

# Synthesis and Structure of Bismuth Copper Vanadate, $\text{BiCu}_2\text{VO}_6$

Ivana Radosavljevic, John S. O. Evans, and Arthur W. Sleight<sup>1</sup>

*Department of Chemistry and Center for Advanced Materials Research, Oregon State University, Corvallis, Oregon 97331*

Received April 3, 1998; in revised form June 12, 1998; accepted June 16, 1998

---

The new compound  $\text{BiCu}_2\text{VO}_6$  was synthesized, and its structure was determined from single-crystal X-ray diffraction data collected at 150 and 298 K. This compound crystallizes in space group  $P2_1/n$  with  $Z = 12$  at both temperatures. At room temperature,  $a = 13.4932(1)$  Å,  $b = 7.8224(1)$  Å,  $c = 15.7972(1)$  Å, and  $\beta = 113.113(1)^\circ$ . The structure contains  $(\text{BiO}_2)^-$  chains and  $(\text{VO}_4)^{3-}$  tetrahedra with three crystallographically distinct sites for both  $\text{Bi}^{3+}$  and  $\text{V}^{5+}$ . There are six crystallographically distinct sites for  $\text{Cu}^{2+}$ ; four show a square-pyramidal environment, and two are in distorted octahedra. The square pyramids share edges and corners, forming  $\text{Cu}_4\text{O}_{14}$  units. © 1998 Academic Press

---

## INTRODUCTION

A growing number of compounds with the  $\text{BiA}_2\text{MO}_6$  formula have been found where  $M$  may be pentavalent V, As, or P (1–8). The  $A^{2+}$  cation can be Ca, Mg, Cd, Pb, or Cu, but not all these combinations of  $A$  and  $M$  have yet given compounds. The structures have certain similarities in that they all contain  $(\text{BiO}_2)^-$  chains and  $(\text{MO}_4)^{3-}$  tetrahedra. There are, however, very considerable variations in the coordination of the  $\text{Bi}^{3+}$  and  $A^{2+}$  cations as well as in the orientation of the tetrahedra. One of these compounds,  $\text{BiCa}_2\text{VO}_6$ , appears to be ferroelectric (3).

## EXPERIMENTAL

A polycrystalline sample of  $\text{BiCu}_2\text{VO}_6$  was synthesized by the solid-state reaction of  $\text{Bi}_2\text{O}_3$  (Atomergic Chemetals, 99.9%),  $\text{CuO}$  (Cerac, 99.9%), and  $\text{NH}_4\text{VO}_3$  (Johnson Matthey, 99.99%). Stoichiometric quantities of the reagents were ground and heated in an alumina crucible at  $750^\circ\text{C}$  for 20 h. The powder X-ray diffraction pattern for indexing purposes was recorded on a Siemens D5000 diffractometer from  $2$  to  $60^\circ 2\theta$ . Although most of the medium- and high-intensity reflections could be indexed on an orthorhombic cell of dimensions similar to those of previously

reported phases in the  $\text{BiM}_2\text{AO}_6$  ( $M = \text{Mg, Cu, Ca; A} = \text{V, As, P}$ ) family, there remained unindexed reflections.

Single-crystal growth was carried out by melting a small amount of the polycrystalline sample at  $1000^\circ\text{C}$  followed by slow cooling it to  $600^\circ\text{C}$  at a rate of  $3^\circ\text{C/h}$  and then to room temperature at a rate of  $5^\circ\text{C/min}$ . Dark-brown needle-shaped crystals with well-developed faces were obtained. The chemical composition of several crystals was analyzed, using an SX-50 electron microprobe. The results confirmed a Bi:Cu:V ratio of 1:2:1.

Single-crystal X-ray diffraction data were collected both at room temperature and at 150 K. Both data sets were collected on an Enraf-Nonius DIP 2000 image plate diffractometer with Mo radiation, using the same collection method. A total of 60 frames, each corresponding to a  $3^\circ$  oscillation interval, were recorded with exposure time of 900 s per frame. The images obtained were processed using the XDisplayF, Denzo, and Scalepack programs of the HKL software suite (9). A total of 13,944 reflections were measured at room temperature and merged to 3326 unique reflections with an agreement factor of  $R_{\text{merge}} = 9.0\%$ . At 150 K, a total of 13,889 reflections were measured and merged to 3371 unique reflections with an agreement factor of  $R_{\text{merge}} = 9.7\%$ .

