JOURNAL OF SOLID STATE CHEMISTRY 97, 228–232 (1992)

A New Bismuth Strontium Vanadate, $BiSr_2V_3O_{11}$, with Both Orthovanadate and Pyrovanadate Groups

JINFAN HUANG AND ARTHUR W. SLEIGHT

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Received June 14, 1991; in revised form September 23, 1991

A new bismuth strontium vanadate, $BiSr_2V_3O_{11}$, has been synthesized, and its structure was determined from single crystal X-ray diffraction data. This compound may be represented by the descriptive formula $BiSr_2(VO_4)(V_2O_7)$, indicating one orthovanadate group and one pyrovanadate group in each formula unit. The compound crystallizes in the triclinic space group $P\bar{1}$ with a = 7.0332(6) Å, b = 10.213(2) Å, c = 6.982(2) Å, α = 96.01(2)°, β = 92.87(2)°, γ = 99.16(2)°, V = 491.3(1) Å^3, and Z = 2. The Bi atom is 7-coordinated to oxygen atoms with Bi–O distances from 2.208(8) to 2.88(1) Å. Two types of Sr atoms were found: one with a coordination number of 9 and the other with one of 7. For the orthovanadate group, the average V–O bond length is 1.72 Å and the O–V–O angles are in the range of 103.9(4)° to 116.2(4)°. For the pyrovanadate group, the average V–O bond length is 1.716 Å and the V–O–V angle is 125.3°.

Introduction

We have been synthesizing new oxides containing bismuth. One system that we have been investigating is the pseudo-ternary Bi_2O_3–SrO–V_2O_5. Several new compounds in this system have been identified. In this paper, we report the preparation and crystal structure of a new mixed ortho-vanadate–pyrovanadate $BiSr_2V_3O_{11}$.

Experimental

Reagents used to explore the Bi/Sr/V/O system were $SrCO_3$ (J. T. Baker Inc., 99.9%), NH_4VO_3 (J. T. Baker Inc., 99.1%), and Bi_2O_3 (J. T. Baker Inc., 99.6%). To grow single crystals of $BiSr_2V_3O_{11}$, a 4 : 6 : 1 mixture in a molar ratio of $SrCO_3$, NH_4VO_3, and Bi_2O_3 was melted at 1240°C. After holding at this temperature for 10 min, the sample was cooled to room temperature at the rate of 15°C/hr. Several light yellow crystals were analyzed with an X-50 electron microprobe using Bi_2O_3, $SrCO_3$, and $Pb_5Cl(VO_4)_3$ as standards. The averaged results indicated the composition of the title compound.

A crystal of dimensions 0.1 × 0.15 × 0.15 mm was mounted on a glass fiber for data collection. Details of the data collection, reduction, and refinement are summarized in Table I. The cell dimensions were refined by a least-squares analysis of 22 reflections in the range of 30.23° < 2θ < 43.86° that had been centered on a Rigaku AFC6R diffractometer. A total of 5750 data were collected with the ω-2θ scan technique at a scan width, $\Delta\omega = (1.63 + 0.3 \tan \theta)°$. The intensities of three standard reflections measured every 300 reflections throughout data collection exhibited excursion of less than 2.5%.

0022-4596/92 $3.00

TABLE I

CRYSTAL DATA AND INTENSITY COLLECTION FOR $BiSr_2V_3O_{11}$

Empirical formula	$BiSr_2V_3O_{11}$
Formula weight	713.04
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	7.0332(6)
b (Å)	10.213(2)
c (Å)	6.982(2)
α (°)	96.01(2)
β (°)	92.87(2)
γ (°)	99.16(2)
V (Å^3)	491.3(1)
Z	2
Diffractometer	Rigaku AFC6R
Radiation	MoK_α(λ = 0.71069 Å) Graphite-monochromated
Temperature	23°C
Maximum 2θ (°)	60
Data collected	$-12 < h < 12$, $-17 < k < 17$, $-11 < l < 11$
Scan speed (degrees/min)	16.0 in ω and 32 in 2θ
No. unique data with $F_0^2 > 3\sigma(F_0^2)$	2362
Data/parameter ratio	15.34
R	0.043
R_w	0.059

