JOURNAL OF SOLID STATE CHEMISTRY **100**, 170–178 (1992)

Synthesis, Crystal Structure, and Optical Properties of a New Bismuth Magnesium Vanadate: $BiMg_2VO_6$

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Received December 19, 1991; accepted February 20, 1992

A new bismuth magnesium vanadate, $BiMg_2VO_6$, has been synthesized and structurally characterized from single crystal X-ray diffraction data. It crystallizes in orthorhombic symmetry with a = 7.9136(6) Å, b = 12.246(2) Å, c = 5.444(2) Å, V = 527.6(2) Å^3, z = 4, and a space group of *Cmcm* (No. 63). An unusual fivefold coordination is found for Mg. The five O atoms bound to Mg form a square pyramidal coordination polyhedron with Mg–O bond lengths ranging from 1.973(7) to 2.066(3) Å. The Bi atom is coordinated by four O atoms with Bi–O bond lengths 2.213(2) Å forming a square pyramid. The V atom bonds to four O atoms with V–O distances from 1.672(6) to 1.725(5) Å; all the O–V–O angles are very close to the value of an ideal VO_4 tetrahedron. The $BiMg_2VO_6$ structure may be viewed as connected chains of edge-shared BiO_4 units and corner-shared MgO_5 units extending along the c axis. These chains are then connected to each other through the VO_4 tetrahedra and edge sharing of the MgO_5 units. The absorption edge (about 450 nm) determined from the photothermal deflection technique is consistent with results from the excitation–emission spectrum. An emission band around 650 nm was observed. The IR spectrum of this compound is also reported.

Introduction

Bismuth-containing compounds frequently have interesting optical properties. For example, Bi^{III} is an attractive activator for luminescent materials (*1–10*). The luminescence of these materials can be seen in quite different wavelength regions, depending on the environment of Bi^{III} in the crystals. Red luminescence is observed in $BaSO_4 : Bi^{III}$ and $Bi_4Ge_3O_{12}$ at low temperatures, while in other materials such as $LaGaO_3 : Bi^{III}$ or $La_2SO_6 : Bi^{III}$, UV emission is observed. Although this complicated optical behavior can be difficult to completely understand, it provides many possibilities for application of these materials. For example, $Bi_4Ge_3O_{12}$ is now well established for luminescence applications.

We have been preparing complex oxides which contain bismuth, vanadium, and at least one other cation. This exploratory program starts with no preconceived notions about the composition, structure, or properties of the compounds to be prepared. After consideration of the composition and structure of a new compound, appropriate properties are determined. Novel compounds prepared to date include $BiSr_2V_3O_{11}$, $BiBa_2V_3O_{11}$, and a new nonlinear optical

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0022-4596/92 $5.00

material (11). In this paper we report the synthesis, crystal structure, and the optical properties of a new bismuth magnesium vanadium oxide, $BiMg_2VO_6$.

Experimental

Single crystals of the title compound were grown from Bi_2O_3 flux in a platinum crucible. The reactants were Bi_2O_3 (99.9%, Aldrich), reagent MgO (J. T. Baker), and NH_4VO_3 (99.5%, AESAR). A mixture of these reagents in the molar ratio Bi : Mg : V = 2 : 2 : 1 was first heated at 700°C for 12 hr and 800°C for 6 hr. It was then heated to 1000°C and held at this temperature for 5 min, cooled to 500°C at a rate of 15°C/hr, and finally furnace cooled to room temperature. Clear light yellow needle crystals with dimensions up to 0.5 × 0.5 × 3 mm were obtained.

The chemical compositions of several crystals were analyzed using an SX-50 microprobe. The standards were Bi_2O_3, $CaMgSi_2O_6$, and $Pb_5Cl(VO_4)_3$ for Bi, Mg, and V, respectively. The average of these results gave a Bi : Mg : V ratio of 1 : 2 : 1.