Structure solution and refinement of both data sets were performed using the Oxford Crystals suite (10). Details about the crystal, data collection, and refinement are given in Tables 1 and 2.

Powder diffraction data for Rietveld refinement were collected on a Siemens D5000 diffractometer using  $\text{CuK}\alpha_1$  radiation. The scan was performed in the range from  $12$  to  $100^\circ 2\theta$ , using a step size of  $0.02^\circ$  and a step count time of 8 s. Rietveld refinement was performed using the GSAS software suite (11).

## SOLUTION AND REFINEMENT OF STRUCTURE

The structure of  $\text{BiCu}_2\text{VO}_6$  was solved from room temperature single-crystal data. The 60 diffraction images were used to determine and refine the unit cell parameters. Indexing gave a monoclinic cell with the parameters  $a = 13.471(1)$  Å,  $b = 7.812(1)$  Å,  $c = 15.760(1)$  Å, and  $\beta = 113.10(1)^\circ$ . More

<sup>1</sup>To whom correspondence should be addressed. E-mail: sleighta@chem.orst.edu.

**TABLE 1**  
Crystal Data

Chemical formula	BiCu <sub>2</sub> VO <sub>6</sub>	
Molecular weight	483.0103	
Crystal color	Dark brown	
Crystal size (mm)	0.1 × 0.1 × 0.3	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	
<i>Z</i>	12	
Temperature (K)	298	150
<i>a</i> (Å)	13.471(1)	13.453(1)
<i>b</i> (Å)	7.812(1)	7.808(1)
<i>c</i> (Å)	15.760(1)	15.753(1)
$\beta$ (deg)	113.10(1)	113.12(1)
<i>V</i> (Å <sup>3</sup> )	1525.51	1521.77
Density (g/cm <sup>3</sup> )	6.311	6.327

reliable and accurate cell parameters obtained by least-squares refinement of the powder diffraction data are  $a = 13.4932(1)$  Å,  $b = 7.8224(1)$  Å,  $c = 15.7972(1)$  Å, and  $\beta = 113.113(1)^\circ$ . The systematic absences in the pattern ( $h00$ :  $h = 2n + 1$ ,  $0k0$ :  $k = 2n$ ,  $00l$ :  $l = 2n$ ,  $h0l$ :  $h + l = 2n$ ) indicated space group *P*2<sub>1</sub>/*n* (No. 14). Structure solution was initiated by direct methods using the program SIR92 (12). Three bismuth, six copper, and three vanadium unique sites were found. Subsequent Fourier difference map syntheses revealed 18 oxygen sites, thus completing the asymmetric unit of 30 atoms.

A full-matrix refinement of a total of 122 parameters (scale factor, extinction parameter, 90 positional parameters, 30 isotropic temperature factors) was performed. Agreement factors achieved were  $R = 13.19\%$  and  $wR = 15.14\%$ . An empirical absorption correction using the program Difabs (13) was then applied. Further refinement and the application of an optimal weighting scheme (third-order Chebyshev polynomial) led to the final agreement

**TABLE 2**  
Data Collection and Refinement

	Enraf-Nonius DIP 2000	
Diffractometer	Enraf-Nonius DIP 2000	
Temperature (K)	298	150
Wavelength (Å)	0.71073	0.71073
Number of measured reflections	13,944	13,889
Number of independent reflections	3326	3371
Cut-off	$I > 4\sigma I$	$I > 4\sigma I$
Number of observed reflections	2067	2061
Number of parameters	122	122
Number of reflections/number of parameters	16	16
$\Delta\rho_{\min}$ (e/Å <sup>3</sup> )	- 5.18	- 7.31
$\Delta\rho_{\max}$ (e/Å <sup>3</sup> )	+ 6.03	+ 6.12
Extinction parameter	88.5(5)	105.0(5)
Goodness-of-fit indicator, S	1.13	1.08
<i>R</i> (%)	8.35	7.78
<i>wR</i> (%)	7.50	8.17

