_6$, and $BiMnPO_5$ (18, 19). Here we report on $BiMnVO_5$ and $BiMnAsO_5$. All these Mn(II) oxides are prepared under vacuum or inert gas.

EXPERIMENTAL

Reactants were Bi_2O_3 (99.9%, CERAC), MnO (99.9%, CERAC), As_2O_5 (99.9%, Alfa), and V_2O_5 (99.9%, Johnson Matthey). Appropriate quantities of reactants were intimately mixed by grinding together in an agate mortar. For preparation of polycrystalline $BiMnVO_5$, reactants with a 1 : 1 : 1 ratio were sealed in an evacuated silica ampoule and heated at 700°C for 30 h, and then quenched to room temperature. A pellet of $BiMnVO_5$ was placed in an alumina boat, sealed in an evacuated silica ampoule, heated at 775°C for 12 h, and cooled to 500°C at 0.03°C per minute. Block-like, orange crystals of $BiMnVO_5$ were obtained. This color is very similar to that of $BiVO_4$ and is due to a charge transfer transition, O 2*p*/Bi 6*s* to V 3*d*. For the preparation of polycrystalline $BiMnAsO_5$, the reactants with a 1:1:1 ratio were sealed in an evacuated silica ampoule and heated at 800°C for 30 h and quenched. A small amount of $BiMnAsO_5$ sample was sealed in an evacuated silica ampoule, heated at 875°C for 12 h, and cooled to 550°C at a rate of 0.03°C per minute. Block-like, colorless crystals of $BiMnAsO_5$ were obtained.

X-ray diffraction powder patterns of the products were obtained on a Siemens D5000 diffractometer using Cu*K*α radiation. Single-crystal X-ray diffraction data were obtained at room temperature on a Rigaku AFC6R diffractometer with monochromatic Mo*K*α radiation ($\lambda = 0.71069$ Å). No decay in intensity was noted during data collections. The observed intensities were corrected for Lorentz, polarization and absorption. Data reduction was carried out using a local program, capable of creating a data file containing the crystal-dependent direction cosines of the diffracted and reverse incident beam, for purposes of correction of absorption anisotropy effects. Correction for the effects of absorption anisotropy was carried out using the program SORTAV, as programmed in the software collection WinGX v1.64.02 (20). Structure

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solution was carried out using Patterson map interpretation as programmed in SHELXS-90 (21), and refined using full-matrix least-squares refinement on F^2 using the program SHELXL-97 (22).

RESULTS

Crystal data and refinement summaries are given for BiMnVO$_5$ and BiMnAsO$_5$ in Table 1. Final atomic coordinates, isotropic displacement parameters, and bond valences (23) are in Table 2 for both compounds. Anistropic displacement parameters are in Table 3. Bond distances and angles are in Table 4. The Mn$_2$O$_{10}$ and Bi$_2$O$_8$ units are shown in Figs. 1 and 2. Each of the units in Figs. 1 and 2 is connected to a tetrahedron in Fig. 3. The extended connectivity is shown in Fig. 4. The X-ray diffraction powder patterns calculated based on these structures closely matched our observed powder patterns.

TABLE 1
Crystal Data and Structure Refinement for BiMnVO$_5$ and BiMnAsO$_5$

Empirical formula	BiMnVO$_5$	BiMnAsVO$_5$
Formula weight	394.86	418.84
Temperature	290(2) K	290(2) K
Wavelength	0.71073 Å	0.71073 Å
Space group	$P\bar{1}$	$P\bar{1}$
a	6.912(4) Å	6.868(1) Å
b	6.991(2) Å	6.905(2) Å
c	5.354(1) Å	5.360(1) Å
α	108.55(2)°	109.47(2)°
β	95.98(4)°	95.91(2)°
γ	109.73(4)°	109.32(2)°
Volume	224.3(2) Å^3	219.57(8) Å^3
Z	2	2
Density (calculated)	5.846 Mg/m^3	6.335 Mg/m^3
Absorption coefficient	43.854 mm^{-1}	50.283 mm^{-1}
F(000)	342	362
Crystal size	0.10 × 0.10 × 0.10 mm^3	0.10 × 0.10 × 0.10 mm^3
Theta range for data collection	3.22–27.56°	3.24–27.53°
Index ranges	$-1\le h\le 8, -9\le k\le 8, -6\le l\le 6$	$-8\le h\le 8, -8\le k\le 8, -1\le l\le 6$
Reflections collected	1272	1310
Independent reflections	1020 [R(int) = 0.0364]	994 [R(int) = 0.0352]
Completeness to theta = 27.53°	99.6%	99.7%
Absorption correction	Semi-empirical	
Max. and min. transmission	0.5311 and 0.0795	0.6628 and 0.1929
Refinement method	Full-matrix least squares on F^2	
Data/restraints/parameters	1020/12/74	994/0/73
Goodness-of-fit on F^2	1.069	1.141
Final R indices [$I > 2$sigma(I)]		
$R1$/w$R2$	0.0374/0.0943	0.0358/0.0895
R indices (all data)		
$R1$/w$R2$	0.0430/0.0968	0.0366/0.0899
Largest diff. peak and hole	2.466 and −2.655 e.Å^{-3}	2.471 and −3.516 e.Å^{-3}

