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$[Bi_{12}O_{14}E_{12}]_n$ Columns and Lone Pairs E in $Bi_{13}Mo_4VO_{34}E_{13}$: Synthesis, Crystal Structure, and Chemistry of the Bi_2O_3–MoO_3–V_2O_5 System

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DEDICATED TO JOACHIM STRÄHLE ON HIS 60TH BIRTHDAY

A new phase, $Bi_{13}Mo_4VO_{34}E_{13}$ (E: Bi(III) lone pair) was found in the Bi_2O_3–MoO_3–V_2O_5 system and its formula determined via single crystal analysis and confirmed by solid state synthesis. It crystallizes in the monoclinic system, space group $P2/c$, with cell parameters $a = 11.652(7)$ Å, $b = 5.7923(8)$ Å, $c = 24.420(9)$ Å, $\beta = 101.38(6)^\circ$, and $Z = 2$. The crystal structure is built up by infinite $[Bi_{12}O_{14}E_{12}]_n$ columns surrounded by 10 (Mo, V)O_4 tetrahedra, situated on layers parallel to (100) and (001), with an extra Bi atom located at the intersection of these "(Mo, V)O_4 layers" in between two tetrahedra. The $Bi_{13}Mo_4VO_{34}E_{13}$ structure is in general agreement with that of R. N. Vannier *et al.* (1996, *J. Solid State Chem.* 111, 118) giving a structural formulation $Bi_{26}M_{10}O_{68}$ but with their chemical formulations giving $Bi_{26}Mo_{10}O_{69}$ or $Bi_{26}Mo_6V_4O_{67}$ and hypothetical nonstoichiometry $Bi_{26}M_{10}O_\delta$. Taking into account the cell dimensions and structural details of $Bi_{13}Mo_4VO_{34}E_{13}$, which show that a reported phase like $Bi_6Mo_2O_{15}$ could also be isostructural, a new hypothesis based on the possible replacement of BiO_4E trigonal bipyramid and/or BiO_3E tetrahedra for MoO_4 tetrahedra strengthens the probability that there is a continuous solid solution in the Bi_2O_3–MoO_3 system between the compositions 1.43 Bi_2O_3: 1 MoO_3 and 1.75 Bi_2O_3: 1 MoO_3. Synthesis and cell dimensions of various compositions supporting these ideas are given. The domain of existence for such phases can extend in the pseudo-ternary Bi_2O_3–MoO_3–V_2O_5 system up to the phase $Bi_{13}Mo_4VO_{34}$; this triangular area excludes $Bi_{26}Mo_{10}O_{69}$ and $Bi_{26}Mo_6V_4O_{67}$ compositions. © 1997 Academic Press

INTRODUCTION

Recently we have reported the synthesis of a new Aurivillius phase $Bi_4V_2O_{10}$ or $(Bi_2O_2)_2V_2O_6$ in which $(Bi_2O_2)_{2n}$ layers alternate with $(V_2O_6)_n$ layers; the vanadium oxidation state is IV. The $(V_2O_6)_n$ layers are built of VO_5 square pyramids sharing basal plane corners (1). This work was then extended to the $Bi_4V_2O_{10}$–$Bi_4V_2O_{11}$ system, the latter phase having been isolated and studied by several authors (2–4). A new series $(Bi_2O_2)_2V^{5+}_{2-2x}V^{4+}_{2x}O_{7-x}$ was then demonstrated to exist for $x = 0.33$, 0.50, and 0.66. This series is characterized by oxygen nonstoichiometry attributed to the simultaneous presence of VO_6 octahedra and VO_5 square pyramids (SP) in the $(V_2O_{7-x})_n$ layers and implying the presence of vanadium in two different oxidation states, V and IV. Another phase with a large homogeneity range $(Bi_2O_2)_2V_{2y}O_{4y+2}$ (with $1 \leq y \leq 4$) was found between $(Bi_2O_2)_2V_2O_6$ and vanadium dioxide VO_2. This compositional range is achieved via a continuous condensation of the vanadium oxygen network between the $(Bi_2O_2)_{2n}$ layers, with the VO_5 SP's sharing more and more edges with increasing y value (5). The series has been related to the CaV_nO_{2n+1} ($n = 2, 3, 4$) series of compounds (6).

Further extension of this work to M^*–V, Mo, W–O or related systems with ns^2 lone pair (E) elements M^* (7–8) is urgently needed. We report here the results of an investigation on the pseudo-binary system $Bi_4V_2O_{11}$–Bi_2MoO_6. The idea was to alter the layers of the transition metals $(MoO_4)_n$ and $(V_2O_7)_n$ by mixing coordination polyhedra, such systems being candidates for original physical properties.

The formula for such a system can be written formally as

$$(Bi_2O_2)_2Mo^{6+}_{2-2x}V^{5+}_{2x}O_{8-x} \quad \text{with } 0 \leq x \leq 1.$$

In fact, this study allowed us to detect from a melted mixture corresponding to $x = 0.5$, an unknown phase characterized by an original X-ray powder pattern, together with $BiVO_4$. From an X-ray single crystal study the formula of this phase was determined to be $Bi_{13}Mo_4VO_{34}$. The present paper describes the results of our chemical and structural investigations, with emphasis on the stereochemical role of the lone pair E of the bismuth atoms in their III oxidation state and the structural relationship of $(Bi_{12}O_{14}E_{12})_n$ columns of this phase with the high temperature γ form of Bi_2MoO_6.

Owing to the obvious connections with known phases of the Bi_2O_3–MoO_3 system, notably $Bi_6Mo_2O_{15}$, a chemical study of this system was made. In the meantime, a paper was published by Vannier *et al.* (9) reporting $Bi_{26}Mo_{10}O_{69}$ and $Bi_{26}Mo_6V_4O_{67}$ crystal structures, but this leads to a quite inadequate nonstoichiometry chemistry interpretation.