The structure was solved and refined with the programs from the TEXAN crystallographic software package (*1*). The positions of the atoms Bi, Sr, and V were determined from direct methods SHELXS (*2*). The oxygen atoms were located from subsequent analyses of difference electron density maps. No atoms are found at a center of symmetry. After the refinement of the model with isotropic thermal parameters on each atom, an empirical absorption correction using the program DIFABS (*3*) was applied which resulted in transmission factors ranging from 0.83 to 1.26. The data were also corrected for Lorentz and polarization effects. Final least-squares on $|F|$ with anisotropic thermal parameters on each atom resulted in $R = 0.043$ and $R_w = 0.059$. Atomic positional and isotropic thermal parameters are given in Table II, and the anisotropic thermal parameters are given in Table III.

Polycrystalline $BiSr_2V_3O_{11}$ was prepared by heating the appropriate quantities of $SrCO_3$, NH_4VO_3, and Bi_2O_3 at 850°C for 24 hr in air. The X-ray powder diffraction pattern of the product compares well to the pattern calculated with the program LAZY-PULVERIX (*4*) using the results of the single crystal X-ray structure determination.

Description of the Structure

The structure of $BiSr_2V_3O_{11}$ is shown in Fig. 1. Selected bond distances and angles are given in Table IV. Trivalent bismuth shows its normal highly irregular coordination to oxygen (Fig. 2a). Such irregular coordination is presumed to be due to hybridization of the 6s and 6p orbitals

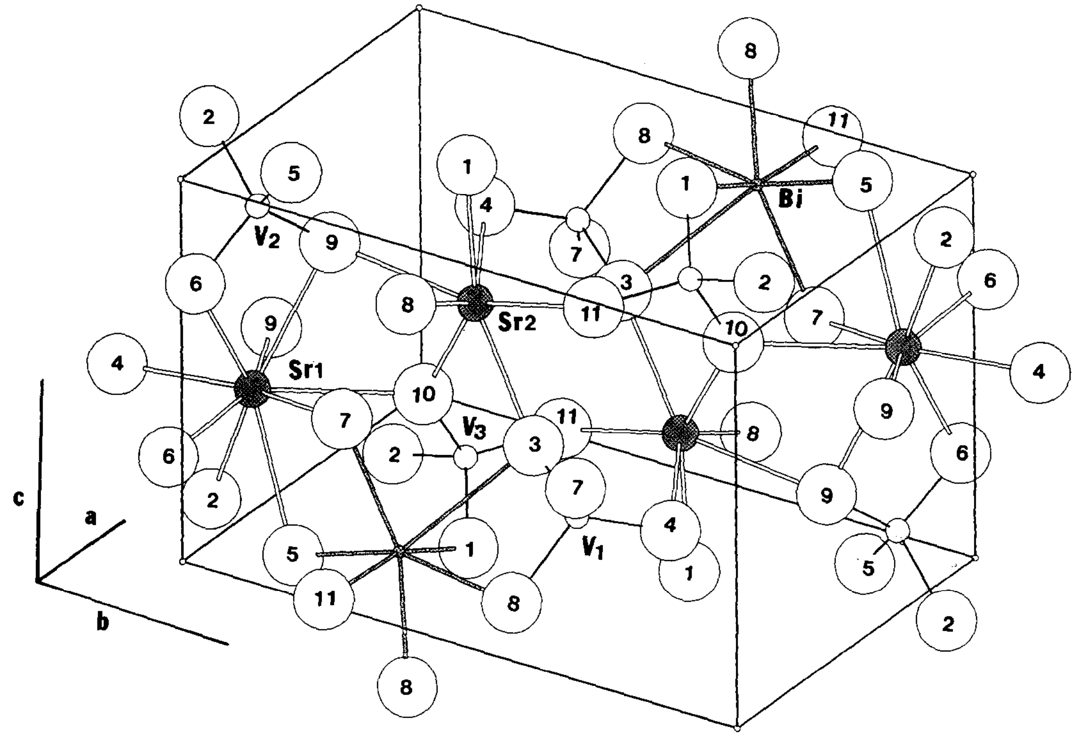

FIG. 1. Structure of $BiSr_2V_3O_{11}$ showing unit cell outline. The large numbered circles are oxygen atoms.