TABLE 2
Atom Positions and Isotropic Displacement Factors for BiMnVO$_5$ and BiMnAsO$_5$[a]

	x	y	z	U(eq)[b]	BV sum
Bi	0.2431(1)	0.4681(1)	0.9074(1)	7(1)	3.164
	0.2441(1)	**0.4738(1)**	**0.9160(1)**	**8(1)**	**3.149**
Mn	0.3671(3)	0.2217(3)	0.3244(4)	8(1)	2.053
	0.3652(2)	**0.2098(2)**	**0.3232(3)**	**8(1)**	**1.987**
V	0.1787(3)	0.8818(3)	0.6577(4)	6(1)	5.059
As	**0.1765(1)**	**0.8784(1)**	**0.6522(2)**	**7(1)**	**4.987**
O(1)	0.342(2)	0.775(2)	0.783(2)	11(2)	2.087
	0.336(1)	**0.776(1)**	**0.782(1)**	**12(1)**	**2.102**
O(2)	0.914(2)	0.706(2)	0.567(2)	12(2)	1.948
	0.9182(9)	**0.708(1)**	**0.570(1)**	**10(1)**	**1.928**
O(3)	0.500(1)	0.551(1)	0.264(2)	6(2)	2.274
	0.5034(9)	**0.549(1)**	**0.264(1)**	**6(1)**	**2.288**
O(4)	0.243(2)	0.918(2)	0.380(2)	13(2)	1.837
	0.238(1)	**0.901(1)**	**0.366(1)**	**14(1)**	**1.694**
O(5)	0.212(2)	0.128(1)	0.906(2)	9(2)	2.130
	0.216(1)	**0.125(1)**	**0.902(1)**	**12(1)**	**2.110**

[a] Bold values are for BiMnAsO$_5$.

[b] Equivalent isotropic displacement parameters (Å^2 × 10^3), where U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

DISCUSSION

We conclude that BiMnVO$_5$ and BiMnAsO$_5$ are isostructural with BiNiAsO$_5$, BiPbVO$_5$, and Bi(Na,Bi)VO$_5$

TABLE 3
Anisotropic Displacement Parameters (Å^2 × 10^3) for BiMnVO$_5$ and BiMnAsO$_5$[a]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Bi	7(1)	7(1)	7(1)	2(1)	1(1)	3(1)
	8(1)	**8(1)**	**9(1)**	**4(1)**	**2(1)**	**3(1)**
V	7(1)	2(1)	7(1)	2(1)	−1(1)	2(1)
As	**8(1)**	**5(1)**	**7(1)**	**2(1)**	**−0(1)**	**2(1)**
Mn	10(1)	6(1)	7(1)	2(1)	2(1)	2(1)
	9(1)	**7(1)**	**6(1)**	**3(1)**	**1(1)**	**2(1)**
O(1)	7(5)	8(4)	19(5)	4(4)	4(4)	5(4)
	8(3)	**12(3)**	**17(3)**	**10(3)**	**2(2)**	**4(2)**
O(2)	10(5)	13(4)	11(4)	3(3)	3(3)	4(4)
	5(3)	**12(3)**	**12(3)**	**1(2)**	**4(2)**	**4(2)**
O(3)	6(2)	6(2)	6(2)	3(2)	2(2)	1(2)
	4(3)	**9(3)**	**3(3)**	**1(2)**	**1(2)**	**3(2)**
O(4)	17(5)	8(4)	12(4)	5(3)	3(4)	5(4)
	16(3)	**17(3)**	**13(3)**	**9(3)**	**9(3)**	**7(3)**
O(5)	10(2)	8(2)	11(2)	5(2)	2(2)	4(2)
	19(3)	**5(3)**	**11(3)**	**4(2)**	**1(3)**	**3(2)**