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EXPERIMENTAL

Samples of ternary oxides were synthesized using a solid state reaction. The starting materials Bi_2O_3, MoO_3, and V_2O_5 (99.99% Aldrich Chem. Co.) were weighed out according to the desired composition. The first mixture corresponded to the composition $Bi_8Mo_2V_2O_{23}$, i.e.,

$$2Bi_2MoO_6 + Bi_4V_2O_{11} \quad \text{or} \quad 4Bi_2O_3 + 2MoO_3 + V_2O_5 \rightarrow Bi_8Mo_2V_2O_{23}.$$

The powder mixture was ground in an agate mortar, placed in a platinum crucible, heated at 550°C for 24 hr, quenched to room temperature, heated again at 850°C for 24 hr, and cooled to room temperature at 50°C/hr. The X-ray pattern of the resulting powder, obtained with a Seifert XRD 3000 diffractometer (Cu$K\alpha$), was rather complex but included lines corresponding to the well-known phase $BiVO_4$. Despite some similarities with the powder pattern of $Bi_6Mo_2O_{15}$ (10), it was clear that an unknown phase was responsible for the other peaks of the diffractogram. On the composition line $Bi_6Mo_2O_{15}$–$BiVO_4$ of the pseudo-ternary diagram Bi_2O_3–MoO_3–V_2O_5 (Fig. 1), it can be seen that

$$Bi_6Mo_2O_{15} + 2BiVO_4 \rightarrow \text{“}Bi_8Mo_2V_2O_{23}\text{” (point P)}.$$

It was decided to grow single crystals from this mixture. To do so, the following protocol was applied: melting at 950°C for 1 hr, cooling to 900°C at 2°C/hr, cooling to 850°C at 10°C/hr, and finally cooling to room temperature at

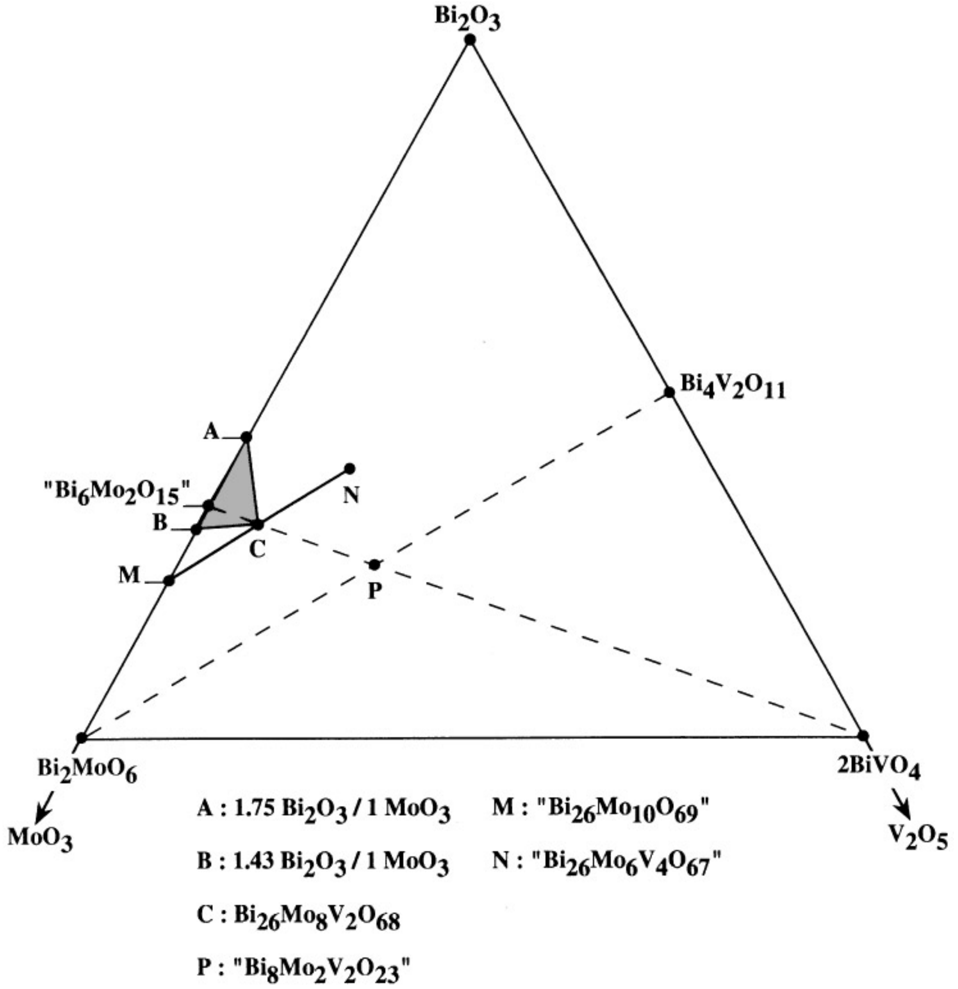

FIG. 1. Schematic representation of the Bi_2O_3–Bi_2MoO_6–2$BiVO_4$ ternary diagram. The shaded area ABC represents the possibility to have various stoichiometries between the postulated solid solution in the Bi_2O_3–MoO_3 system, i.e., $[BiE]_2[Bi_{12}O_{14}E_{12}]_2[MoO_4]_{8+1.33x}[BiO_3E]_{2(1-x)}[BiO_4E]_{0.67x}$ and the $Bi_{26}Mo_8V_2O_{68}$ phase (point C). M and N represent the Vannier's *et al.* phases. The P point is the starting mixture which gives by solid reaction a mixture of the presently reported $Bi_{26}Mo_8V_2O_{68}$ phase (point P) and $BiVO_4$.

50°C/hr. Nice yellow crystals were obtained. A single crystal was selected by studies on Weissenberg (Cu$K\alpha$) and precession (Mo$K\alpha$) cameras. It crystallized in the monoclinic system with the possible space groups $P2/c$ or Pc. The powder pattern of ground crystals was indexed with the cell parameters and the space group derived from the single crystal data (Table 1).

The structure of the single crystal was determined after data collection using an Enraf Nonius CAD4 diffractometer (Mo$K\alpha$). Experimental conditions are summarized in Table 1. The collected intensity of *hkl* reflections were corrected for the Lorentz polarization effect. Numerical absorption and secondary extinction corrections were also applied. Following an EDX investigation indicating the presence of Bi, Mo, and V atoms in this complex oxide, the relevant scattering factors including anomalous dispersion were introduced into the calculations. The structure was determined using Patterson functions followed by subsequent Fourier and difference Fourier analysis. The refinement by least squares in the space group $P2/c$, including both positions and thermal parameters of the atoms, gave a final agreement index, $R = 0.088$ (Table 1). The rough formula that emerged from this detailed structural analysis was $\mathrm{Bi}_{13}\mathrm{Mo}_4\mathrm{VO}_{34}$ with two formula units per cell. Positional and thermal parameters are listed in Table 2 and main interatomic distances in Table 3.