TABLE II

POSITIONAL PARAMETERS AND B_{eq} FOR $BiSr_2V_3O_{11}$

Atom	x	y	z	B_{eq}[a]
Bi	0.92832(6)	0.36010(4)	0.15052(7)	0.68(1)
Sr(1)	0.7491(1)	0.0202(1)	0.3478(1)	0.46(3)
Sr(2)	0.6124(1)	0.3639(1)	−0.3394(2)	0.77(3)
V(1)	0.8890(2)	0.6660(2)	0.3588(3)	0.24(5)
V(2)	0.7642(3)	0.0379(2)	−0.1591(2)	0.26(5)
V(3)	0.5731(3)	−0.2645(2)	−0.1327(3)	0.33(5)
O(1)	0.603(1)	0.3459(8)	0.009(1)	0.8(3)
O(2)	0.659(1)	−0.0940(8)	−0.029(1)	0.7(3)
O(3)	0.252(1)	0.4733(8)	−0.420(1)	1.3(3)
O(4)	0.738(1)	−0.2310(8)	0.300(1)	0.9(3)
O(5)	0.880(1)	0.1484(8)	0.028(1)	1.0(3)
O(6)	0.086(1)	0.012(1)	0.319(1)	1.0(3)
O(7)	0.941(1)	0.2639(9)	0.462(1)	1.1(3)
O(8)	0.974(1)	0.3943(8)	−0.169(1)	0.7(3)
O(9)	0.604(1)	0.0975(8)	0.702(1)	0.7(3)
O(10)	0.540(1)	0.238(1)	0.336(1)	1.3(3)
O(11)	0.258(1)	0.3660(9)	0.175(1)	1.1(3)

[a] $B_{eq} = (8\pi^2/3)U_{ij}\sum_i\sum_j a_i^* a_j^* a_i a_j$.

TABLE III

ANISOTROPIC THERMAL PARAMETERS ($\times 10^{-3}$ Å^2) FOR THE ATOMS OF $BiSr_2V_3O_{11}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	8.7(2)	6.7(2)	10.5(2)	1.3(1)	0.6(1)	0.9(1)
Sr(1)	4.8(4)	8.6(4)	3.0(5)	−2.5(3)	2.1(3)	0.8(4)
Sr(2)	6.6(5)	18.9(5)	3.1(5)	0.2(4)	0.1(4)	1.5(4)
V(1)	2.8(8)	3.4(7)	3.5(8)	2.1(6)	1.9(6)	−0.2(6)
V(2)	4.3(8)	4.2(7)	1.6(8)	1.5(6)	1.2(6)	0.1(6)
V(3)	4.2(8)	5.0(8)	4.2(8)	2.6(6)	1.9(6)	0.9(6)
O(1)	8(4)	8(4)	17(5)	3(3)	5(3)	5(3)
O(2)	16(4)	5(3)	5(4)	−4(3)	3(3)	0(3)
O(3)	27(5)	7(4)	14(5)	−4(3)	10(4)	5(3)
O(4)	6(4)	11(4)	21(5)	5(3)	0(3)	4(4)
O(5)	21(4)	1(3)	16(5)	2(3)	−5(4)	−1(3)
O(6)	12(4)	18(4)	13(4)	10(3)	7(3)	3(4)
O(7)	13(4)	12(4)	14(4)	2(3)	−2(3)	0(4)
O(8)	9(4)	10(4)	9(4)	3(3)	4(3)	2(3)
O(9)	6(3)	13(4)	10(4)	5(3)	0(3)	2(3)
O(10)	23(5)	19(4)	10(4)	6(4)	−1(4)	4(4)
O(11)	15(4)	14(4)	15(5)	7(3)	10(3)	2(3)

