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Synthesis and Characterization of Bismuth Magnesium Phosphate and Arsenate: $BiMg_2PO_6$ and $BiMg_2AsO_6$

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Two new compounds, $BiMg_2PO_6$ and $BiMg_2AsO_6$, have been synthesized and structurally characterized by single crystal and powder X-ray diffraction. Both compounds crystallize in the orthorhombic space group *Cmcm* (No. 63) with four formula units per unit cell. They are isostructural with bismuth magnesium vanadate, $BiMg_2VO_6$. The cell parameters for $BiMg_2PO_6$ are $a = 7.801(2)$, $b = 11.888(3)$, $c = 5.273(2)$ Å, $V = 489.0(2)$ Å^3 and for $BiMg_2AsO_6$ are $a = 7.9142(5)$, $b = 12.1637(8)$, $c = 5.3898(4)$ Å, $V = 518.9(2)$ Å^3. The formula for this series of compounds may be written as $(BiO_2)MgAO_4$ to emphasize the $(BiO_2)^{1-}$ chains and the $(AO_4)^{3-}$ tetrahedral groups isolated from one another. Between these chains and tetrahedral groups sit Mg^{2+} cations in an unusual fivefold coordination to oxygen. No emission bands were observed from $BiMg_2PO_6$ and $BiMg_2AsO_6$ under excitation with UV or visible radiation. The IR spectra of these compounds are compared to that of $BiMg_2VO_6$.

Introduction

The structure of $BiMg_2VO_6$ was recently reported (*1*). This structure is unusual in that the magnesium cations are coordinated to five oxygens. Furthermore, this structure contains a new motif in the form of $(BiO_2)^-$ chains. In view of the unusual structural features of $BiMg_2VO_6$, possible isostructural compounds were sought. Here we report the structure of the new compounds $BiMg_2PO_6$ and $BiMg_2AsO_6$.

Experimental

(*1*). *Synthesis*

The powder samples of $BiMg_2PO_6$ and $BiMg_2AsO_6$ were prepared by solid state reactions. The reactants were Bi_2O_3 (J. T. Baker Inc., 99.6%), reagent MgO (J. T. Baker Inc.), and reagent $(NH_4)_2HPO_4$ (E. M. Science) or As_2O_5 (Johnson Matthey Electronics). Combined differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) experiments at a heating rate of 15°C/min were first performed on each stoichiometric mixture of the reagents to investigate the appropriate reaction conditions for synthesis. In the mixture of $\frac{1}{2}Bi_2O_3 + 2MgO + (NH_4)_2HPO_4$, the decomposition of $(NH_4)_2HPO_4$ started at 160°C and completed at about 400°C. The product $BiMg_2PO_6$ melts congruently at 1170°C. From the DTA results, there is no significant thermal event related to the solid state reaction which suggests a small enthalpy change for this reaction. The mixture of Bi_2O_3 + $4MgO + As_2O_5$ showed no discernible thermal events on heating except for the melting of Bi_2O_3, but the melting point of $BiMg_2AsO_6$ was estimated to be 1160°C.

For the synthesis of $BiMg_2PO_6$, a mixture of Bi_2O_3, MgO, and $(NH_4)_2HPO_4$ with a Bi : Mg : P ratio of 1 : 2 : 1 was ground in an agate mortar under hexane and then heated at 400°C for 2 hr to decompose the $(NH_4)_2HPO_4$. After grinding, it was heated

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at 700°C for 12 hr, 800°C for 12 hr, 1000°C for 12 hr and was ground at the end of each period of the heating. The synthesis of $BiMg_2AsO_6$ was carried out in two ways: one preparation was in air with a 5% excess of As_2O_5 and another preparation was in a sealed quartz tube. The reaction conditions for the preparation in air were similar to those of the Bi–Mg–P–O system, while the preparation in a sealed quartz tube involved heating predried reagents at very low rate (5°C/hr) and holding at 200°C for 12 hr, 300°C for 12 hr, 400°C for 12 hr, 600°C for 24 hr, and 800°C for 72 hr. The main products from these procedures are the title compounds; only a small amount of Bi_2O_3 impurity was identified from the X-ray powder patterns.

