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Synthesis and Structure of New $BiMn_2MO_6$ Compounds Where *M*=P, As, or V

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The new compounds $BiMn_2PO_6$, $BiMn_2AsO_6$, and $BiMn_2VO_6$ have been prepared and shown to be structurally related to several other BiA_2MO_6 compounds. The structure of $BiMn_2PO_6$ was refined from neutron powder diffraction data in space group *Pnma* with $a=12.04$ Å, $b=5.37$ Å, $c=8.13$ Å, and $Z=4$. It contains $(BiO_2)^{1-}$ chains and $(PO_4)^{3-}$ tetrahedra. The observed fivefold coordination for the Mn^{2+} cations is unusual for Mn in this oxidation state. © 2002 Elsevier Science (USA)

1. INTRODUCTION

Bismuth-containing oxides have been shown to have interesting properties such as high oxygen ion conductivity, bright yellow pigment, and selective oxidation catalysts (1–3). Complex oxides of the type BiA_2MO_6 have been reported for $A=$ Mg, Ca, Cd, Pb, Cu, and Zn with $M=$ P, As, or V (4–15). The structures of nearly all of these compounds have $(BiO_2)^{1-}$ chains and $(MO_4)^{3-}$ tetrahedra. The coordination of the A^{2+} cation is variable, including an unusual fivefold coordination for the smaller cations. The orientation of the tetrahedra is also variable. In the case of ferroelectric $BiCa_2VO_6$ and $BiCa_2AsO_6$, all tetrahedra point in the same direction along the polar axis of the crystal. All previously reported BiA_2MO_6 compounds could be prepared in air, but synthesis of $BiMn_2MO_6$ compounds requires protection from air during synthesis.

2. EXPERIMENTAL

Reactants were Bi_2O_3 (99.9%, CERAC), MnO (99.9%, CERAC), $NH_4H_2PO_4$ (AR, Mullinckrodt), As_2O_5 (99.9%, Alfa), and V_2O_5 (99.9%, Johnson Mathey). Appropriate quantities of reactants were intimately mixed by grinding together in an agate mortar. For preparation of $BiMn_2PO_6$, the reactant mixture was first heated at 600°C under flowing Ar for 6 h to decompose the $NH_4H_2PO_4$ and eliminate ammonia and water. After grinding this sample, it was heated again at 800°C for 48 h either under flowing Ar or in an evacuated silica ampoule. For preparation of $BiMn_2VO_6$, reactants were sealed in an evacuated silica ampoule and heated at 700°C for 30 h. For the preparation of $BiMn_2AsO_6$, the reactants were sealed in an evacuated silica ampoule and heated at 800°C for 24 h.

X-ray diffraction powder patterns of the products were obtained on a Siemens D5000 diffractometer using Cu$K\alpha$ radiation. Powder neutron diffraction data for $BiMn_2PO_6$ were collected on BT-l at the NIST Center for Neutron Research using a wavelength of 1.5402 Å. Structure refinements utilized GSAS software (16).

3. RESULTS

The X-ray diffraction powder patterns (Fig. 1) were readily indexed on the basis of an orthorhombic unit cell by

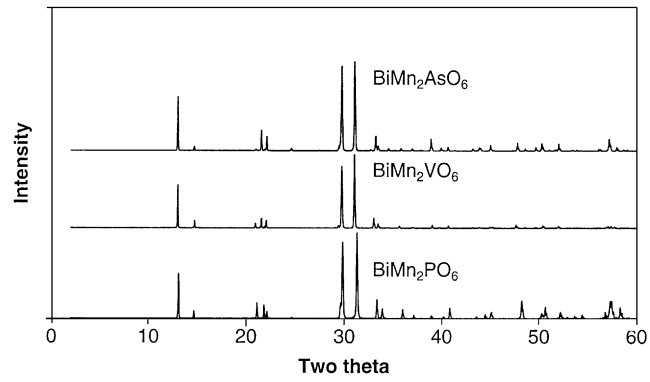

FIG. 1. X-ray diffraction powder patterns for $BiMn_2PO_6$, $BiMn_2AsO_6$, and $BiMn_2VO_6$.