**TABLE 3**  
Atomic Positional Parameters, Temperature Factors, and Bond Valence Sums

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> (Å <sup>2</sup> )	BV sum
Bi(1)	0.40756(7)	0.0116(1)	0.06077(7)	0.0043(3)	2.97
Bi(2)	0.62129(7)	- 0.0112(1)	0.28720(7)	0.0038(3)	3.11
Bi(3)	0.41265(7)	0.0111(1)	0.38016(7)	0.0036(3)	3.14
Cu(1)	0.5878(3)	0.3183(4)	0.4470(3)	0.0073(7)	2.14
Cu(2)	0.5762(2)	- 0.3140(4)	0.4443(3)	0.0054(7)	2.05
Cu(3)	0.4301(3)	- 0.2915(4)	0.2326(3)	0.0071(7)	2.12
Cu(4)	0.4461(3)	0.3041(4)	0.2396(3)	0.0078(7)	1.97
Cu(5)	0.5765(2)	- 0.3171(4)	0.1010(3)	0.0046(7)	2.10
Cu(6)	0.5841(2)	0.3221(4)	0.1046(3)	0.0057(7)	2.07
V(1)	0.3081(3)	0.4991(6)	0.3466(3)	0.0083(8)	5.13
V(2)	0.6924(3)	0.5197(6)	0.3158(3)	0.0056(8)	5.39
V(3)	0.3103(3)	- 0.5214(6)	0.0405(3)	0.0082(9)	5.14
O(1)	0.504(1)	0.175(2)	- 0.002(2)	0.003(3)	2.18
O(2)	0.518(1)	0.176(3)	0.170(2)	0.009(4)	2.14
O(3)	0.513(1)	- 0.171(2)	0.172(2)	0.007(4)	2.18
O(4)	0.522(1)	- 0.158(2)	0.337(2)	0.005(4)	2.45
O(5)	0.534(1)	0.163(2)	0.347(2)	0.007(4)	2.39
O(6)	0.493(2)	- 0.170(2)	0.497(2)	0.011(4)	2.20
O(7)	0.622(1)	0.507(3)	0.534(1)	0.016(4)	2.20
O(8)	0.350(2)	0.323(3)	0.306(2)	0.013(4)	1.95
O(9)	0.342(2)	- 0.329(3)	0.301(2)	0.024(5)	2.07
O(10)	0.329(1)	- 0.012(2)	0.185(1)	0.010(3)	1.91
O(11)	0.593(1)	0.502(3)	0.364(1)	0.008(3)	2.15
O(12)	0.751(1)	0.210(2)	0.155(1)	0.008(4)	1.91
O(13)	0.628(1)	- 0.498(3)	0.196(1)	0.011(4)	2.15
O(14)	0.715(1)	- 0.125(2)	0.147(1)	0.006(3)	2.00
O(15)	0.392(1)	- 0.501(2)	0.160(1)	0.006(3)	2.06
O(16)	0.614(1)	- 0.495(2)	0.029(1)	0.007(3)	1.97
O(17)	0.716(2)	- 0.131(3)	0.511(2)	0.027(5)	1.75
O(18)	0.758(1)	0.214(2)	0.523(2)	0.010(4)	1.89

factors of  $R = 8.35\%$  and  $wR = 7.50\%$ . The final atomic positional and thermal parameters are given in Table 3. Bond valence sums (14,15) are also given in this table.

Data collection was also performed at 150 K, and the structure was found to be largely unchanged. All cell edges

**TABLE 4**  
Powder X-Ray Diffraction Data Collection and Refinement

Diffractometer	Siemens D5000
Temperature (K)	298
Wavelength (Å)	1.5406
Scan range (deg 2 $\theta$ )	12-100
Step size (deg)	0.02
Step time (s)	8
Number of data points	4399
Number of observed reflections	1624
Number of variables	35
$\chi^2$	4.66
<i>R</i> <sub>p</sub> (%)	8.77
<i>wR</i> <sub>p</sub> (%)	12.05
<i>R</i> <sub>F</sub> (%)	5.21