The single crystals of $BiMg_2PO_6$ were grown from the melt. A polycrystalline sample of $BiMg_2PO_6$ was melted at 1230°C and was held at this temperature for 10 min, then it was cooled to 600°C at the rate of 15°C/hr and finally cooled to room temperature by simply turning the power to the furnace off. Two types of crystals were obtained from this process, light yellow needles of $BiMg_2PO_6$ and colorless crystals of $Mg_3(PO_4)_2$. Several needle crystals were analyzed with an SX-50 electron microprobe using Bi_2O_3, $CaMgSi_2O_6$, and $Ca_5(PO_4)_3(F_{0.5}Cl_{0.5})$ as standards for Bi, Mg, and P; the averaged results indicated a Bi : Mg : P ratio of 1 : 2 : 1.

(2). *Structure Analysis*

A crystal of $BiMg_2PO_6$ was mounted on a glass fiber for data collection. Details of the data collection, reduction, and refinement are summarized in Table 1. The cell dimensions were determined by a least-squares analysis of 19 reflections that had been centered on a Rigaku AFC6R diffractometer in the range of $25.18 < 2\theta < 47.69°$. The data were collected with the ω-2θ scan technique at a scan width $\Delta\omega = (1.10 + 0.3 \tan \theta)°$. The intensities of three standard reflections, measured every 300 reflections throughout data collection, exhibited no significant fluctuation.

TABLE 1

CRYSTAL DATA AND INTENSITY COLLECTION FOR $BiMg_2PO_6$

Color	light yellow
Size, mm	0.15 × 0.15 × 0.15
Crystal system	Orthorhombic
Space group	*Cmcm* (No. 63)
a (Å)	7.801(2)
b (Å)	11.888(3)
c (Å)	5.273(2)
Volume (Å^3)	489.0(2)
Z	4
Formula weight	384.56
Calculated density, g/cm^3	5.223
Diffractometer	Rigaku AFC6R
Radiation	Mo$K\alpha$ (λ = 0.71069 Å) Graphite-monochromated
Temperature	23°C
μ (Mo), cm^{-1}	364.77
Maximum 2θ (°)	70.0
Data collected	$-12 \le h \le 12$, $0 \le k \le 19$, $-8 \le l \le 8$
Scan method	$\omega - 2\theta$
Scan speed (deg/min)	16.0 in ω, and 32 in 2θ
No. of data collected	2251
No. unique data with $F_0^2 > 3\sigma(F_0^2)$	648
R_{int}	0.063
Absorption correction	DIFABS
Transmission factors, range	0.77–1.21
Refinement method	full-matrix least-squares on $\|F\|$
Parameters varied	33
Data/parameter ratio	17.18
R	0.031
R_w	0.038
Goodness of fit indicator	1.48
Secondary extinction coeff., mm	3.4731×10^{-6}

The crystal structure of $BiMg_2PO_6$ was solved and refined based on the single crystal X-ray diffraction data with the programs from TEXSAN crystallographic software package (*2*). The positions of three heavy atoms determined from direct methods SHELXS (*3*) are identical to those of $BiMg_2VO_6$. Therefore, the starting structure model for the least-squares refinement was

TABLE II

POSITIONAL PARAMETERS AND B_{eq}

Atom	Site	x	y	z	B_{eq}[a] (Å^2)
			A. $BiMg_2PO_6$		
Bi	4c	$\frac{1}{2}$	0.09642(3)	$\frac{1}{4}$	0.48(2)
P	4c	0	0.1979(2)	$\frac{1}{4}$	0.49(8)
Mg	8g	0.3040(4)	0.4022(2)	$\frac{1}{4}$	0.5(1)
O(1)	8e	0.3295(7)	0	$\frac{1}{2}$	0.7(2)
O(2)	8f	0	−0.1242(5)	0.509(1)	0.7(2)
O(3)	8g	0.664(1)	−0.2322(6)	$\frac{1}{4}$	2.2(3)
			B. $BiMg_2AsO_6$		
Bi	4c	$\frac{1}{2}$	0.0930(4)	$\frac{1}{4}$	0.34(8)
As	4c	0	0.1987(9)	$\frac{1}{4}$	1.2(3)
Mg	8g	0.305(2)	0.408(2)	$\frac{1}{4}$	0.9(4)
O(1)	8e	0.329(5)	0	$\frac{1}{2}$	0.7(8)
O(2)	8f	0	−0.118(3)	0.491(6)	0.7(8)
O(3)	8g	0.673(7)	−0.229(5)	$\frac{1}{4}$	3.0(16)

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

taken from $BiMg_2VO_6$ (*1*). After the refinement of the model with isotropic thermal parameters on each atom, an empirical absorption correction using the program DIFABS (*4*) was applied. The data were also corrected for Lorentz and polarization effects. Final least-squares refinement on $|F|$ with anisotropic thermal parameters on each atom resulted in the final residuals $R = 0.031$ and $R_w = 0.038$. The final atomic positional and isotropic thermal parameters are given in Table IIA, and the anisotropic thermal parameters are given in Table III.