Single crystal X-ray diffraction data were collected on a Rigaku AFC6R diffractometer. Details of the data collection, re-

TABLE I

CRYSTAL DATA AND INTENSITY COLLECTION FOR $BiMg_2VO_6$

Color	Light yellow
Size (mm)	0.1 × 0.1 × 0.15
Crystal system	Orthorhombic
Space group	*Cmcm*(No. 63)
a (Å)	7.9136(6)
b (Å)	12.246(2)
c (Å)	5.444(2)
Volume (Å^3)	527.6(2)
z	4
Formula weight	404.53
Calculated density (g/cc)	5.093
Diffractometer	Rigaku AFC6R
Radiation	Mo$K\alpha$ (λ = 0.71069 Å) Graphite-monochromated
Temperature	23°C
μ (Mo) (cm^{-1})	351.2
Maximum 2θ (°)	80.0
Data collected	$-15 \le h \le 15$, $-22 \le k \le 22$, $-9 \le l \le 9$
Scan method	$\omega - 2\theta$
Scan speed (deg/min)	16.0 in ω, and 32 in 2θ
No. of data collected	5228
No. of unique data with $F_0^2 > 3\sigma(F_0^2)$	851
R_{int}	0.057
Absorption correction	DIFABS
Transmission factors, range	0.82–1.32
Refinement method	Full-matrix least-squares on $\lvert F \rvert$
Parameters varied	33
Data/parameter ratio	25.79
R	0.029
R_w	0.037
Goodness of fit indicator	1.76
Secondary extic. coeff. (mm)	1.156(1) × 10^{-6}

duction, and the refinement are summarized in Table I. The cell dimensions were determined by a least-squares analysis of 21 reflections in the range $29.3^\circ \leq 2\theta$ (Mo$K\alpha$) $\leq 38.8^\circ$ that had been centered on the diffractometer. The intensity data were collected using the ω-2θ scan technique, and a scan width of $\Delta\omega = (1.48 + 0.3 \tan \theta)^\circ$ was used. The intensities of three standard reflections, monitored every 300 reflections throughout data collection, exhibited excursion of less than 2.5%.

The structure was solved and refined with the use of computer programs from the TEXSAN crystallographic software package (*12*). A trial structure based on the positions of Bi, Mg, and V which were determined from direct methods, SHELXS (*13*), was first refined. The O atoms were then located from subsequent analyses of difference electron density maps. After the refinement of the model with isotropic thermal parameters on each atom, an empirical absorption correction using the program DIFABS (*14*) was applied. The data were also corrected for Lorentz and polarization effects. Final least-squares analysis on $|F|$ with anisotropic thermal parameters on each atom resulted in $R = 0.029$ and $R_W = 0.037$.

A polycrystalline sample of BiMg$_2$VO$_6$ was synthesized by solid state reaction using the reactants mentioned earlier. Stoichiometric quantities were mixed in an agate mortar and ground under hexane. This reactant mixture was heated at 800°C for 4 days. An X-ray diffraction powder pattern of the sample was obtained on a Siemens D5000 diffractometer with Si as an internal standard. The observed *d* spacings and intensities are given in Table II. The structure parameters from our single crystal X-ray study were used to calculate the theoretical X-ray powder diffraction pattern using the computer program Lazy-pulverix (*15*), and this result is also given in Table II. The agreement between the calculated and the experimental diffraction pattern is very good.

TABLE II

INDEXED X-RAY POWDER PATTERN FOR BiMg$_2$VO$_6$

			Calcd.		Obsd.	
h	*k*	*l*	*d*	I/I_0	*d*	I/I_0
1	1	0	6.647	72	6.655	79
0	2	0	6.123	9	6.124	11
1	1	1	4.212	9	4.215	10
0	2	1	4.069	35	4.069	38
2	0	0	3.957	31	3.958	36
1	3	1	3.019	100	3.019	100
2	2	1	2.837	81	2.837	80
0	0	2	2.722	20	2.722	22
0	4	1	2.669	3	2.668	3
3	1	0	2.579	8	2.579	9
1	1	2	2.519	19	2.519	21
2	4	0	2.421	11	2.421	11
1	5	0	2.340	11	2.340	10
2	0	2	2.243	10	2.242	11
2	4	1	2.212	9	2.212	9
3	3	1	2.052	12	2.052	11
0	6	0	2.041	6	2.040	6
0	4	2	2.034	4	2.033	5
4	0	0	1.979	8	1.978	8
3	1	2	1.872	22	1.871	19
2	6	0	1.814	4	1.812	3
3	5	0	1.795	16	1.794	12
4	2	1	1.779	14	1.778	14
1	5	2	1.774	21	1.773	17
0	2	3	1.740	4	1.739	4
4	4	0	1.662	4	1.661	3
0	6	2	1.633	8	1.631	8
1	7	1	1.630	10	1.629	8
1	3	3	1.623	15	1.622	12
4	0	2	1.600	6	1.599	5
2	2	3	1.593	15	1.592	11