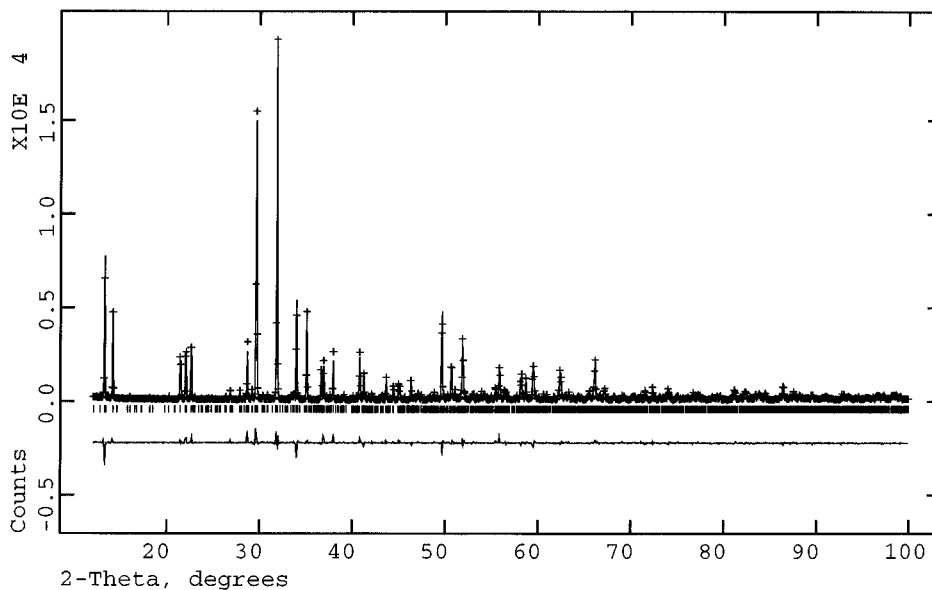


FIG. 1. Observed, calculated, and difference X-ray diffraction patterns for  $\text{BiCu}_2\text{VO}_6$ .

were found to be somewhat smaller:  $a = 13.453(1) \text{ \AA}$ ,  $b = 7.808(1) \text{ \AA}$ ,  $c = 15.753(1) \text{ \AA}$ , and  $\beta = 113.12(1)^\circ$ . No change in space group was indicated, and the room temperature structure was used as the initial model for low-temperature data refinement. The final agreement factors obtained were  $R = 7.78\%$  and  $wR = 8.17\%$ .

The structure obtained from the single-crystal data was used as the initial model for the Rietveld refinement of powder diffraction data. The purpose of this refinement was mainly to confirm the purity of the powder sample. Atomic positional parameters were therefore kept fixed. The scale factor, diffractometer zero point, lattice parameters, background, and profile coefficients were initially refined. The observed data were then corrected for the surface roughness effects using the method of Suortti (16). Cation temperature factors were allowed to refine freely, while those of oxygens

were constrained to be the same. During the final cycles of refinement a total of 35 parameters were varied, giving the profile agreement factors of  $R_p = 8.77\%$ ,  $wR_p = 12.05\%$ , and  $R_F = 5.21\%$ . Details of the refinement are given in Table 4. Observed, calculated, and difference profiles are shown in Fig. 1.

### DESCRIPTION OF STRUCTURE

The structure of  $\text{BiCu}_2\text{VO}_6$  (Fig. 2) is considerably more complex than that of other  $\text{BiA}_2\text{MO}_6$  compounds. Other members of the  $\text{BiM}_2\text{VO}_6$  family can be described using an orthorhombic cell of approximate dimensions  $a \sim 12$ ,  $b \sim 8$ , and  $c \sim 5 \text{ \AA}$ . In  $\text{BiCu}_2\text{VO}_6$ , the crystal class has

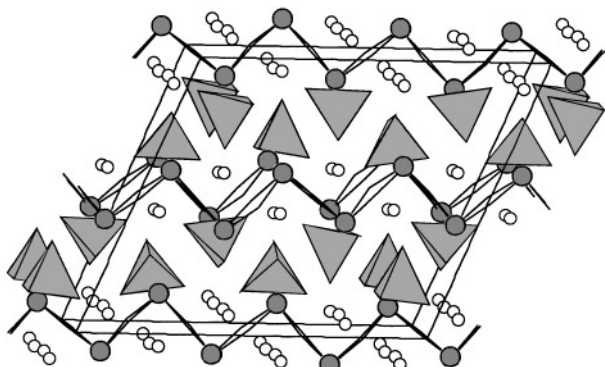


FIG. 2. Structure of  $\text{BiCu}_2\text{VO}_6$  as  $\text{VO}_4$  tetrahedra and  $\text{BiO}_2$  chains. Open circles are Cu atoms.