TABLE 1
Crystallographic Parameters of $\mathrm{Bi}_{13}\mathrm{Mo}_4\mathrm{VO}_{34}$

Crystal data	
Formula	$\mathrm{Bi}_{13}\mathrm{Mo}_4\mathrm{VO}_{34}$
Crystal system	monoclinic
Space group	$P2/c$
a [Å]	11.652(7)
b [Å]	5.7923(8)
c [Å]	24.420(9)
β [°]	101.38(6)
V [Å^3]	1616(1)
Z	2
Molecular weight	3695.4
ρ calc [g/cm^3]	7.60
μ[Mo$K\alpha$ cm^{-1}]	689
Morphology	parallelepiped
Color	yellow
Dimension (mm)	0.075×0.15×0.38
Data collection	
Temperature [°C]	20
Wavelength [Mo$K\alpha$] [Å]	0.71069
Monochromator	graphite
Scan mode	ω–2θ
Scan width [°]	$0.80+0.35\tan\theta$
Take-off-angle [°]	3.9
Max Bragg angle [°]	25
$T_{\max}$ [s]	80
Control reflections:	
Intensity (every 3600 s)	3 1 −2/6 0 −4/0 −1 −6
Orientation (every 150 refl.)	3 3 8/6 4 −6/3 5 −4
Structure refinement	
Reflections for cell refinement	25 with $6° \leq \theta \leq 19°$
Reflections collected	4875
Reflections unique measured	1634
Reflections unique used	1634
Parameters refined	141
R_{int}	0.057
Weighting w^{-1}	$\sigma^2(F)+0.0035F^2$
Secondary extinction g	7×10^{-5}
$R=\sum\lvert\lvert F_0\rvert-\lvert F_c\rvert\rvert/\sum\lvert F_0\rvert$	0.088
$R_w=[\sum w(\lvert F_0\rvert-\lvert F_c\rvert)^2/[\sum wF_0^2]^{1/2}$	0.092

DESCRIPTION OF THE STRUCTURE

A projection of the structure onto the (010) plane is shown in Fig. 2. The atom numbering scheme is presented in Fig. 3 in a partial view slightly rotated for clarity. The cell contents include:

- two infinite $(\mathrm{Bi}_{12}\mathrm{O}_{14})_n$ columns parallel to [010] containing a twofold axis, centered on the c axis at 1/4 and 3/4 and making a kind of rose in the projection along b;
- ten $(\mathrm{Mo,V})\mathrm{O}_4$ tetrahedra making a crown around these columns;
- two Bi atoms occupying (at 50%) two closed crystallographic positions around the symmetry center in site $2b$ (1/2 1/2 0 and 1/2 1/2 1/2), assuming the coherence of the network linking the crowns formed by the $(\mathrm{Mo,V})\mathrm{O}_4$ tetrahedra along both the a and the c axis in planes parallel to (100) at $c/2$ and parallel to (001) at $a/2$.

The $(\mathrm{Bi}_{12}\mathrm{O}_{14}E_{12})_n^{8n+}$ columns are built from Bi1 to Bi6 with their lone pairs E and from O1 to O8 atoms. The bismuths are situated at the corners of Bi_6 octahedra. Pairs of such Bi_6 octahedra are edge-connected in planes perpendicular to b, the direction of the edge-connection rotating 90° from level to level and being interconnected along the [010] as shown in Fig. 4. Bismuth atoms in the trivalent state have a typical one-sided coordination owing to the steric effect of their $6s^2$ lone pair E. For the sake of clarity in the description of the structure, we have deliberately chosen to label only the shortest Bi–O bonds within the columns and not longer interatomic distances between Bi's within the columns and oxygens of the $(\mathrm{Mo,V})\mathrm{O}_4$ tetrahedra. The latter interactions, while weak, nonetheless represent real interactions. The Bi1 and Bi2 atoms closest to the twofold axis and bound to O1 and O2 oxygen atoms on the twofold axis exhibit fourfold coordination, i.e., Bi1–O1, O3, O8, O7b and Bi2–O2c, O5c, O4c, O6d, forming typical distorted trigonal bipyramidal BiO_4E polyhedra. The lone pairs of both Bi1 and Bi2 point practically along the direction of the column. The other bismuths at the periphery of the column, i.e., Bi3, Bi4, Bi5, and Bi6, are threefold coordinated leading to BiO_3E tetrahedra sharing corners, the lone pairs then pointing in directions quasi-perpendicular to the column