Combined DTA and TGA at a rate of 5°C/min was first performed on a reactant mixture to determine the reaction pathway to BiMg$_2$VO$_6$. The decomposition of NH$_4$VO$_3$ began at 200°C and was complete by about 400°C. There is an exothermic peak at 640°C and a small endothermic peak at 720°C. The X-ray powder pattern of the mixture heated at 700°C for 2 days indicates a small amount of the title compound and a

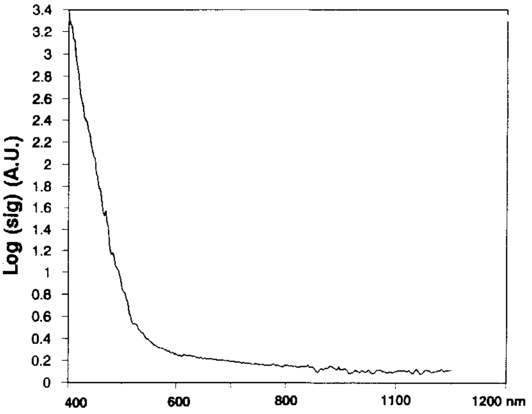

FIG. 1. The photothermal deflection spectroscopy spectrum of $BiMg_2VO_6$.

large amount of $Mg_3(VO_4)_2$. After the mixture was heated at 800°C for 4 days, the X-ray powder pattern of the light yellow powder product indicates the pure title compound. Heating to above 800°C indicates that $BiMg_2VO_6$ starts to decompose into $Mg_3(VO_4)_2$ and $BiVO_4$ at about 840°C.

A second harmonic generation (SHG) effect was sought using a Nd^{3+} : YAG laser 1064-nm beam. A significant signal was not observed, thus confirming the centric space group for the structure of $BiMg_2VO_6$. An electronic absorption spectrum was obtained from the photothermal deflection spectroscopy (PDS) (*16*) technique, the details of which will be reported elsewhere (*17*). Figure 1 shows the PDS spectrum of the title compound. The fluorescence spectrum was recorded using a grating monochromator and an AMINCO photomultiplier interfaced with a computer. A xenon lamp dispersed by a grating monochromater was used as the source of excitation. The spectrum containing excitation and luminescence information is given in Fig. 2. The infrared spectrum of $BiMg_2VO_6$ with a KBr pellet was obtained on a Nicolet-5PC FTIR spectrometer, and the result is given in Fig. 3.

Structure Description

One unit cell of the $BiMg_2VO_6$ structure is shown in Fig. 4. The atomic positions and isotropic thermal factors are given in Table III, and the anisotropic thermal parameters for each atom are given in Table IV. Selected bond distances and angles are given in Table V.

Each Bi atom of $BiMg_2VO_6$ is coordinated to four coplanar oxygen atoms which form a rectangle. These rectangles share edges to form a chain where the Bi atoms are alter-

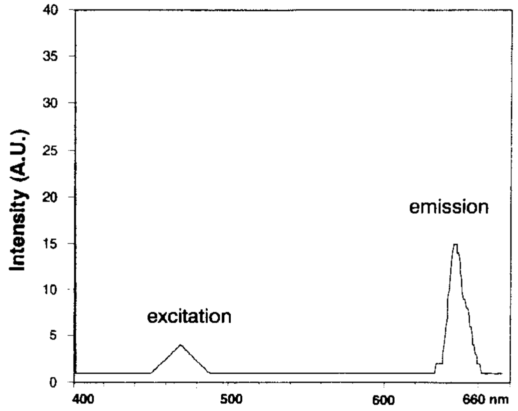

FIG. 2. Excitation–emission spectrum of $BiMg_2VO_6$.