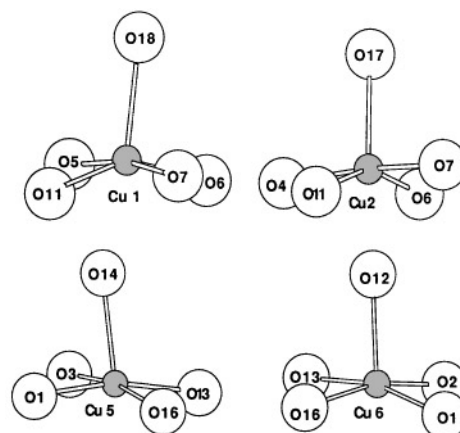


FIG. 3. The four copper atoms in fivefold coordination.

**TABLE 5**  
Selected Bond Lengths (Å) and Angles (Deg)

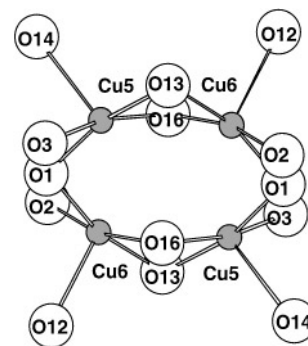
Bi(1)–O(2)	2.195(21)	O(1)–Bi(1)–O(1)	73.1(6)
–O(3)	2.268(20)	O(1)–Bi(1)–O(3)	113.1(7)
–O(1)	2.296(21)	O(2)–Bi(1)–O(10)	78.6(7)
–O(1)	2.302(21)	O(2)–Bi(1)–O(18)	86.0(7)
–O(10)	2.571(19)		
–O(18)	2.841(19)		
Bi(2)–O(4)	2.129(20)	O(2)–Bi(2)–O(5)	72.8(8)
–O(3)	2.218(20)	O(2)–Bi(2)–O(4)	111.4(7)
–O(5)	2.237(21)	O(3)–Bi(2)–O(12)	87.2(7)
–O(2)	2.340(21)	O(3)–Bi(2)–O(14)	64.7(7)
–O(12)	2.707(19)		
–O(14)	3.080(19)		
Bi(3)–O(6)	2.227(27)	O(4)–Bi(3)–O(6)	73.8(9)
–O(6)	2.236(26)	O(5)–Bi(3)–O(6)	111.6(8)
–O(5)	2.242(20)	O(4)–Bi(3)–O(8)	121.4(8)
–O(4)	2.280(20)	O(4)–Bi(3)–O(9)	59.0(7)
–O(8)	2.689(19)	O(4)–Bi(3)–O(10)	70.3(7)
–O(10)	2.834(19)		
–O(9)	2.926(20)		
Cu(1)–O(5)	1.896(22)	O(5)–Cu(1)–O(11)	90.8(8)
–O(7)	1.941(23)	O(6)–Cu(1)–O(7)	98.4(8)
–O(11)	1.962(20)	O(7)–Cu(1)–O(11)	81.7(8)
–O(6)	2.012(26)	O(7)–Cu(1)–O(18)	89.4(8)
–O(18)	2.280(19)		
Cu(2)–O(7)	1.914(23)	O(4)–Cu(2)–O(11)	89.7(8)
–O(4)	1.980(21)	O(4)–Cu(2)–O(7)	88.4(9)
–O(11)	1.982(21)	O(7)–Cu(2)–O(11)	81.7(8)
–O(6)	1.990(26)	O(6)–Cu(2)–O(17)	87.3(9)
–O(17)	2.265(25)		
Cu(3)–O(9)	1.917(29)	O(3)–Cu(3)–O(4)	81.9(9)
–O(4)	1.924(20)	O(4)–Cu(3)–O(9)	86(1)
–O(15)	1.942(19)	O(9)–Cu(3)–O(10)	85.3(8)
–O(3)	1.974(21)	O(9)–Cu(3)–O(15)	98.2(9)
–O(10)	2.525(19)	O(4)–Cu(3)–O(10)	82.9(7)
–O(11)	2.852(19)		
Cu(4)–O(15)	1.923(19)	O(11)–Cu(4)–O(15)	90.0(9)
–O(8)	1.955(25)	O(2)–Cu(4)–O(5)	86.3(9)
–O(5)	1.972(21)	O(8)–Cu(4)–O(15)	97.3(8)
–O(2)	2.002(22)	O(5)–Cu(4)–O(8)	83.3(9)
–O(11)	2.668(19)	O(4)–Cu(4)–O(10)	82.9(7)
–O(10)	2.871(20)		
Cu(5)–O(1)	1.879(23)	O(3)–Cu(5)–O(13)	95.0(8)
–O(13)	1.980(20)	O(1)–Cu(5)–O(3)	84.0(9)
–O(16)	1.981(20)	O(1)–Cu(5)–O(16)	97.3(8)
–O(3)	2.007(21)	O(1)–Cu(5)–O(14)	90.4(9)
–O(14)	2.284(17)	O(3)–Cu(5)–O(14)	85.7(7)
Cu(6)–O(13)	1.933(22)	O(2)–Cu(6)–O(13)	95.7(9)
–O(2)	1.962(22)	O(1)–Cu(6)–O(16)	94.7(9)
–O(1)	1.966(23)	O(13)–Cu(6)–O(16)	81.6(8)
–O(16)	1.999(19)	O(12)–Cu(6)–O(13)	92.7(7)
–O(12)	2.242(18)	O(12)–Cu(6)–O(16)	95.0(7)