TABLE 2
Positional and Thermal Atomic Parameters of $Bi_{13}Mo_4VO_{34}$

Atom	Site	Occ. factor	x	y	z	B_{eq} (Å^2)^a $^*B_{iso}$
Bi1	4g	1	0.0386(2)	0.4147(5)	0.3273(1)	1.1(1)
Bi2	4g	1	0.1582(2)	−0.0878(5)	0.2450(1)	1.3(1)
Bi3	4g	1	0.2377(2)	0.0066(5)	0.4004(1)	1.4(1)
Bi4	4g	1	0.3587(2)	0.4977(6)	0.3211(1)	1.4(1)
Bi5	4g	1	0.2727(2)	0.4973(5)	0.1579(1)	1.5(1)
Bi6	4g	1	−0.0826(2)	0.0027(5)	0.4099(1)	1.3(1)
Bi7	4g	0.5	0.5125(8)	0.498(2)	0.0074(4)	3.4(1)*
Mo/V1	2f	0.8/0.2	1/2	0.007(2)	1/4	2.2(2)*
Mo/V2	4g	0.8/0.2	0.1691(5)	0.514(1)	0.4875(3)	1.6(1)*
Mo/V3	4g	0.8/0.2	0.4271(6)	−0.006(1)	0.0793(3)	2.0(1)*
O1	2e	1	0	0.247(9)	1/4	0.8(9)*
O2	2e	1	0	0.710(9)	1/4	0.5(8)*
O3	4g	1	0.226(3)	0.272(6)	0.333(1)	0.1(6)*
O4	4g	1	0.238(3)	0.763(7)	0.337(2)	1.1(7)*
O5	4g	1	0.251(4)	0.588(9)	0.239(2)	3.1(9)*
O6	4g	1	0.134(4)	0.251(7)	0.653(2)	1.5(7)*
O7	4g	1	0.137(3)	0.742(7)	0.655(2)	1.0(7)*
O8	4g	1	0.061(3)	0.070(7)	0.367(2)	1.4(7)*
O9	4g	1	0.382(4)	0.182(9)	0.246(2)	3.0(9)*
O10	4g	1	0.483(8)	−0.16(1)	0.183(4)	11.0(1)*
O11	4g	1	0.382(5)	0.04(1)	0.010(3)	4.0(1)*
O12	4g	1	0.310(4)	−0.031(9)	0.100(2)	3.0(9)*
O13	4g	1	0.500(6)	0.71(1)	0.083(3)	5.0(1)*
O14	4g	1	0.466(6)	0.18(1)	0.392(3)	7.0(1)*
O15	4g	1	0.187(6)	0.45(1)	0.057(3)	6.0(1)*
O16	4g	1	0.305(5)	0.472(9)	0.466(2)	3.4(9)*
O17	4g	1	0.118(5)	0.766(9)	0.453(3)	4.0(1)*
O18	4g	1	0.084(6)	0.27(1)	0.474(3)	7.0(1)*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi1	0.012(1)	0.013(1)	0.017(1)	0.0010(9)	0.0066(9)	−0.001(1)
Bi2	0.009(1)	0.013(1)	0.026(2)	−0.0017(9)	0.0061(9)	0.000(1)
Bi3	0.015(1)	0.017(1)	0.020(1)	0.004(1)	0.0018(9)	0.000(1)
Bi4	0.005(1)	0.018(1)	0.028(1)	0.001(1)	0.0048(9)	0.002(1)
Bi5	0.007(1)	0.020(1)	0.028(1)	−0.002(1)	0.0097(9)	−0.005(1)
Bi6	0.015(1)	0.018(1)	0.015(1)	−0.003(1)	0.0070(9)	−0.003(1)

[a] $B_{eq} = 8\pi^2 U_{eq}$; $U_{eq} = 1/3$ trace U.

axis toward the space outside the columns (Fig. 5). Bi–O bond lengths range from 2.09 to 2.23 Å (the O–O interatomic distances for the whole crystal structure fall between 2.5 and 3 Å, in excellent agreement with the known values).

The (Mo, V)O_4 tetrahedra, surrounding the $(Bi_{12}O_{14}E_{12})_n$ columns, form a kind of spiral. We chose to refine the positions of the metal atoms with a combination of Mo and V reflecting the stoichiometry needed to balance the charges and in accordance with the position of the phase on the compsition line $BiVO_4$–$Bi_6Mo_2O_{15}$ in the phase diagram, i.e., 4Mo:1V (for this crystal, absorption corrections are very important and it is difficult to trust even a precise refinement with regard to the ratio Mo:V versus the B(Å^2) thermal parameter). Despite the absence of this degree of freedom, the B factors are quite reasonable, between 1.6 and 2.2 Å^2. We note that thermal vibration affects mainly the (Mo, V)1 O_4 tetrahedron which is in between the columns along [100]. Formally, the average charge of these tetrahedra is $[(Mo, V)O_4]^{2.2-}$. The electrostatic balance of the structure needs three extra positive charges—this is the role of the last bismuth atom, Bi7.

As indicated previously, Bi7 is the link between the two slabs of tetrahedra lying in the planes parallel to (100) and (001). With its lone pair E, it cannot be situated on the center of symmetry and so it occupies, at 50%,

TABLE 3
Interatomic Distances (Å) in $Bi_{13}Mo_4VO_{34}$

Bi1	O1	2.09(2)	Bi5	O5	2.10(6)
Bi1	O8	2.22(4)	Bi5	O7d	2.10(4)
Bi1	O3	2.31(3)	Bi5	O6d	2.16(4)
Bi1	O7a	2.35(4)	Bi5	O15	2.50(7)
Bi1	O2	2.52(3)	Bi6	O6d	2.12(4)
Bi2	O5b	2.19(5)	Bi6	O7a	2.17(4)
Bi2	O2b	2.21(3)	Bi6	O8	2.17(4)
Bi2	O6c	2.41(5)	Bi7	O16f	2.10(5)
Bi2	O4b	2.41(4)	Bi7	O13	2.23(7)
Bi3	O8	2.09(4)	Bi7	O16d	2.43(5)
Bi3	O4b	2.10(4)	Bi7	O13g	2.48(7)
Bi3	O3	2.23(3)			
Bi3	O17b	2.50(6)	Bi7	Bi7g	0.42(2)
Bi4	O3	2.09(3)			
Bi4	O4	2.17(4)			
Bi4	O5	2.22(5)			
MoV1	O9	1.69(5)	MoV2	O17	1.73(5)
MoV1	O9f	1.69(5)	MoV2	O16	1.79(6)
MoV1	O10	1.9(1)	MoV3	O12	1.55(5)
MoV1	O10f	1.9(1)	MoV3	O11	1.68(6)
MoV2	O15h	1.67(8)	MoV3	O14f	1.69(7)
MoV2	O18	1.70(7)	MoV3	O13b	1.86(6)

Symmetry code:
a: $-x, 1-y, 1-z$ b: $x, -1+y, z$ c: $x, -y, -1/2+z$
d: $x, 1-y, -1/2+z$ e: $-x, -y, 1-z$ f: $1-x, y, 1/2-z$
g: $1-x, 1-y, -z$ h: $x, 1-y, 1/2+z$

crystallographic sites slightly off-center (the distance between these sites is 0.42 Å). Bi7 strongly bridges the two (Mo, V)3 O_4 tetrahedra related by the symmetry center, but is also connected to the (Mo, V)2 O_4 tetrahedra via O16.