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $BiSr_2V_3O_{11}$

Bi–O(1)	2.421(8)	Sr(1)–O(2)	2.766(8)
–O(3)	2.882(9)	–O(4)	2.540(9)
–O(5)	2.208(8)	–O(5)	2.828(9)
–O(7)	2.482(9)	–O(6)	2.405(9)
–O(8)	2.324(8)	–O(6)	2.624(9)
–O(8)′	2.482(8)	–O(7)	2.656(9)
–O(11)	2.310(9)	–O(9)	2.806(8)
		O(9)	2.570(8)
V(1) –O(3)	1.706(8)	–O(10)	2.86(1)
–O(4)	1.674(8)		
–O(7)	1.704(9)	Sr(2)–O(1)	2.466(9)
–O(8)	1.792(8)	–O(3)	2.594(8)
		–O(4)	2.661(8)
V(2) –O(2)	1.786(8)	–O(8)	2.709(8)
–O(5)	1.710(9)	–O(9)	2.757(8)
–O(6)	1.665(9)	–O(10)	2.48(1)
–O(9)	1.679(8)	–O(11)	2.86(1)
V(3) –O(1)	1.701(8)		
–O(2)	1.811(8)		
–O(10)	1.66(1)		
–O(11)	1.712(9)		
O(1) –Bi –O(3)	75.5(3)	O(1) –Bi –O(5)	81.4(3)
O(1) –Bi –O(7)	113.2(3)	O(1) –Bi –O(8)′	76.5(3)
O(1) –Bi –O(8)	97.9(3)	O(1) –Bi –O(11)	160.5(3)
O(3) –Bi –O(5)	136.9(3)	O(3) –Bi –O(7)	73.5(3)
O(3) –Bi –O(8)	125.3(3)	O(3) –Bi –O(8)′	61.8(2)
O(3) –Bi –O(11)	120.5(3)	O(5) –Bi –O(7)	83.2(3)
O(5) –Bi –O(8)	82.3(3)	O(5) –Bi –O(8)′	158.9(3)
O(5) –Bi –O(11)	91.4(3)	O(7) –Bi –O(8)	161.1(3)
O(7) –Bi –O(8)′	115.8(3)	O(7) –Bi –O(11)	83.7(3)
O(8) –Bi –O(8)	77.0(3)	O(8)′ –Bi –O(11)	84.6(3)
O(8) –Bi –O(11)	82.3(3)		
O(2) –Sr(1) –O(4)	65.9(3)	O(2) –Sr(1) –O(5)	57.3(2)
O(2) –Sr(1) –O(6)	91.6(3)	O(2) –Sr(1) –O(6)	144.2(3)
O(2) –Sr(1) –O(7)	126.5(3)	O(2) –Sr(1) –O(9)	145.9(2)
O(2) –Sr(1) –O(9)	68.6(3)	O(2) –Sr(1) –O(10)	97.8(3)
O(4) –Sr(1) –O(5)	113.3(3)	O(4) –Sr(1) –O(6)	80.1(3)
O(4) –Sr(1) –O(6)	80.6(3)	O(4) –Sr(1) –O(7)	150.1(3)
O(4) –Sr(1) –O(9)	110.5(3)	O(4) –Sr(1) –O(9)	70.5(3)
O(4) –Sr(1) –O(10)	147.2(3)	O(5) –Sr(1) –O(6)	70.0(2)
O(5) –Sr(1) –O(6)	133.9(3)	O(5) –Sr(1) –O(7)	69.3(3)
O(5) –Sr(1) –O(9)	136.1(2)	O(5) –Sr(1) –O(9)	113.4(3)
O(5) –Sr(1) –O(10)	74.9(3)	O(6) –Sr(1) –O(6)	69.7(3)
O(6) –Sr(1) –O(7)	72.9(3)	O(6) –Sr(1) –O(9)	121.9(3)
O(6) –Sr(1) –O(9)	149.2(3)	O(6) –Sr(1) –O(10)	130.6(3)
O(6) –Sr(1) –O(7)	78.2(2)	O(6) –Sr(1) –O(9)	57.2(2)
O(6) –Sr(1) –O(9)	112.7(3)	O(6) –Sr(1) –O(10)	117.7(3)
O(7) –Sr(1) –O(9)	137.8(3)	O(7) –Sr(1) –O(10)	62.6(3)
O(7) –Sr(1) –O(9)	74.7(3)	O(9) –Sr(1) –O(10)	66.5(3)
O(9) –Sr(1) –O(10)	77.1(3)	O(9) –Sr(1) –O(9)	78.2(3)
O(1) –Sr(2) –O(3)	141.3(3)	O(1) –Sr(2) –O(4)	75.4(3)
O(1) –Sr(2) –O(8)	69.0(3)	O(1) –Sr(2) –O(9)	73.9(3)
O(1) –Sr(2) –O(10)	144.1(3)	O(1) –Sr(2) –O(11)	77.8(3)
O(3) –Sr(2) –O(4)	133.1(3)	O(3) –Sr(2) –O(8)	88.1(3)
O(3) –Sr(2) –O(9)	136.4(3)	O(3) –Sr(2) –O(10)	74.3(3)
O(3) –Sr(2) –O(11)	64.6(3)	O(4) –Sr(2) –O(8)	138.7(3)
O(4) –Sr(2) –O(9)	65.9(2)	O(4) –Sr(2) –O(10)	79.5(3)
O(4) –Sr(2) –O(11)	123.3(2)	O(8) –Sr(2) –O(9)	84.3(2)
O(8) –Sr(2) –O(10)	119.4(3)	O(8) –Sr(2) –O(11)	68.9(3)
O(9) –Sr(2) –O(10)	72.6(3)	O(9) –Sr(2) –O(11)	146.5(3)
O(10)–Sr(2) –O(11)	138.0(3)		
O(3) –V(1) –O(4)	106.3(4)	O(3) –V(1) –O(7)	112.1(5)
O(3) –V(1) –O(8)	104.9(4)	O(4) –V(1) –O(7)	113.3(4)
O(4) –V(1) –O(8)	116.2(4)	O(7) –V(1) –O(8)	103.9(4)
O(2) –V(2) –O(5)	100.3(4)	O(2) –V(2) –O(6)	112.4(4)
O(2) –V(2) –O(9)	113.9(4)	O(5) –V(2) –O(6)	113.1(5)
O(5) –V(2) –O(9)	115.2(4)	O(6) –V(2) –O(9)	102.4(4)
O(1) –V(3) –O(2)	113.4(4)	O(1) –V(3) –O(10)	104.6(5)
O(1) –V(3) –O(11)	108.3(4)	O(2) –V(3) –O(10)	100.0(4)
O(2) –V(3) –O(11)	117.6(4)	O(10)–V(3) –O(11)	112.0(5)