**TABLE 5—Continued**

V(1)–O(9)	1.669(27)	O(8)–V(1)–O(10)	109(1)
–O(8)	1.712(22)	O(7)–V(1)–O(9)	110(1)
–O(10)	1.721(17)	O(8)–V(1)–O(9)	107(1)
–O(7)	1.741(20)	O(9)–V(1)–O(10)	111(1)
V(2)–O(14)	1.610(17)	O(13)–V(2)–O(14)	109(1)
–O(12)	1.652(21)	O(12)–V(2)–O(14)	108.7(9)
–O(13)	1.744(20)	O(11)–V(2)–O(13)	108.6(8)
–O(11)	1.789(18)	O(12)–V(2)–O(13)	110(1)
V(3)–O(18)	1.638(19)	O(15)–V(3)–O(17)	109(1)
–O(17)	1.669(25)	O(16)–V(3)–O(17)	110(1)
–O(16)	1.774(18)	O(15)–V(3)–O(18)	108(1)
–O(15)	1.783(18)	O(15)–V(3)–O(16)	112.1(8)

dropped from orthorhombic to monoclinic and the volume of the unit cell has tripled. The  $b$  axis is the same in the orthorhombic and monoclinic structures, but the  $c$  axis in the monoclinic structure is increased by a factor of 3. The  $a$  axes of the two cells are related by  $a_{\text{ortho}}/a_{\text{mono}} = \sin \beta_{\text{mono}}$ . Fractional atomic coordinates of the final refined structure are given in Table 3 and selected bond distances and angles in Table 5. All the bond valence sums for the  $\text{BiCu}_2\text{VO}_6$  structure (Table 3) are in good agreement with the expected values.

In  $\text{BiCu}_2\text{VO}_6$  there are six crystallographically unique Cu sites showing two different types of coordination environments. Four copper atoms may be described as having a fivefold distorted square-pyramidal coordination to oxygen atoms, although in all cases there is a sixth oxygen atom at 3–3.2 Å. They form four bonds to the basal oxygens at about 2 Å and one to the apical oxygen at about 2.3 Å (Fig. 3). Pairs of square pyramids share an edge to form  $(\text{Cu}_2\text{O}_8)$  dimers, which then share two corners to form the quadrimer units of the formula  $(\text{Cu}_4\text{O}_{14})$  shown in Fig. 4. The intradimer copper–copper distance is about 2.8 Å, very similar to the dimers found in  $\text{BiCu}_2\text{PO}_6$  (4) and  $\text{BiCu}_2\text{AsO}_6$  (5). The remaining two copper atoms are six-coordinated in