DISCUSSION

Based on this structural study, the phase $Bi_{13}Mo_4VO_{34}$ may be more precisely represented by the formula $\mathrm{Bi}E[\mathrm{Bi}_{12}\mathrm{O}_{14}E_{12}][\mathrm{Mo}_{4/5}\mathrm{V}_{1/5})\mathrm{O}_4]_5$. If the (Mo, V)$O_4$ tetrahedra and even the "isolated" Bi atoms do not show in their bonding with oxygen-distinguishable features, one should note the remarkable heavily charged columns $(\mathrm{Bi}_{12}\mathrm{O}_{14}E_{12})_n^{8n+}$, making a kind of infinite polycation similar to those existing in the high temperature form of Bi_2MoO_6 depicted by Buttrey *et al.* (11). Such original strong building units, like Aurivillius's $(\mathrm{Bi}_2\mathrm{O}_2E_2)_n^{2n+}$ layers, must surely exist in other structures. There is a need to store data on such columns in various structures if they exist to extract pertinent information on their charge and lone pair stereochemical activity.

Using our crystallographic data, there it was easy to synthesize the phase, point P in the schematic phase diagram Bi_2O_3–MoO_3–V_2O_5 (Fig. 1), by heating in air at 900°C the starting materials in a platinum crucible:

$$13\ \mathrm{Bi_2O_3} + 8\ \mathrm{MoO_3} + \mathrm{V_2O_5} \rightarrow 2\mathrm{Bi_{13}Mo_4VO_{34}}.$$

An important fact concerning this phase must be pointed out by comparing its cell parameters and space group with those reported for $Bi_6Mo_2O_{15}$ by Miyazawa *et al.* (10) (Table 4). Obviously, both the $Bi_6Mo_2O_{15}$ and $Bi_{13}Mo_4VO_{34}$ structures must be very similar. But a chemical problem arises: how can the structural composition be fitted in the system Bi_2O_3–MoO_3? The crystallographic data imply a formula $\{\mathrm{Bi}E[\mathrm{Bi}_{12}\mathrm{O}_{14}E_{12}][(\mathrm{Mo}_{4/5}, \mathrm{V}_{1/5})\mathrm{O}_4]_5\}_2$ or, for the whole cell, $\mathrm{Bi}_{26}M\mathrm{O}_{68}E_{26}$ with $M = 8\mathrm{Mo} + 2\mathrm{V}$ in the present case. The columns $[\mathrm{Bi}_{12}\mathrm{O}_{14}E_{12}]_n$ and the $[M\mathrm{O}_4]$ tetrahedra cannot be affected by oxygen nonstoichiometry; such a hypothesis would be nonsense. The closest composition of a phase in the Bi_2O_3–MoO_3 system fitting the required structure formulation is

$$13\ \mathrm{Bi_2O_3} + 10\ \mathrm{MoO_3} \rightarrow \mathrm{Bi_{26}Mo_{10}O_{69}}.$$

Such a formula implies an extra oxygen in the cell, in fact, two extra oxygen atoms, owing to the twofold symmetry. The comments of Andersson *et al.* (12) and Galy *et al.* (13) on the crystal chemical understanding of ns^2 lone pair E elements suggest that the lone pair volume is roughly equivalent to an oxygen. For the correct composition of the cell, i.e., $\mathrm{Bi}_{26}\mathrm{Mo}_8\mathrm{V}_2\mathrm{O}_{68}E_{26}$, the volume per (O, E) is 17, 2 $Å^3$—a standard value, indicating that the atomic packing is rather dense and it is rather hard to see where any additional oxygen could be added!

We therefore made a chemical hypothesis concerning the apparent formation of such phase "$Bi_{26}Mo_{10}O_{69}$" based on the fact that $\mathrm{Bi}_{26}\mathrm{Mo}_8\mathrm{V}_2\mathrm{O}_{68}E_{26}$ is the result of electrostatic charge balance stabilization by the presence of some V substituting for Mo. The "$Bi_{26}Mo_{10}O_{69}$" having been synthesized in an alumina crucible, we propose that some aluminium atoms could have substituted for Mo, the formula "$\mathrm{Bi}_{26}\mathrm{Mo}_{9.33}\mathrm{Al}_{0.66}\mathrm{O}_{68}E_{26}$" being perfectly stoichiometric as well as perfectly electrically balanced.

Following the same synthetic protocol as described above, powders of Bi_2O_3, MoO_3, and Al_2O_3 were mixed, finely ground, and heated at 900°C in a platinum crucible. Nice yellow single crystals were obtained and fully characterized by X-ray diffraction. The cell parameters and space group are reported in Table 4. Their close relationship with "$Bi_{26}Mo_{10}O_{69}$" (Table 4) prompted us to undertake a full structure determination. It was initially carefully checked by EDX on single crystals that aluminium was present. The refinement was carried out with a mixture of Mo and Al in the $M\mathrm{O}_4$ tetrahedra in the ratio $Mo_{14/15}Al_{1/15}$ or $[(Mo_{9.333}Al_{0.667})O_4]$.

The atomic architecture is very similar to that of $\mathrm{Bi}_{26}\mathrm{Mo}_8\mathrm{V}_2\mathrm{O}_{68}E_{26}$. Again we note around the strongly