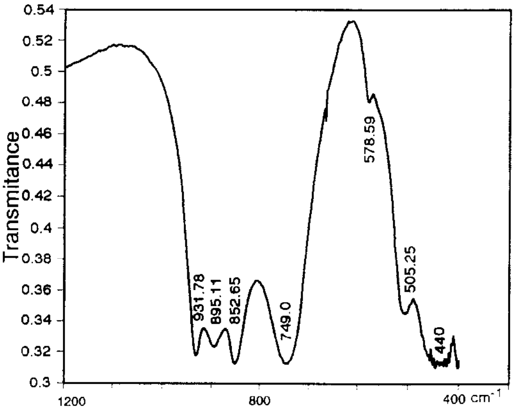

FIG. 3. Infrared spectrum of $BiMg_2VO_6$.

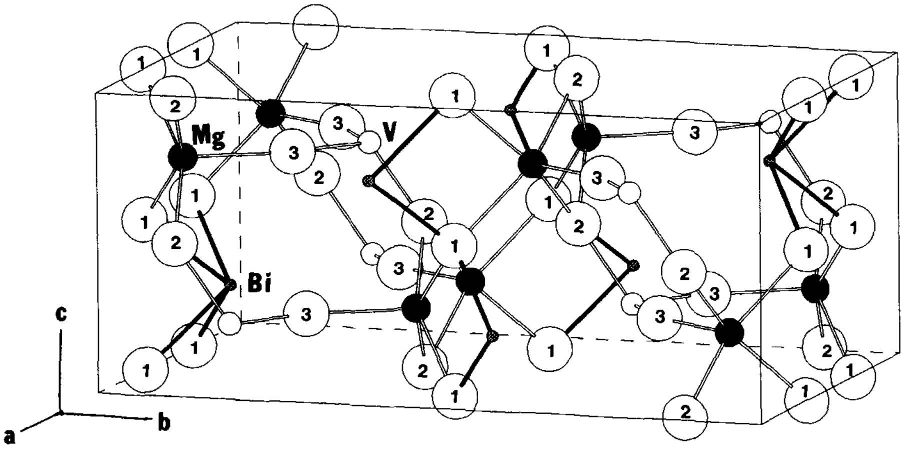

FIG. 4. Labeled sketch of the contents of a unit cell of $BiMg_2VO_6$. The big circles with numbers are oxygen atoms.

nately displaced 1.1 Å above and below the plane of the oxygen atoms (Fig. 5). This is essentially the same arrangement for bismuth as found in the Bi_2O_2 sheets of the Aurivilluis phases (*18*, *19*). The oxygen coordination to bismuth is 4 in the Bi_2O_2 sheets but is only 2 in the BiO_2 chains of $BiMg_2VO_6$. Another difference between

TABLE III

POSITIONAL PARAMETERS AND B_{eq} FOR $BiMg_2VO_6$

Atom	Site	x	y	z	$B_{eq}{}^a$
Bi	4c	1/2	0.09221(2)	1/4	0.62(1)
V	4c	0	0.1979(1)	1/4	0.70(3)
Mg	8g	0.3084(3)	0.4113(2)	1/4	0.67(5)
O(1)	8e	0.3319(5)	0	1/2	0.7(1)
O(2)	8f	0	−0.1163(4)	0.492(1)	0.9(1)
O(3)	8g	0.673	−0.2242(7)	1/4	3.3(3)