**FIG. 4.** The  $\text{Cu}_4\text{O}_{14}$  unit.

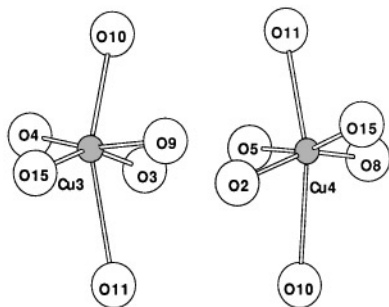


FIG. 5. The two copper atoms in sixfold coordination.

a distorted octahedral environment (Fig. 5), with bond lengths ranging from 2.2 Å (equatorial oxygens) to about 3 Å (axial oxygens). These octahedra alternately share an edge and a corner, forming rows that run perpendicular to the  $(\text{BiO}_2)^-$  chains (Fig. 6). The copper-copper distance between the edge-sharing octahedra is 3.17 Å, while that between the corner-sharing ones is 4.66 Å.

One of the more flexible aspects of the structure of the  $\text{BiA}_2\text{MO}_6$  compounds is the coordination number of the  $A^{2+}$  cation. This can be as high as seven, as it is for  $\text{Ca}^{2+}$  in  $\text{BiCa}_2\text{VO}_6$  (3). Fivefold coordination is found for  $\text{Mg}^{2+}$  in  $\text{BiMg}_2\text{MO}_6$  compounds (1,2). However, this fivefold coordination is highly irregular compared to the square-pyramidal coordination found for some  $\text{Cu}^{2+}$  in  $\text{BiCu}_2\text{VO}_6$  and  $\text{BiCu}_2\text{PO}_6$  (4). Sixfold coordination is found in the  $\text{BiA}_2\text{MO}_6$  series for the first time for part of the  $A$  cations in  $\text{BiCu}_2\text{VO}_6$ .

Bismuth atoms form  $(\text{BiO}_2)^-$  chains parallel to the  $z$  axis as in all the known  $\text{BiA}_2\text{MO}_6$  phases. There are three unique bismuth sites (Fig. 7). Two of them are six-coordinate. They form four short bonds to the oxygens in the  $(\text{BiO}_2)^-$  chains at about 2.2–2.3 Å and two more bonds to oxygens at distances between 2.6 and 3.1 Å. The third bismuth atom is located near the six-coordinate copper atoms and, consequently, there are more oxygen atoms in its vicinity. In addition to the four short bonds to the oxygens in the  $(\text{BiO}_2)^-$  chains, there are three additional bonds to oxygens, ranging in length from 2.7 to 3.0 Å. All  $\text{BiA}_2\text{MO}_6$  phases have  $\text{BiO}_2$  chains with four short Bi–O distances (2.2–2.3 Å). The longer Bi–O bonds found in  $\text{BiCu}_2\text{VO}_6$  are considerably shorter than those found in  $\text{BiCa}_2\text{VO}_6$  (3) and  $\text{BiMg}_2\text{MO}_6$  phases (1,2), where they are at least 3.0 Å.

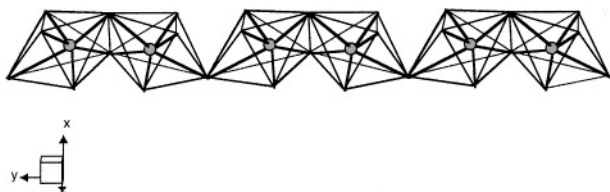


FIG. 6. Chain formed by corner- and edge-sharing of distorted  $\text{CuO}_6$  octahedra.

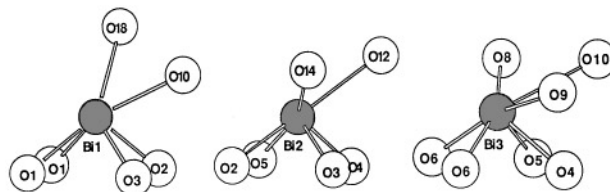


FIG. 7. Coordination polyhedra for the three bismuth atoms.

However, in  $\text{BiCu}_2\text{PO}_6$  there is a fifth Bi–O distance at 2.5 Å (4).