An X-ray powder diffraction pattern of $BiMg_2PO_6$ sample was obtained on a Siemens D5000 diffractometer with Si as an internal standard. The observed *d* spacings and intensities are given in Table IV. 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 (*5*), and this result is also given in Table IV. The agreement between the calculated and the experimental diffraction pattern is very good.

The crystal structure of $BiMg_2AsO_6$ was refined from X-ray powder diffraction data obtained from a Siemens D5000 diffractometer with Cu$K\alpha$ radiation. The data were collected at room temperature in the 2θ range of 2° to 150° and increments of 0.02°

TABLE III

ANISOTROPIC THERMAL PARAMETERS (Å^2) FOR THE ATOMS OF $BiMg_2PO_6$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	0.0064(2)	0.0055(2)	0.0064(2)	0	0	0
P	0.008(1)	0.005(1)	0.006(1)	0	0	0
Mg	0.004(1)	0.010(1)	0.006(1)	0.0004(8)	0	0
O(1)	0.006(2)	0.011(2)	0.008(8)	0	0	0.000(2)
O(2)	0.007(2)	0.011(2)	0.008(2)	0	0	0.004(2)
O(3)	0.033(4)	0.025(4)	0.025(3)	−0.026(3)	0	0

TABLE IV

INDEXED X-RAY POWDER PATTERN FOR $BiMg_2PO_6$ AND $BiMg_2AsO_6$ ($CuK\alpha_1$)

	$BiMg_2PO_6$				$BiMg_2AsO_6$		
h k l	Calcd. d (Å)	Calcd. I/I_0	Obsd. d	Obsd. I/I_0	Obsd. d (Å)	Calcd. I/I_0	Obsd. I/I_0
1 1 0	6.522	92	6.524	85	6.634	61	66
0 2 0	5.944	9	5.946	8	6.082	4	3
1 1 1	4.101	19	4.102	19	4.183	3	4
0 2 1	3.947	39	3.944	38	4.034	40	42
2 0 0	3.901	31	3.902	33	3.955	36	37
0 4 0	2.972	10	2.973	9	3.041	6	6
1 3 1	2.935	100	2.936	100	2.999	100	100
2 2 1	2.774	91	2.774	90	2.825	84	81
0 0 2	2.637	20	2.636	21	2.695	21	22
0 4 1	2.589	4	2.590	4	2.648	1	1
3 1 0	2.540	9	2.542	10	2.578	6	6
1 1 2	2.444	23	2.444	23	2.497	16	18
2 4 0	2.364	14	2.366	13	2.411	9	11
3 1 1	2.289	7	2.290	7	2.326	1	1
1 5 0	2.274	11	2.275	10	2.325	13	14
2 0 2	2.184	9	2.186	10	2.227	12	13
2 4 1	2.157	10	2.158	9	2.201	5	6
3 3 1	2.010	11	2.012	11	2.046	14	13
0 6 0	1.981	6	1.982	5	2.027	5	5
0 4 2	1.972	7	1.973	6	2.017	4	4
4 0 0	1.950	8	1.952	7	1.979	9	7
3 1 2	1.829	25	1.831	23	1.863	18	18
2 6 0	1.767	4	1.767	3	1.804	3	3
3 5 0	1.755	17	1.756	18	1.788	16	16
4 2 1	1.748	15	1.750	13	1.776	14	14
1 5 2	1.722	20	1.723	19	1.761	22	23
0 2 3	1.686	4	1.686	3	1.723	4	4
4 4 0	1.631	6	1.632	5	1.658	3	3
0 6 2	1.584	9	1.584	21	1.620	6	7
1 7 1	1.583	11			1.618	5	5
1 3 3	1.574	16	1.575	15	1.608	14	14
4 0 2	1.568	6	1.569	5	1.595	7	7
2 2 3	1.547	15	1.548	15	1.580	14	14

with a counting time of 10 sec per step. All the reflections can be indexed with orthorhombic cell in the space group *Cmcm*, and the compound appeared to be isostructural with $BiMg_2VO_6$ and $BiMg_2PO_6$. Thus, we used the structural parameters of $BiMg_2VO_6$ as the starting model. The structure refinement was carried out with the Rietveld method using the GSAS program (*6*). A pseudo-Voigt profile-function without crystallite preferred orientation was used. Final least-squares refinement on 300 reflections with 15 structural parameters and 3 cell parameters resulted in the final residuals R_I =