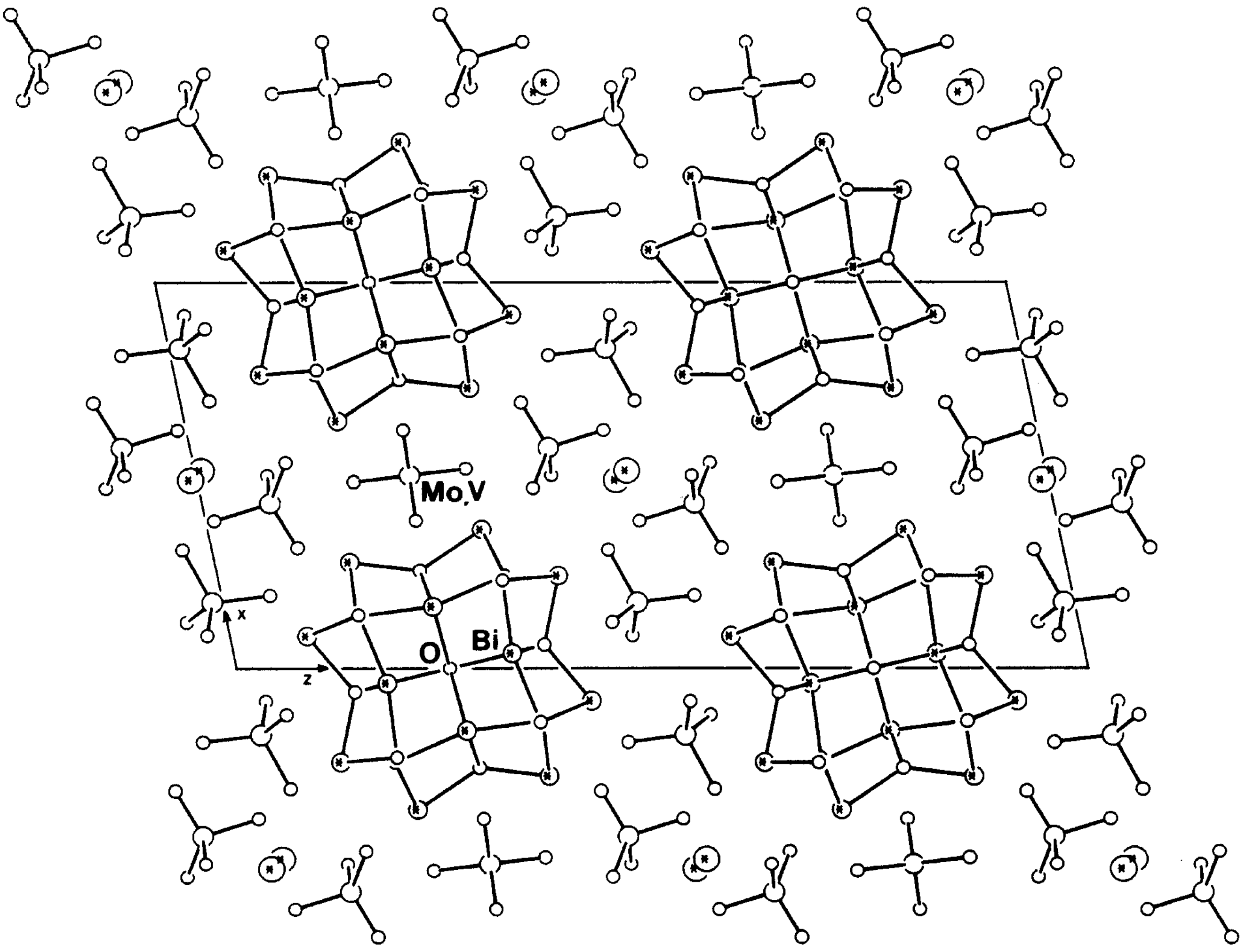

FIG. 2. Projection of the crystal structure of $Bi_{13}Mo_4VO_{34}$ onto the (010) plane.

established $(B_{12}O_{14}E_{12})_n^{8n+}$ columns the high thermal vibration of the oxygens of the (Mo, Al)O_4 tetrahedra, indicating strong libration of these polyhedra around the metal atom position.

Note that the cell parameters of $Bi_{26}(Mo, Al)_{10}O_{68}$ are larger than those of $Bi_{26}Mo_8V_2O_{68}$ and very close to those reported for "$Bi_{26}Mo_{10}O_{69}$" by Vannier *et al.* (9) (Table 4).

Have the preceding authors stabilized, by working in an alumina crucible, the phase $Bi_{26}Mo_{9.33}Al_{0.67}O_{68}E_{26}$ by a smooth attack on the Al_2O_3 container by Bi_2O_3 or MoO_3 or both oxides? We cannot tell, although such a hypothesis is clearly plausible. In any event, it is clear that the formula "$Bi_{26}Mo_{10}O_{69}$" is doubtful. We would like to propose three other possible ways by which it might be possible to explain the formation of a phase in the Bi_2O_3–MoO_3 system having the $Bi_{26}Mo_8V_2O_{68}$ structure.

The first proposal is that an extra Bi(III) is present, substituting for Mo like Al(III); then the formula would be $Bi_{26}Mo_{9.33}Bi_{0.67}O_{68}E_{26.67}$. But this idea, although possible, is difficult to justify. Bi(III) with its lone pair E is a large cation and cannot easily enter into the type of tetrahedra welcoming Mo(VI), V(V), or Al(III) in spite of large oxygen vibrations. It might be assumed that when Bi eventually substitutes totally for Mo, one of the edges of tetrahedron expands considerably with the BiE being bonded on one side to the fourth oxygen and making a distorted trigonal bipyramid BiO_4E, E situated on an apex of the equatorial plane.

Such a hypothesis would allow us to remain within the Bi_2O_3–MoO_3 system,

$$13.33\ Bi_2O_3 + 9.33\ MoO_3 \rightarrow Bi_{26}Mo_{9.33}Bi_{0.67}O_{68}E_{26.67}$$

or 1.43 Bi_2O_3:1 MoO_3, represented by point B (Fig. 1). Data of single crystals prepared close to this point are listed in Table 4. Taking into account the fact that Bi makes (BiO_4E) trigonal bipyramids larger than (AlO_4) ones, we should expect the unit cell to be expanded, which is indeed