$^a B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

TABLE IV

ANISOTROPIC THERMAL PARAMETERS (Å²) FOR THE ATOMS OF $BiMg_2VO_6$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.0081(1)	0.0076(2)	0.0079(2)	0	0	0
V	0.0127(5)	0.0067(5)	0.0072(6)	0	0	0
Mg	0.0035(7)	0.013(1)	0.009(1)	0.0002(6)	0	0
O(1)	0.004(1)	0.016(2)	0.007(2)	0	0	0.000(1)
O(2)	0.006(1)	0.020(2)	0.010(2)	0	0	0.005(2)
O(3)	0.063(5)	0.048(4)	0.016(3)	−0.049(4)	0	0

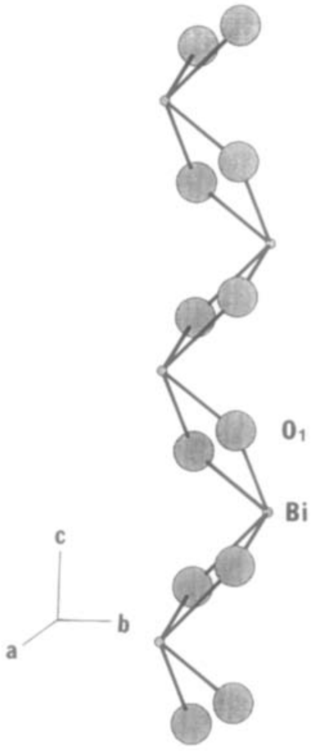

FIG. 5. Chain structure formed from BiO_4 square pyramids.

$BiMg_2VO_6$ and the Aurvillius phases is the presence of a fifth oxygen bound to Bi of the Bi_2O_2 sheets which is not present in $BiMg_2VO_6$. Thus, the bismuth coordination in the Bi_2O_2 sheets is properly regarded as 5 while it is only 4 in $BiMg_2VO_6$. The Bi–O distance in the Bi_2O_2 sheets is about 2.31 Å, whereas it is only 2.21 Å in the chains of $BiMg_2VO_6$. We attribute this shorter distance to the lower coordination numbers of both bismuth and oxygen.

The Mg atom bonds to five oxygen atoms with Mg–O bond lengths ranging from 1.973(7) to 2.066(3) Å and forms an irregular square pyramidal coordination polyhedron. Two O(1) and two O(2) atoms form the distorted square. The Mg atom is about 0.4 Å above the square, and O(3) completes the coordination around Mg. As might be expected from the repulsions between oxygens around Mg, the Mg–O(3) bond length (1.973 Å) is shorter than the others (two at 2.036 Å and two at 2.066 Å). The Mg–O distances in $BiMg_2VO_6$ are very close to those observed in the five-coordinate Mg-containing compounds $Mg[Me_3AsO)_5](ClO_4)_2$ (1.92 to 2.05 Å) (*20*) and $Mg_3Ti_4P_6O_{24}$ (2.0021 to 2.1182 Å) (*21*) and are reasonable compared to the sum of crystal radii for Mg^{II} and O^{-II} for the four-coordinate case (1.87 Å) and for the six-coordinate case (2.16 Å) (*22*).

The V atom coordinates to four O atoms

TABLE V

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $BiMg_2VO_6$

Bi–O(1) × 4	2.213(2)	Mg–O(1) × 2	2.066(3)
		–O(2) × 2	2.036(4)
		–O(3)	1.973(7)
V–O(2) × 2	1.725(5)		
–O(3) × 2	1.672(6)		
O(1) – Bi – O(1) × 2	75.91(9)	O(1) – Bi – O(1) × 2	118.63(7)
O(1) – Bi – O(1) × 2	73.9(2)		
O(2) – V – O(2)	109.2(4)	O(3) – V – O(3)	110.4(7)
O(2) – V – O(3) × 4	109.3(2)		
O(1) – Mg – O(1)	82.4(1)	O(1) – Mg – O(2) × 2	156.0(2)
O(1) – Mg – O(2) × 2	93.5(2)	O(1) – Mg – O(3) × 2	98.7(3)
O(2) – Mg – O(2)	80.6(2)	O(2) – Mg – O(3) × 2	105.3(3)