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TABLE 1
Cell Edges of $BiMn_2MO_6$ Compounds

Compound	a (Å)	b (Å)	c (Å)
$BiMn_2PO_6$	12.031(1)	5.3652(5)	8.1225(7)
$BiMn_2AsO_6$	12.009(1)	5.3734(5)	8.2092(7)
$BiMn_2VO_6$	12.002(1)	5.4421(5)	8.2378(7)

TABLE 2
Details of Neutron Diffraction Data Collection and Refinement for $BiMn_2PO_6$

Z	4
Calc. density(g/cm^3)	5.633 g/cm^3
Space group	*Pnma*
a (Å)	12.0425(4)
b (Å)	5.3704(1)
c (Å)	8.1288(2)
Cell volume, (Å^3)	525.71(2)
Zero point ($^\circ\theta$)	0.0197
Wavelength (Å)	1.5402
Data range ($^\circ 2\theta$)	10–140
Step size ($^\circ 2\theta$)	0.05
Time per step(s)	300
Number of data points	3300
Number of reflections	568
Number of variables	68
R_p(%)	4
wR_p(%)	4.94
χ^2	1.698

TABLE 3
Atomic Coordinates and Isotropic Thermal Parameters for $BiMn_2PO_6$

Atom	*Site*	x/a	y/b	z/c	U_{iso} (Å^2)	BVsum[a]
Bi	4*c*	0.0950(2)	0.25	0.0120(5)	0.0155(5)	2.956
Mn(1)	4*c*	0.1032(6)	0.75	0.6924(6)	0.0090(9)	1.986
Mn(2)	4*c*	0.0991(7)	0.75	0.2952(7)	0.0216(9)	1.974
P	4*c*	0.1970(3)	0.25	0.4744(7)	0.0144(8)	5.032
O(1)	8*d*	−0.0033(3)	0.0050(7)	0.1634(2)	0.0148(5)	2.269
O(2)	8*d*	0.1249(2)	0.4859(4)	0.4922(5)	0.0212(6)	1.942
O(3)	4*c*	0.2895(4)	0.25	0.5983(6)	0.0318(9)	1.811
O(4)	4*c*	0.2414(3)	0.25	0.2965(5)	0.0272(9)	1.825

[a] Bond valence sum

TABLE 4
$BiMn_2PO_6$ Anisotropic Displacement Parameters

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.015(1)	0.013(1)	0.018(1)	0.0	0.003(1)	0.0
Mn(1)	0.014(3)	0.010(3)	0.002(3)	0.0	0.004(3)	0.0
Mn(2)	0.034(4)	0.029(4)	0.002(3)	0.0	0.000(1)	0.0
P	0.016(2)	0.009(2)	0.018(3)	0.0	−0.006(2)	0.0
O(1)	0.028(1)	0.007(1)	0.009(1)	0.005(1)	0.001(2)	0.000 (1)
O(2)	0.023(2)	0.018(1)	0.023(1)	0.009(1)	0.004(2)	−0.001(2)
O(3)	0.031(3)	0.039(3)	0.026(2)	0.0	−0.020(2)	0.0
O(4)	0.011(2)	0.050(3)	0.021(3)	0.0	0.009(2)	0.0

analogy to other BiA_2MO_6 compounds. The refined cell edges for the $BiMn_2MO_6$ compounds are given in Table 1. Refinement of the neutron data for $BiMn_2PO_6$ proceeded smoothly in space group *Pnma*, and details are given in Table 2. Figure 2 compares the observed and calculated intensities. Refined atomic coordinates and isotropic displacement factors are in Table 3. Anisotropic displacement factors are given in Table 4. Selected interatomic