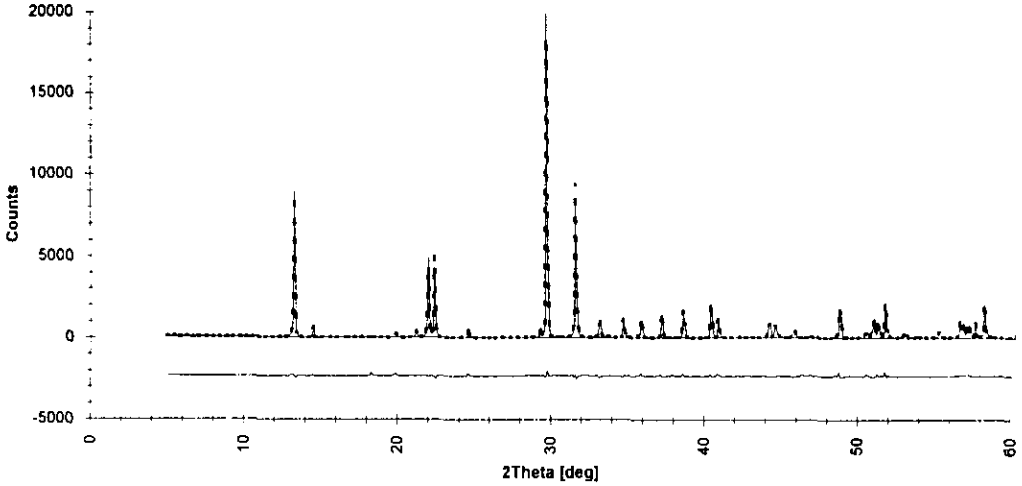

FIG. 1. Observed, calculated, and difference X-ray powder diffraction of $BiMg_2AsO_6$.

6.31, $R_P = 14.1$, $R_{WP} = 19.62$, and $R_F = 7.88$. The refined cell dimensions are $a = 7.9142(5)$, $b = 12.1637(8)$, $c = 5.3898(4)$ Å and $V = 518.9(2)$ Å^3. Table IV gives the d values and the observed and the calculated intensities. Figure 1 shows the observed pattern in the range of 5° < 2θ < 60°, as well as the calculated and difference patterns

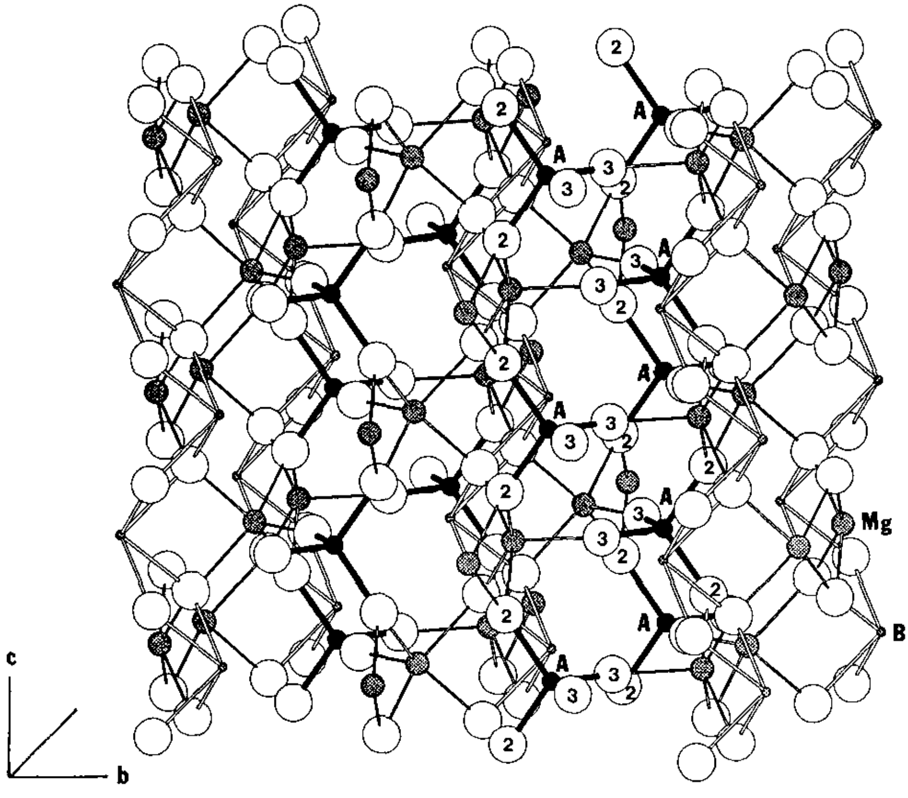

FIG. 2. Full structure of $BiMg_2AO_6$ showing several unit cells and AO_4^{3-} groups.