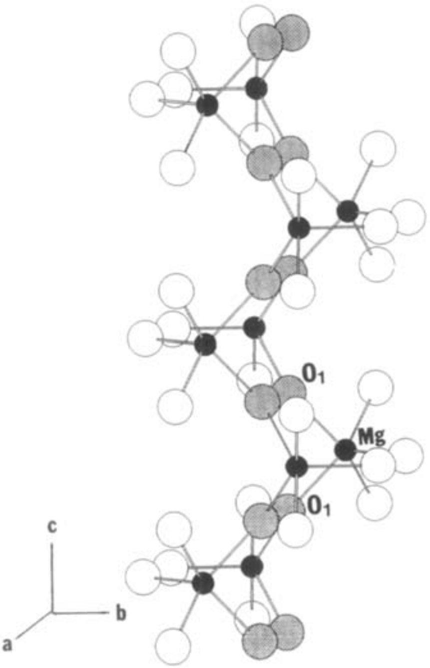

FIG. 6. Chain structure formed from MgO$_5$ square pyramids.

with V–O distances from 1.672(6) to 1.725(5) Å. All the O–V–O angles are very close to the value of an ideal tetrahedral VO$_4$ group.

The O(1) atom coordinates to two Bi and two Mg atoms, forming an irregular OM$_4$ tetrahedron; the M–O–M angles are in the range of 100.7°(5) to 117.4°(6). The coordination number of the O(2) atom is 3: one bond to V and two bonds to Mg, and the values of three M–O(2)–M angles [two V–O(2)–Mg at 128.5°(1) and one at Mg–O(2)–Mg at 96.3(2)] indicate that three O–M bonds are almost in a plane. The O(3) atom only bonds to two cations (V and Mg); the V–O–Mg angle is 157.6°(7).

The formula of BiMg$_2$VO$_6$ can be rewritten as (BiO$_2$)$^-$Mg$_2^{2+}$(VO$_4$)$^{3-}$ to stress the strong covalent bonding within the BiO$_2$ chains and within the VO$_4$ tetrahedra which are isolated from each other. The bonds of magnesium would then be described as ionic bonds to oxygens which are covalently bound to either bismuth or vanadium. This view allows for some understanding of the unusual coordination of Mg. Cations residing in a network of covalently bonded atoms frequently have unusual, low symmetry environments, e.g., alkali cations in zeolites.

We may also consider the structure of BiMg$_2$VO$_6$ in terms of the linking of the MgO$_5$ polyhedra. The MgO$_5$ square pyramids share corners to form a zigzag MgO$_4$ chains along the *c* axis (Fig. 6). The BiO$_2$ and MgO$_4$ chains thus are parallel to each other and share O(1) between them (Fig. 7). The three-dimensional structure of BiMg$_2$VO$_6$ is constructed by the connection of the BiO$_2$ and MgO$_4$ chains through the VO$_4$ tetrahedra and edge sharing of the MgO$_5$ polyhedra (Fig. 8).

Discussion

The environment of bismuth is not close to being an inversion center; thus, we do

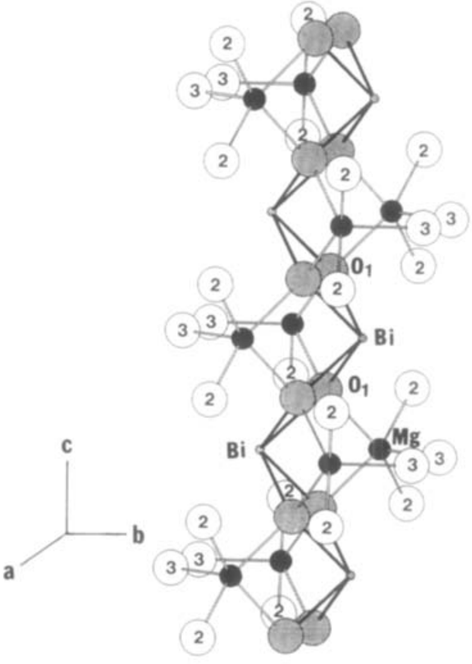

FIG. 7. The basic structure unit of the 2MgO$_4$–BiO$_2$ chain.