[a] Values for BiMnAsO$_5$ are in bold. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+\cdots+2hka^*b^*U^{12}]$.

TABLE 4
Bond Lengths (Å) and Angles (deg) for $BiMnVO_5$ and $BiMnAsO_5$[a]

Bi–O(3)	2.102(9)	Mn–O(3)	2.318(9)
Bi–O(3)	**2.093(6)**	**Mn–O(3)**	**2.359(6)**
Bi–O(3)	2.242(8)	O(3)–Bi–O(3)	76.1(3)
Bi–O(3)	**2.230(6)**	**O(3)–Bi–O(3)**	**76.2(3)**
Bi–O(5)	2.309(6)	O(3)–Bi–O(5)	82.4(3)
Bi–O(5)	**2.323(9)**	**O(3)–Bi–O(5)**	**81.7(2)**
Bi–O(1)	2.353(10)	O(3)–Bi–O(5)	76.9(3)
Bi–O(1)	**2.342(6)**	**O(3)–Bi–O(5)**	**75.7(2)**
Bi–O(2)	2.382(9)	O(3)–Bi–O(1)	77.6(3)
Bi–O(2)	**2.430(7)**	**O(3)–Bi–O(1)**	**76.9(2)**
Bi–Bi(1)	3.422(2)	O(3)–Bi–O(1)	105.6(3)
Bi–Bi	**3.402(1)**	**O(3)–Bi–O(1)**	**108.3(2)**
Mn–Mn	3.442(4)	O(5)–Bi–O(1)	158.5(3)
Mn–Mn	**3.516(3)**	**O(5)–Bi–O(1)**	**156.3(2)**
V–O(4)	1.668(9)	O(3)–Bi–O(2)	76.8(3)
As–O(4)	**1.675(7)**	**O(3)–Bi–O(2)**	**75.7(2)**
V–O(1)	1.734(9)	O(3)–Bi–O(2)	150.4(3)
As–O(1)	**1.691(6)**	**O(3)–Bi–O(2)**	**148.9(2)**
V–O(2)	1.734(10)	O(5)–Bi–O(2)	87.9(3)
As–O(2)	**1.683(6)**	**O(5)–Bi–O(2)**	**87.2(2)**
V–O(5)	1.733(9)	O(1)–Bi–O(2)	79.9(3)
As–O(5)	**1.693(6)**	**O(1)–Bi–O(2)**	**77.9(2)**
Mn–O(4)	2.132(10)	O(4)–V–O(1)	108.9(5)
Mn–O(4)	**2.118(7)**	**O(4)–As–O(1)**	**109.2(3)**
Mn–O(3)	2.143(8)	O(4)–V–O(2)	107.3(5)
Mn–O(3)	**2.150(6)**	**O(4)–As–O(2)**	**107.4(3)**
Mn–O(1)	2.143(9)	O(1)–V–O(2)	112.2(5)
Mn–O(1)	**2.166(7)**	**O(1)–As–O(2)**	**111.7(3)**
Mn–O(5)	2.166(9)	O(4)–V–O(5)	111.0(5)
Mn–O(5)	**2.178(7)**	**O(4)–As–O(5)**	**113.6(3)**
Mn–O(2)	2.256(10)	O(1)–V–O(5)	108.6(4)
Mn–O(2)	**2.275(6)**	**O(1)–As–O(5)**	**105.9(3)**
O(2)–V–O(5)	108.9(5)	O(3)–Mn–O(2)	78.8(3)
O(2)–As–O(5)	**109.1(3)**	**O(3)–Mn–O(2)**	**78.0(2)**
O(4)–Mn–O(3)	101.0(3)	O(1)–Mn–O(2)	167.1(4)
O(4)–Mn–O(3)	**103.8(3)**	**O(1)–Mn–O(2)**	**163.8(2)**
O(4)–Mn–O(1)	102.6(4)	O(5)–Mn–O(2)	86.5(3)
O(4)–Mn–O(1)	**104.7(3)**	**O(5)–Mn–O(2)**	**86.1(3)**
O(1)–Mn–O(3)	97.7(4)	O(4)–Mn–O(3)	179.7(4)
O(1)–Mn–O(3)	**97.0(2)**	**O(4)–Mn–O(3)**	**178.6(2)**
O(4)–Mn–O(5)	101.6(3)	O(3)–Mn–O(3)	79.1(3)
O(4)–Mn–O(5)	**102.7(3)**	**O(3)–Mn–O(3)**	**77.6(2)**
O(3)–Mn–O(5)	152.9(3)	O(1)–Mn–O(3)	77.6(3)
O(3)–Mn–O(5)	**149.4(2)**	**O(1)–Mn–O(3)**	**75.2(2)**
O(1)–Mn–O(5)	91.7(4)	O(5)–Mn–O(3)	78.2(3)
O(1)–Mn–O(5)	**91.0(3)**	**O(5)–Mn–O(3)**	**76.0(2)**
O(4)–Mn–O(2)	90.2(4)	O(2)–Mn–O(3)	89.6(3)
O(4)–Mn–O(2)	**91.5(3)**	**O(2)–Mn–O(3)**	**88.6(2)**