Vanadium in  $\text{BiCu}_2\text{VO}_6$  is in a distorted tetrahedral environment, with bond angles ranging from 105 to 113°. The  $(\text{VO}_4)^{3-}$  tetrahedra share all of their corners with the copper-oxygen polyhedra in a way that makes it possible to view this structure as consisting of sheets (Fig. 8). Copper coordination polyhedra and the  $(\text{BiO}_2)^-$  chains form slabs parallel to the (100) plane; the linkage along the  $x$  direction is provided by the  $(\text{VO}_4)^{3-}$  tetrahedra. Very similar sheets are found in the orthorhombic  $\text{BiCu}_2\text{PO}_6$  (4). In most of the  $\text{BiA}_2\text{MO}_6$  compounds, there is only type of  $\text{MO}_4$  tetrahedron from a crystallographic point of view, and this tetrahedron lies on a symmetry element, usually a mirror plane. This results in the tetrahedra having definite orientations with respect to the crystallographic axes. In  $\text{BiCu}_2\text{VO}_6$ , however, none of the three distinct  $\text{VO}_4$  tetrahedra lie on any symmetry element. Thus, these tetrahedra do not point in directions along the axes of the unit cell.

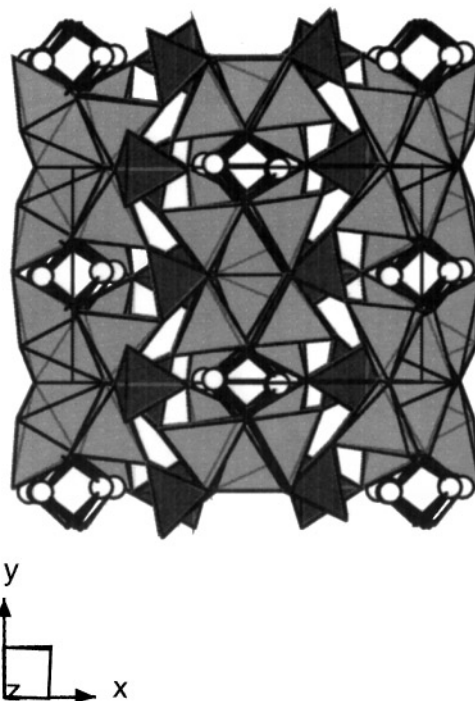


FIG. 8.  $\text{BiCu}_2\text{VO}_6$  looking down the  $\text{BiO}_2$  chains where circles are Bi atoms. Sheets are formed by connecting Cu–O and V–O polyhedra.

## ACKNOWLEDGMENT

This work was supported through NSF Grant DMA-9308530.

## REFERENCES

1. J. Huang and A. W. Sleight, *J. Solid State Chem.* **100**, 170 (1992).
2. J. Huang, Q. Gu, and A. W. Sleight, *J. Solid State Chem.* **105**, 599 (1993).
3. I. Radosavljevic, J. S. O. Evans, and A. W. Sleight, *J. Solid State Chem.* **137**, 143 (1998).
4. F. Abraham, M. Ketatni, G. Mairesse, and B. Mernari, *Eur. J. Solid State Inorg. Chem.* **31**, 313 (1994).
5. I. Radosavljevic, J. S. O. Evans, and A. W. Sleight, *J. Solid State Chem.* (submitted).
6. A. Mizrahi, J. P. Wignacourt, and H. Steinfink, *J. Solid State Chem.* **133**, 516 (1997).
7. A. Mizrahi, J. P. Wignacourt, M. Drache, and P. Conflant, *J. Mater. Chem.* **5**, 901 (1995).
8. N. Tancret, S. Obbade, F. Abraham, F. Kzaiber, and B. Mernari, *J. Phys.* (in press).
9. Z. Otwinowski and W. Minor, in "Methods in Enzymology" (C. W. Carter, Jr., and R. M. Sweet, Eds.), p. 276. Academic Press, New York, 1996.
10. D. J. Watkin, J. R. Carruthers, and P. W. Betteridge, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1985.
11. A. C. Larson and R. B. Von Dreele, "LANSCE," Los Alamos National Laboratory, Los Alamos, NM, 1994.
12. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, and M. Camalli, *J. Appl. Crystallogr.* **27**, 435 (1994).
13. D. Stewart and N. Walker, *Acta Crystallogr., Sect. A* **39**, 158 (1983).
14. I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B* **41**, 244 (1985).
15. N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B* **47**, 192 (1991).
16. P. Suortti, *J. Appl. Crystallogr.* **5**, 325 (1972).