of bismuth with a resulting lone pair of electrons in effect occupying a coordination site. The environment for bismuth may be described as a distorted, capped octahedron (*5*), although the distortion is very large. In this description, a lower triangle of oxygens (Fig. 2a) may be defined by O(5), O(11), and O(8) and an upper triangle by O(1), O(7), and O(8)′. The Bi–O distances in this "octahedron" range from 2.208 to 2.482 Å. The cap oxygen is O(3) with a longer Bi–O distance of 2.88 Å.

The environment of the 9-coordinate strontium (Fig. 2b) may be viewed as an irregular monocapped square antiprism (*5*). The environment of the 7-coordinate strontium (Fig. 2c) may be viewed as an irregular tetragonal base-trigonal base coordination polyhedron (*5*). As expected, the average Sr–O bond length from heptacoordinated Sr(2) (2.647 Å) is slightly shorter than that from the nonacoordinated Sr(1) atom (2.672 Å).

The V(1) atom is surrounded by four oxygen atom neighbors that form a distorted tetrahedral orthovanadate group. The O–V–O angles are in the range of 103.9° to 116.2°. The pyrovanadate group is formed from the VO_4 tetrahedra of V(2) and V(3) atoms through the bridging atom O(2). As observed in other pyrovanadates (*6–10*), the V–O bond lengths for the bridging oxygen atom (1.786 and 1.811 Å) are longer than those for the other six oxygen atoms. The V(3)–O(2)–V(2) angle of 125.3° is very close to those observed in α-$Sr_2V_2O_7$ (121.2° and 123.0°) (*9*) and β-$Sr_2V_2O_7$ (123° and 124°) (*10*).