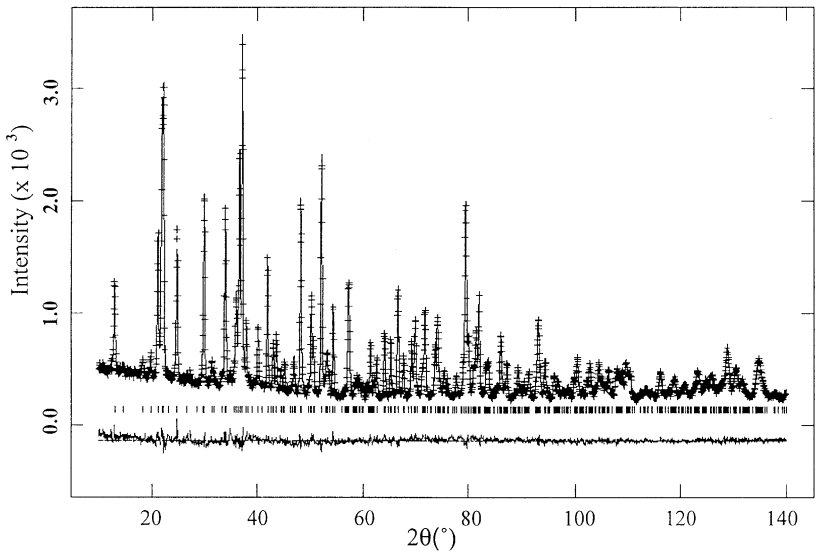

FIG. 2. Observed (points) and calculated (line) neutron diffraction patterns for $BiMn_2PO_6$.

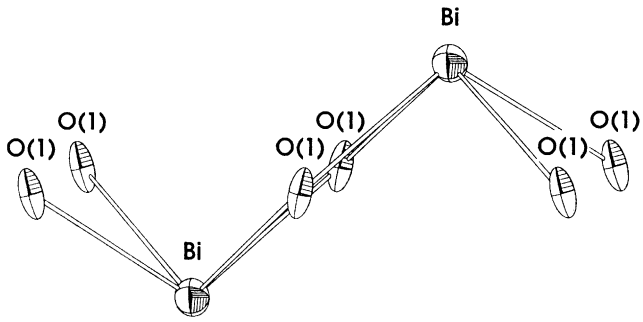

FIG. 3. $(BiO_2)^{1-}$ chain in $BiMn_2PO_6$.

distances and angles are in Table 5. Based on these distances, bond valences (17) were calculated (Table 3) and found to be very close to the ideal values. Both $BiMn_2PO_6$ and $BiMn_2AsO_6$ were off-white in color with $BiMn_2AsO_6$ being somewhat darker. The color of $BiMn_2VO_6$ was red-brown as might be expected for a vanadate. The similarity of the X-ray diffraction patterns (Fig. 1) and the unit cells (Table 1) for $BiMn_2PO_6$, $BiMn_2AsO_6$, and $BiMn_2VO_6$ suggests that the three compounds are isostructural.

TABLE 5
Selected Interatomic Distances (Å) and Angles (deg) for $BiMn_2PO_6$

	O(1)	O(2)	O(3)	O(4)
Bi	2.155(4) × 2			2.908(5)
	2.265(4) × 2			
P		1.543(3) × 2	1.502(6)	1.542(6)
Mn(1)	2.134(5) × 2	2.175(5) × 2		2.054(8)
Mn(2)	2.132(6) × 2	2.161(5) × 2	2.088(8)	
O(1)–Bi–O(1)	75.2(2)			
O(1)–Bi–O(1)	73.9(1)			
O(1)–Bi–O(4)	117.4(4)			
O(1)–Bi–O(1)	117.4(1)			
O(1)–Bi–O(4)	73.9(2)			
O(1)–Bi–O(4)	74.4(1)			
O(1)–Mn(1)–O(1)	76.1(3)			
O(1)–Mn(1)–O(2)	151.8(4)			
O(1)–Mn(1)–O(2)	94.4(1)			
O(1)–Mn(1)–O(4)	106.7(2)			
O(2)–Mn(1)–O(2)	81.4(2)			
O(2)–Mn(1)–O(4)	101.5(2)			
O(1)–Mn(2)–O(1)	80.0(3)			
O(1)–Mn(2)–O(2)	151.3(4) × 2			
O(1)–Mn(2)–O(2)	91.9(2) × 2			
O(1)–Mn(2)–O(3)	89.2(2) × 2			
O(2)–Mn(2)–O(2)	82.0(3)			
O(2)–Mn(2)–O(3)	118.4(3) × 2			
O(2)–P–O(2)	110.4(3)			
O(2)–P–O(3)	110.8(3) × 2			
O(2)–P–O(4)	106.4(3) × 2			
O(3)–P–O(4)	111.9(4)			