[a] Values for $BiMnAsO_5$ are in bold.

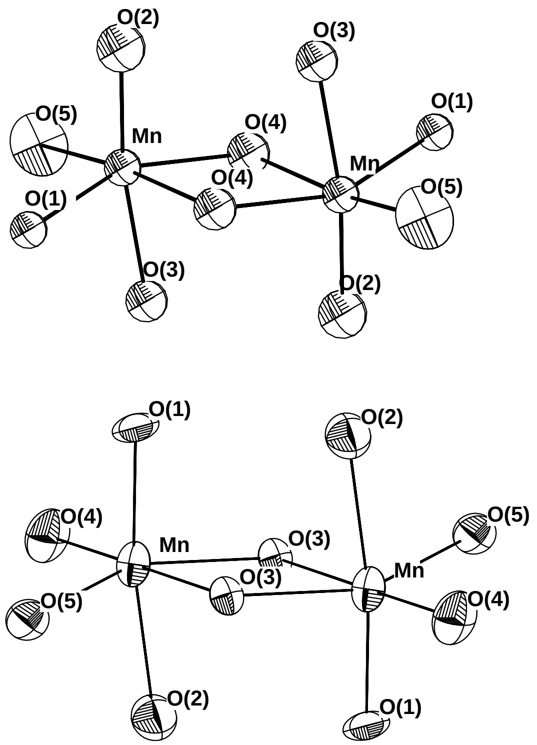

FIG. 1. The Mn_2O_{10} dimer in $BiMnPO_5$ (upper) and in $BiMnVO_5$ (lower).

(24–26). The structure of $BiPbVO_5$ was previously reported in space group *P*1, and in that report the authors considered both *P*1 and $P\bar{1}$ as the possible space group (25). Their decision to choose space group *P*1 was largely based on a statistical analysis of structure factors (see, for example, Ref. 27). However, it should be noted that these structure factor statistics are calculated based on the assumption that there is a uniform distribution of atomic positions in the unit cell. Cases where application of these statistical criteria to distinguish between centrosymmetric and noncentrosymmetric structures fail are known to be those where this basic criterion is not observed; for example, where there is a small number of independent atoms in the unit cell, or the composition of the cell is strongly heterogeneous (28). Both of these cases are present in this general structural type. Namely, there are eight independent atoms, with two of them being extremely heavy (Bi and Pb). The final criterion to distinguish between the correctness of the centric or acentric structures should be the extent to which the introduction of the new set of variables improves the final refinement, as reflected in the calculated residuals (a good discussion of these criteria can be found in Ref. 29). In addition, careful examination of the observed intensities for anomalous dispersion effects (which, ultimately, reflect themselves on the calculated residuals) and, if available, the study of other physical effects that can only arise from noncentrosymmetric materials such as pyro- or piezoelectricity, optical activity, or second harmonic optical effect. For a list of several types of effects dependent on a noncentrosymmetric structure see Ref. (30). Statistical analysis of the structure factors we collected for Bi(Na,Bi)VO_5 (26), $BiMnVO_5$, and $BiMnAsO_5$ also suggested that these structures should be acentric. Nonetheless, we obtained good refinements in $P\bar{1}$, and there was no justification to drop the symmetry to