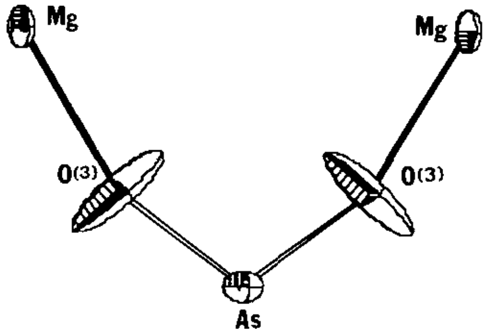

FIG. 3. Vibrational ellipsoids for O(3) and linked atoms.

from the final refinement. Table IIB gives the atomic positional and isotropic thermal parameters.

(3). Spectroscopy Analysis

The fluorescence properties of $BiMg_2PO_6$ and $BiMg_2AsO_6$ were examined using a grating monochromator and an AMINCO photomultiplier interfaced with a computer. Light from a xenon lamp dispersed by a grating monochromator was used as the source of excitation. The infrared spectra of these compounds in KBr pellets were obtained on a Nicolet-5PC FTIR spectrometer.

Results and Discussion

Figure 2 shows the structure for $BiMg_2AO_6$ compounds with the BiO_2 chains running along the *c* axis. All bismuth atoms and all oxygen atoms of these chains are crystallographically equivalent. There is only one type of AO_4 tetrahedral unit, and its true symmetry is reduced to *C2v*. The Mg^{2+} cations bond to oxygens of the BiO_2 chains and to both types of oxygen of the AO_4 units. The coordination numbers for

TABLE V

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)

	A. $BiMg_2PO_6$		
Bi –O(1) × 4	2.196(3)	Mg –O(1) × 2	2.043(4)
		–O(2) × 2	2.073(4)
		–O(3)	1.935(7)
P –O(2) × 2	1.545(5)		
–O(3) × 2	1.526(7)		
O(1)–Bi–O(1) × 2	73.8(1)	O(1)–Bi–O(1) × 2	117.1(1)
O(1)–Bi–O(1) × 2	74.6(2)		
O(2)–P–O(2)	111.04(4)	O(3)–P–O(3)	114.0(7)
O(2)–P–O(3) × 4	108.0(2)		
O(1)–Mg–O(1)	80.4(2)	O(1)–Mg–O(2) × 2	152.5(2)
O(1)–Mg–O(2) × 2	92.2(2)	O(1)–Mg–O(3) × 2	100.5(3)
O(2)–Mg–O(2)	82.3(3)	O(2)–Mg–O(3) × 2	106.9(3)
	B. $BiMg_2AsO_6$		
Bi –O(1) × 4	2.22(1)	Mg –O(1) × 2	2.046(9)
		–O(2) × 2	2.045(9)
		–O(3)	1.958(9)
As –O(2) × 2	1.706(10)		
–O(3) × 2	1.631(10)		
O(1)–Bi–O(1) × 2	75.3(5)	O(1)–Bi–O(1) × 2	118.7(6)
O(1)–Bi–O(1) × 2	74.6(6)		
O(2)–As–O(2)	109.6(4)	O(3)–As–O(3)	114.4(9)
O(2)–As–O(3) × 4	108.2(9)		
O(1)–Mg–O(1)	82.4(9)	O(1)–Mg–O(2) × 2	153.2(8)
O(1)–Mg–O(2) × 2	93.1(8)	O(1)–Mg–O(3) × 2	101.0(9)
O(2)–Mg–O(2)	82.3(8)	O(2)–Mg–O(3) × 2	105.8(8)