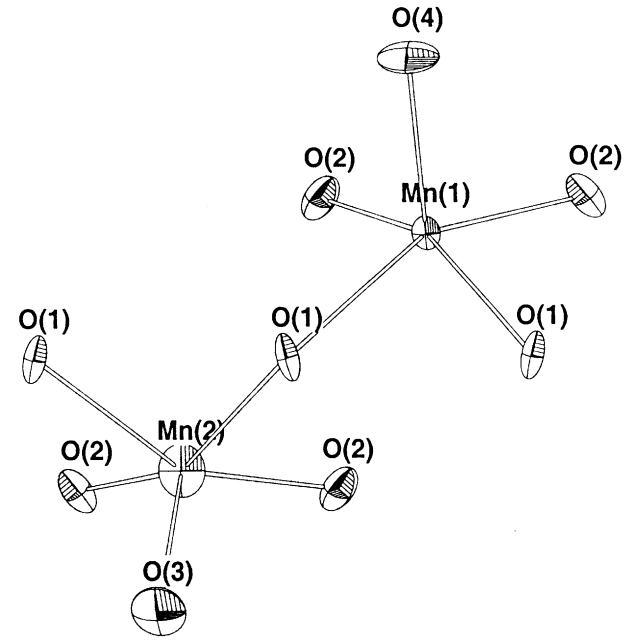

FIG. 4. Coordination of Mn(II) cations in $BiMn_2PO_6$.

4. DISCUSSION

The $(BiO_2)^{1-}$ chain (Fig. 3) in $BiMn_2PO_6$ is essentially the same as found in the other BiA_2MO_6 compounds, and the $(PO_4)^{3-}$ tetrahedron is quite regular (Table 5). There

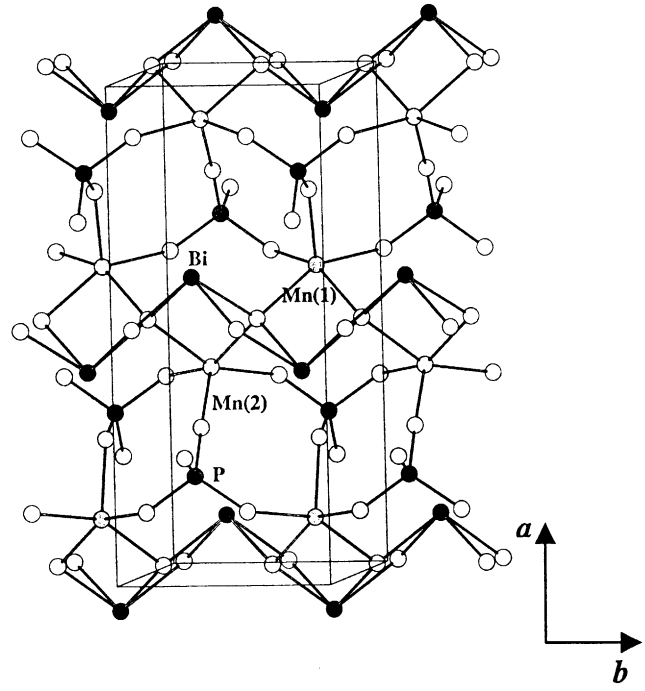

FIG. 5. Overall structure of $BiMn_2PO_6$.