Nine of the eleven oxygen atoms are coordinated by three cations. Atom O(8) is surrounded by Sr(2), V(1), and two Bi atoms, forming a distorted tetrahedra coordinated polyhedron. Likewise, atom O(9) bonds to four atoms: Sr(1), Sr(1), Sr(2), and V(2).

Related Compositions

Attempts were made to synthesize derivatives with Ba or Ca partially or completely

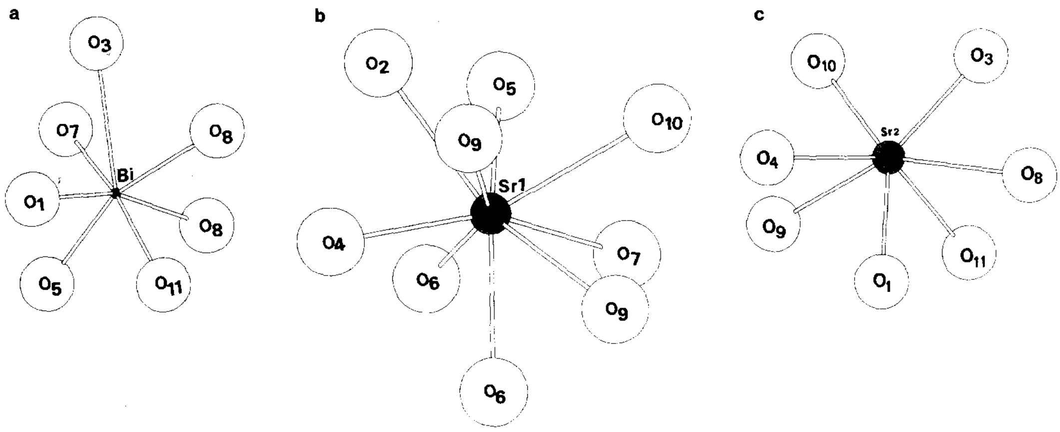

FIG. 2. Coordination polyhedra of Bi, Sr(1), and Sr(2). The upper oxygen coordinated to bismuth is O(8)′ in the text and in Table IV.

substituting for Sr. Attempts were also made to synthesize derivatives with Pb substituting for Bi using La for Sr to balance the charge. Only in the case of a Ca substitution for Sr was there clear evidence for substantial substitution as shown by a significant decrease in the *d* values of peaks. A compound with the formula $BiBa_2V_3O_{11}$ was, however, prepared. This compound crystallizes in an orthorhombic system, and the cell dimensions obtained from the single crystal X-ray diffraction data are a = 5.640(3) Å, b = 24.012(4) Å, and c = 7.750(4) Å. The details of this structure will be reported.

Acknowledgment

This research was supported through the Oregon Metals Initiative which includes contributions from the Oregon Lottery, Teledyne Wah Chang Albany, and Pacific Power and Light.

References

1. Molecular Structure Corporation, TEXSAN, The Woodlands, TX (1989).
2. "Crystallographic Computing 3" (G. M. Sheldrick, C. Kruger, and R. Goddard, Eds.), pp. 175–189, Oxford Univ. Press, London/New York (1985).
3. N. Walker and D. Stuart, *Acta Crystallog. A* **39**, 158 (1983).
4. K. Yvon, W. Jeitschko, and E. Parthe, *J. Appl. Crystallogr.* **10**, 925 (1977).
5. E. L. Muetterties and C. M. Wright, *Q. Rev.* **21**, 109 (1967).
6. E. E. Sauerbrei, R. Faggiani, and C. Calvo, *Acta Crystallogr. B* **30**, 2907 (1974).
7. R. Gopal and C. Calvo, *Acta Crystallogr. B* **30**, 2491 (1974).
8. M. Quarton, J. Angenault, and A. Rimsky, *Acta Crystallogr. B* **29**, 567 (1974).
9. J. Huang and A. W. Sleight, to be submitted.
10. J. A. Baglio and J. N. Dann, *J. Solid State Chem.* **4**, 87 (1972).