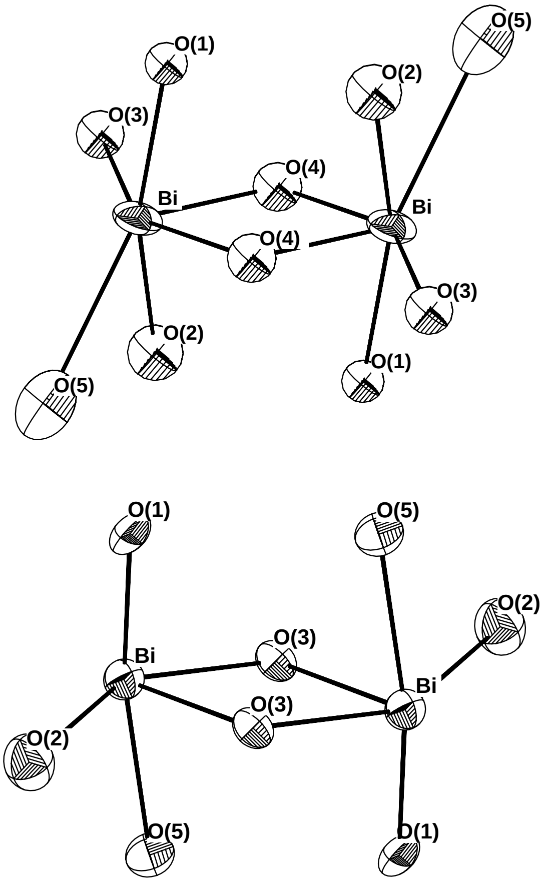

FIG. 2. The Bi_2O_{10} dimer in $BiMnPO_5$ (upper) and the Bi_2O_8 dimer in $BiMnVO_5$ (lower).

$P1$. The authors reporting on the structure of $BiPbVO_5$ appreciated that their structure was very close to centric; we believe that it is likely centric. In support of that, it has been reported that this compound does not produce a second harmonic signal (31).

The $P\bar{1}$ structure of $BiMnVO_5$ and $BiMnAsO_5$ is very similar to the structure of monoclinic $BiMnPO_5$: the same building blocks are involved and the local connectivity is the same (Fig. 3). Further, in both structures there is an inversion center midway between the Mn atoms in the Mn_2 dimer (Fig. 1) and midway between the Bi atoms in the Bi_2 dimer (Fig. 2). On this basis one might expect that the triclinic structure is a distortion of the monoclinic structure. Examination of the extended connectivity, however, shows that the structures are distinctly different, and the monoclinic structure can be viewed as a zigzag version of the triclinic structure (Fig. 4). Both the monoclinic and triclinic structures have all atoms in general positions. Thus, there is the same number of positional parameters in the two structures.

There is a significant difference in the Bi–O bonding when comparing the triclinic and monoclinic structures.

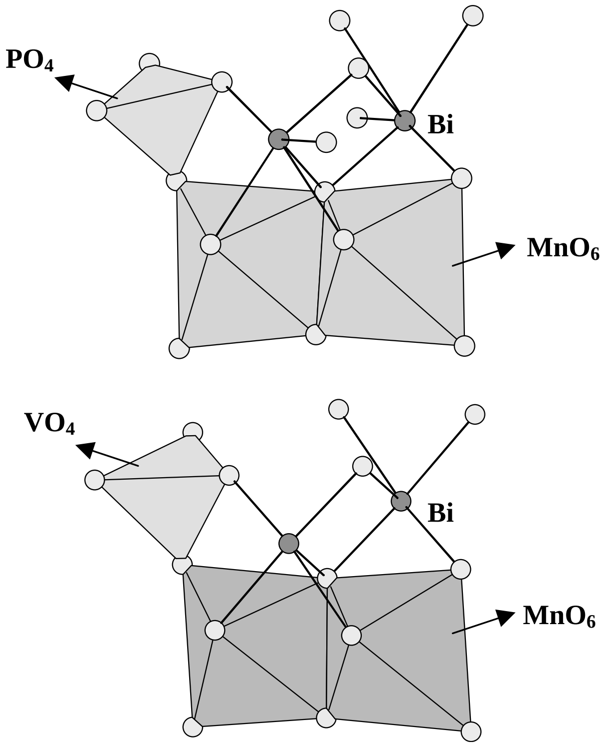

FIG. 3. Local connectivity in $BiMnPO_5$ (upper) and in $BiMnVO_5$ (lower).