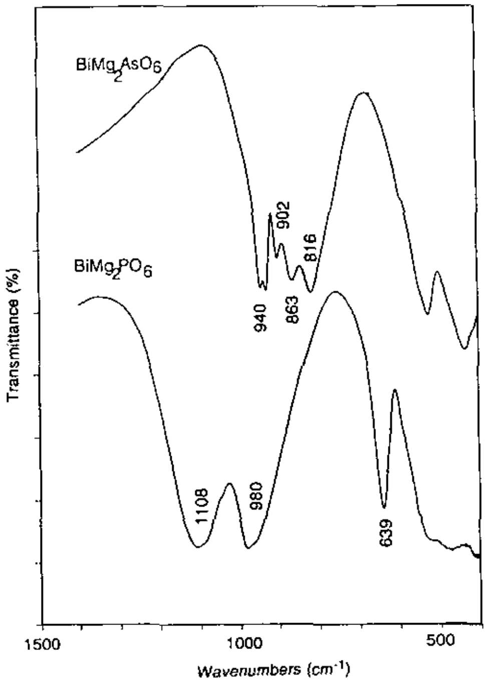

FIG. 4. Infrared spectra of $BiMg_2PO_6$ and $BiMg_2AsO_6$.

O(1) and O(2) are 4 and 3, respectively. The coordination number of O(3) is only 2, and a high thermal parameter is found in all three cases, i.e., $BiMg_2AO_6$ where A is V, P, or As. Examination of the anisotropic thermal parameters shows that this vibration is basically perpendicular to the metal oxygen bonds as expected (Fig. 3).

The unit cell volumes of the $BiMg_2AO_6$ compounds increase with increasing size of the A cation as expected. One might have expected a relatively smaller expansion along the c axis due to the BiO_2 chains running along this direction. However, the expansion is about the same in all directions, and much of the expansion along the BiO_2 chains is due to an increase in the Bi–O bond length (Tables VA and VB).

The IR spectra of $BiMg_2PO_6$ and $BiMg_2AsO_6$ are given in Figure 4. The profile of the spectra below 600 cm^{-1} for all three spectra are very similar, and we believe that these bands arise mainly from the Bi–O vibrations. The absorption bands above 600 cm^{-1} are related to the vibrations of the AO_4^{3-} group. The A atom sits at a $C2v$ symmetry site; therefore, we expect eight IR active ($4A1 + 2B1 + 2B2$) and one Raman active ($A2$) vibrational modes. The frequencies of the bending modes for T_d symmetry VO_4^{3-} and AsO_4^{3-} are well below 700 cm^{-1} (*7, 8*), and the symmetry of the AO_4^{3-} group in $BiMg_2AO_6$ compounds is same as that of the $C2v$ symmetry of SF_4 (*9, 10*). Therefore, we can assign the four bands of $BiMg_2VO_6$ as: 931 cm^{-1} (ν_1), 895 cm^{-1} (ν_8), 852 cm^{-1} (ν_6), 749 cm^{-1} (ν_3). And similarly, for $BiMg_2AsO_6$, 940 cm^{-1} (ν_1), 902 cm^{-1} (ν_8), 863 cm^{-1} (ν_6), 816 cm^{-1} (ν_3). The splitting around 940 cm^{-1} in the spectrum of $BiMg_2AsO_6$ may be due to the coupling to the lattice mode. The spectrum of $BiMg_2PO_6$ is very simple and suggests a higher symmetry of PO_4^{3-} group. From Table VA it is clear that the distortion of PO_4^{3-} group is much smaller if one considers that the four P–O bond lengths are almost equivalent. Therefore, it is a good approximation to use T_d symmetry to assign the three observed IR absorption bands as: 1108 cm^{-1} (ν_3), 980 cm^{-1} (ν_1), and 639 cm^{-1} (ν_4), and the broadening of the first two peaks is due to the distortion from the ideal T_d symmetry. No emission band was observed under the excitation of UV and visible radiation.

Attempts to synthesize the derivatives with Cu, Ni, Co, Zn substituting for Mg were made. No completely isostructural compounds were identified. However, the Cu substituted compound, $BiCu_2VO_6$, crystallizes in the orthorhombic system, and the cell dimensions obtained from the single crystal X-ray diffraction data are $a = 7.821(5)$, $b = 12.407(8)$, $c = 5.269(4)$ Å, $V = 511.3(2)$ Å^3, $Z = 4$, but the space group is now $C222_1$. The Zn substituted compound, $BiZn_2PO_6$, apparently has a monoclinic structure; the cell dimensions determined from powder X-ray diffraction data are $a = 11.575$, $b = 11.907$, $c = 7.904$ Å, $\beta = 97.35°$ and $V = 1080.4$ Å^3. Details about the structures of these compounds will be discussed in forthcoming reports.

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