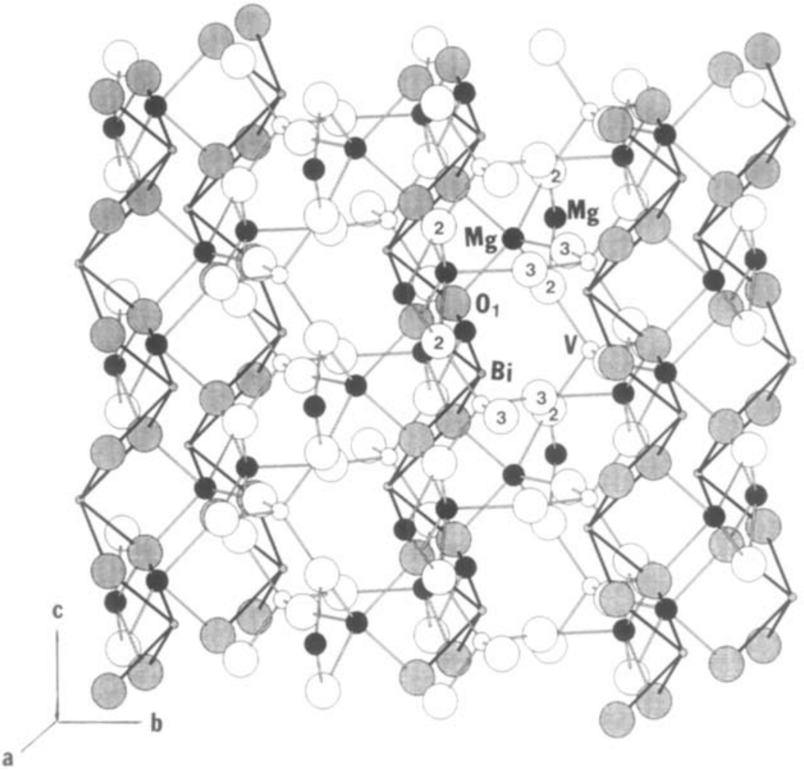

FIG. 8. Full structure of $BiMg_2VO_6$ showing several unit cells.

not expect the structural instability usually observed when Bi^{III} sits at or very close to an inversion center. There is, however, a suggestion of a structural instability in the large thermal parameter for O(3). This oxygen is bound to only two atoms, V and Mg. Therefore, its thermal parameter is expected to be larger than that of O(1) and O(2) which are bound to four and three atoms, respectively. Furthermore, the thermal amplitude is primarily perpendicular to a line connecting Mg and V as expected. A crystallographic study with data collected at low temperatures would be necessary to obtain a good understanding of this situation.

The absorption edge estimated from the PDS technique is about 450 nm, corresponding to a band gap of about 2.75 eV. The excitation–emission spectrum gives the excitation peak at about 450 nm and the luminescence peak at about 650 nm. The excitation peak starts at 450 nm which is consistent with the result from PDS measurement. Details of the electronic band structure and the explanation of these observed results for the title compound will be given in a forthcoming report (*17*).

The stretching frequencies of V–O bonds are usually in the range 1040 to 620 cm^{-1} for four-coordinated vanadium, and the stretching frequencies for Bi–O bonds are below 630 cm^{-1} (*23*). Although we are unable to give definitive assignments to the IR absorption bands, from the reported spectra of Bi-containing oxides and V-containing oxides, we believe those bands above 740 cm^{-1} are related to the stretching modes of the VO_4 group and that the 505.25 and 578.59 cm^{-1} bands may come from the stretching of Bi–O bonds. The broadband around 440

cm^{-1} may be assigned to the antisymmetric VO_4 bending mode. The unusual large splittings of VO_4 stretching bands of $BiMg_2VO_6$ are due to the C_{2v} distortion of the VO_4 group. Similar splittings were observed in $TlVO_4$ and $InVO_4$ (*24*).

Acknowledgments

This work was supported by the Oregon Metals Initiative which is funded through partnership with the Oregon Economic Development Department and Oregon Lottery, the U.S. Bureau of Mines, Teledyne Wah Chang Albany, and Pacific Power and Light.

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