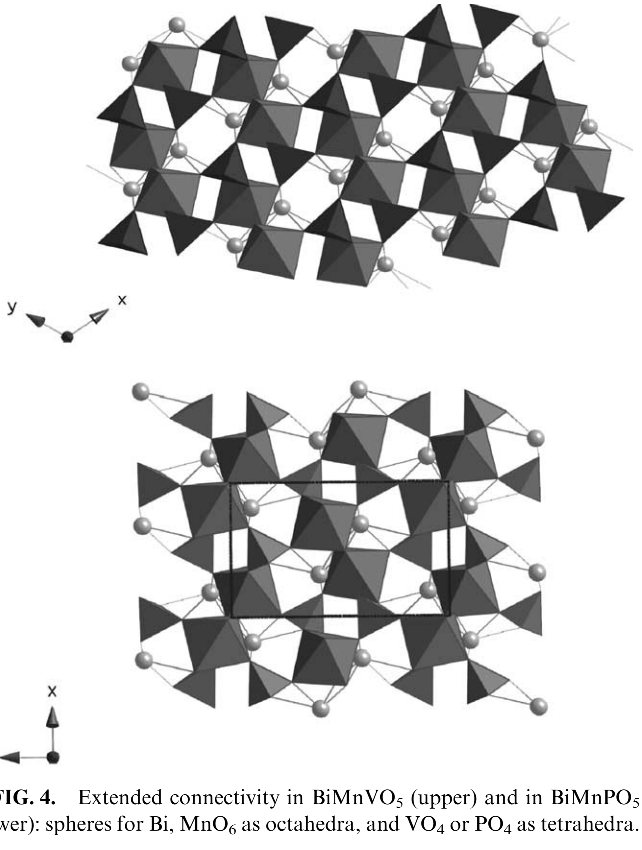

FIG. 4. Extended connectivity in $BiMnVO_5$ (upper) and in $BiMnPO_5$ (lower): spheres for Bi, MnO_6 as octahedra, and VO_4 or PO_4 as tetrahedra.

Figures. 2 and 3 show in $BiMnAsO_5$ a Bi coordination to oxygen of 5 with the longest Bi–O bond length being 2.43 Å. In $BiMnPO_5$, there is a sixth Bi–O distance at 2.76 Å; thus, the Bi coordination was considered to be 6 in that compound. This sixth Bi–O distance in $BiMnAsO_5$ is at 3.15 Å and is shown as a bond in Fig. 4. A consequence of this very long Bi–O distance is that O(4) would be underbonded if it did not form shorter bonds to Mn or V and As. This shortening of Mn, V, and As bonds to O(4) leads to a pronounced distortion of the VO_4 tetrahedron in $BiMnVO_5$ with three V–O bonds of 1.73 Å and one of 1.67 Å.

Two other $BiAVO_5$ compounds ($A = Cd$ or Ca) are known with structure (9, 32) showing similarities and differences with the $BiMnMO_5$ structures discussed above. These structures have different space groups, but are both orthorhombic with $Z = 8$. Both have VO_4 tetrahedra. For $BiCdVO_5$, there are CdO_6 octahedra sharing edges in pairs as in the monoclinic and triclinic $BiMnMO_5$ structures. In $BiCaVO_5$, there are CaO_7 polyhedra sharing edges in pairs. The Bi environment is, however, very different when considering the $BiCaVO_5$ and $BiMnMO_5$ structures on the one hand and the monoclinic and triclinic $BiAMO_5$ structures on the other hand. The latter have "isolated" Bi_2O_{10} or Bi_2O_8 dimers, whereas the former have extended BiO_2 ribbons.

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