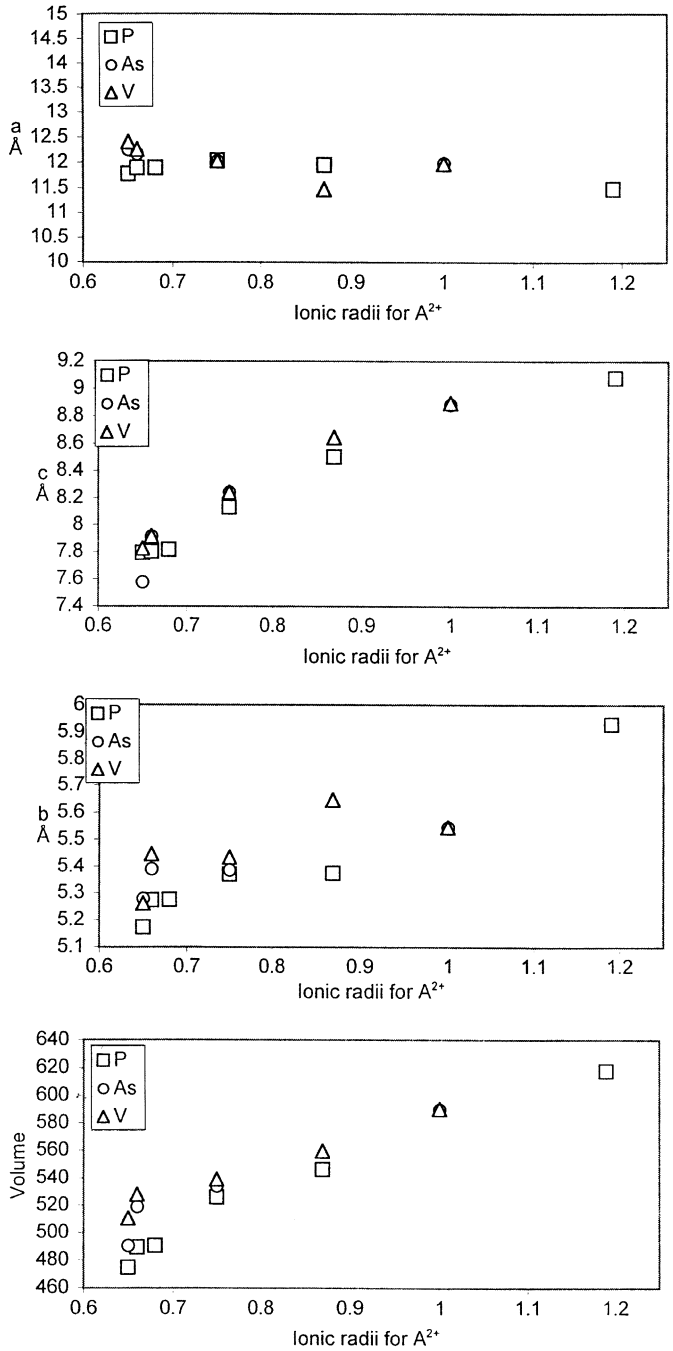

FIG. 6. Plot of *a*, *b*, *c*, and volume vs *A*(II) ionic radii for isostructural BiA_2MO_6 phases.

are two crystallographically distinct Mn^{2+} cations; both are five coordinated to oxygen (Fig. 4), which is an unusual coordination for Mn in this oxidation state. Figure 5 shows how all the structural units in $BiMn_2PO_6$ fit together. The *Pnma* space group we find for $BiMn_2PO_6$ is the same space group found for the structures of $BiMg_2PO_6$, $BiMg_2AsO_6$, $BiMg_2VO_6$, $BiZn_2PO_6$, $BiCu_2AsO_6$, and $BiCu_2PO_6$ at room temperature. However, for both $BiMg_2VO_6$ and $BiZn_2PO_6$, a phase transition occurs above room temperature (12, 14). Small displacements of atoms lead to a higher symmetry structure. This same transition may well occur for $BiMn_2PO_6$ above room temperature.

In Fig. 6, the cell edges and volumes of all the known BiA_2MO_6 isostructural compounds are plotted vs. the ionic radius of the A^{2+} cation. The coordination number of the A^{2+} cation is 5 for the smaller cations but becomes larger for the larger Ca^{2+}, Cd^{2+}, and Pb^{2+} cations. The cell edges normally increase with the ionic radius of the A^{2+} cation as might be expected. However, the *a* cell edge is an exception. This same type of exception in the *a* cell edge is found with increasing size of the M^{5+} cation in our $BiMn_2MO_6$ series (Table 1). The BiA_2MO_6 structure described here is only known for all three M^{5+} cations P, As, and V when *A* is Mg, Cu, or Mn. Although $BiCa_2PO_6$ is given in Table 4 of Ref. (13), the cell dimensions given are those that we report for $BiCa_2VO_6$ (9), and a synthesis of $BiCa_2PO_6$ has apparently never been reported.

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