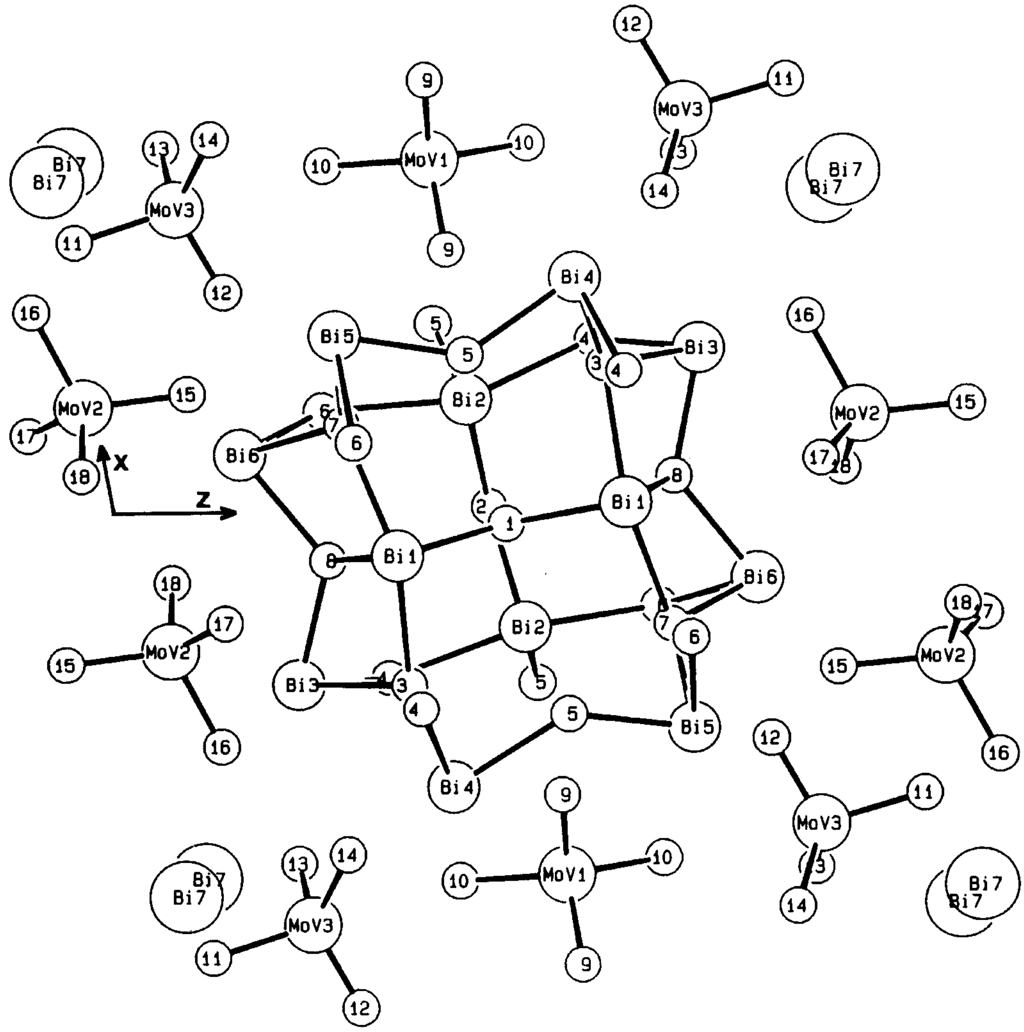

FIG. 3. View of $Bi_{13}Mo_4VO_{34}$ structure: 10 $(Mo,V)O_4$ surrounding the $(Bi_{12}O_{14})_n$ column.

the case (Table 4). We note also that the cell dimensions of such crystals are extremely close to the "$Bi_{26}Mo_{10}O_{69}$" ones (9), their composition (point M) being slightly moved toward MoO_3 in the diagram.

A second hypothesis is based on the possible substitution of BiO_3E tetrahedra for (MoO_4) tetrahedra. We note that the formal charge of $(BiO_3E)^{3-}$ units is exactly the same as $(VO_4)^{3-}$ units but of course its volume must be larger. Thus a simple formula can be proposed, following exactly the structural features,

$$[BiE]_2[Bi_{12}O_{14}E_{12}][MoO_4]_8[BiO_3E]_2,$$

i.e., $Bi_{28}Mo_8O_{66}E_{28}$. The equation of reaction would become

$$14\ Bi_2O_3 + 8\ MoO_3 \rightarrow Bi_{28}Mo_8O_{66}E_{28}$$

or 1.75 Bi_2O_3:1 MoO_3, represented by point A (Fig. 1). Again the crystal data are in agreement with our hypothesis.

The third hypothesis could be based on a partial oxidation of the samples during the synthetic process; then, starting with the same molar ratio as above, we obtain

$$14\ Bi_2O_3 + 8\ MoO_3 + O_2 \rightarrow Bi_{26}Mo_8Bi_2O_{68}E_{26},$$

in which it is necessary to propose that some Bi(III) has been oxidized to Bi(V) forming $(BiO_4)^{3-}$ tetrahedra. This phase belongs to the system Bi_2O_3–MoO_3–Bi_2O_5; the restriction on such a hypothesis is the unlikeliness of Bi(V) fourfold coordination.

To summarize, if a phase, isostructural with $Bi_{28}Mo_8V_2O_{68}E_{26}$, is formed within the Bi_2O_3–MoO_3 system, then it should have a cell composition falling between the following extreme possibilities:

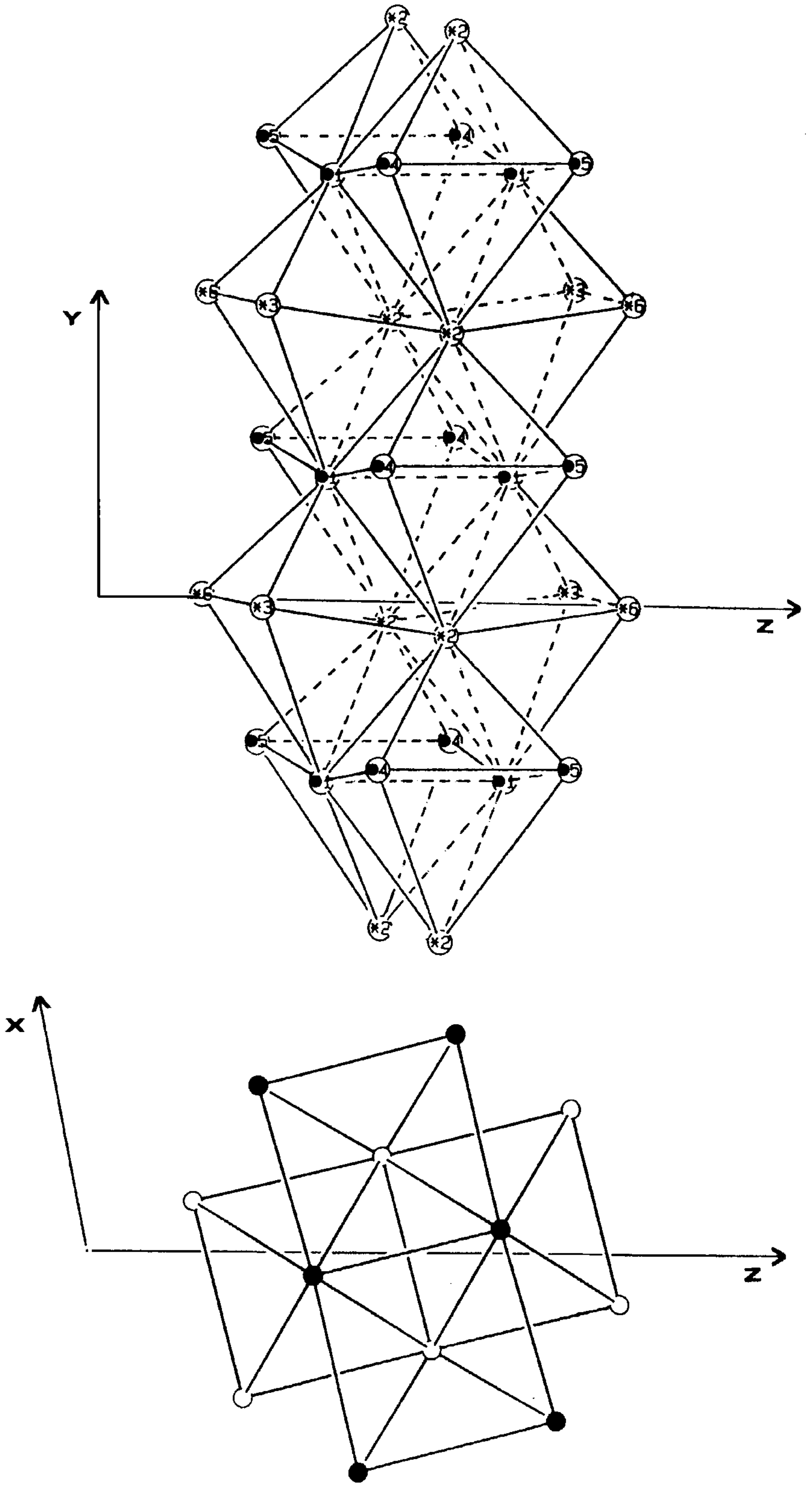

FIG. 4. Bismuth atoms distribution into the $(Bi_{12}O_{14})_n$ column.

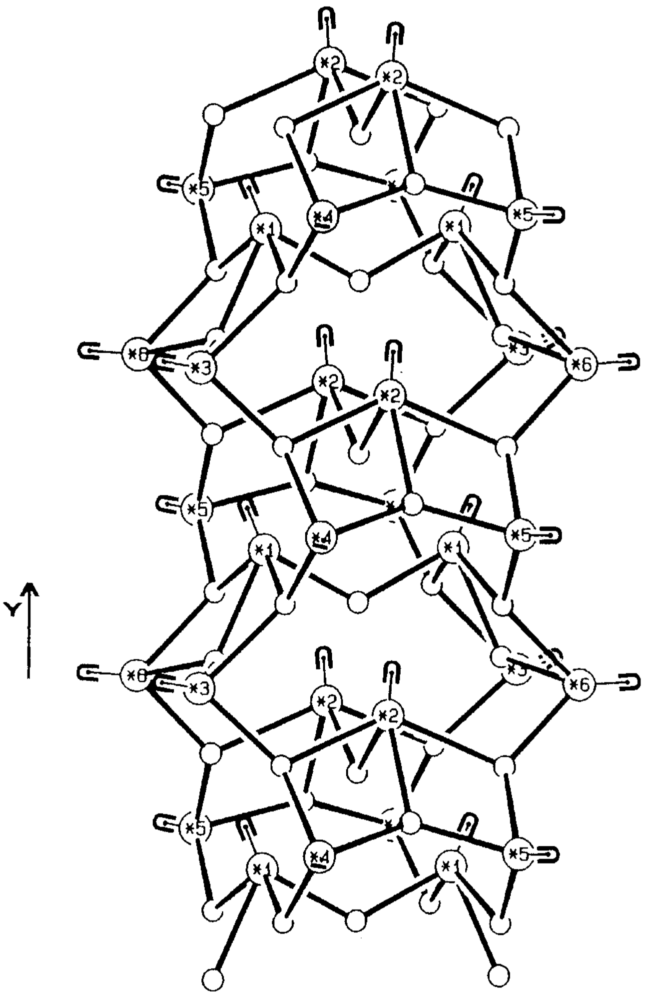

FIG. 5. Arrangement of bismuths, oxygens and lone pairs into the $(Bi_{12}O_{14}E_{12})_n$ columns of $Bi_{13}Mo_4VO_{34}E_{13}$ structure into the [010] direction.

(i) if (BiO_4E) units substitute totally for (MoO_4) tetrahedra,

$$[BiE]_2[Bi_{12}O_{14}E_{12}]_2[MoO_4]_{9.33}[BiO_4E]_{0.67},$$

corresponding to 1.43 Bi_2O_3:1 MoO_3; and

(ii) if (BiO_3E) units substitute totally for (MoO_4) tetrahedra,

$$[BiE]_2[Bi_{12}O_{14}E_{12}]_2[MoO_4]_8[BiO_3E]_2,$$

corresponding to 1.75 Bi_2O_3:1 MoO_3.

It should be noted that a phase such as "$Bi_{26}Mo_{10}O_{69}$" corresponding to 1.30 Bi_2O_3:1 MoO_3 is well outside the extreme limits of any possible solid solution while $Bi_6Mo_2O_{15}$ corresponding to 1.5 Bi_2O_3:1 MoO_3 falls in this domain.

The solid solution can be written as

$$[BiE]_2[Bi_{12}O_{14}E_{12}]_2[MoO_4]_{8+1.33x}[BiO_3E]_{2(1-x)} \times [BiO_4E]_{0.67x},$$

with $0 \le x \le 1$ ($x = 0 \Rightarrow 1.75$ Bi_2O_3:1 MoO_3; $x = 1 \Rightarrow 1.43$ Bi_2O_3:1 MoO_3).

As we already indicated above, Vannier *et al.* (9) reported two important structures corresponding to phases formulated as $Bi_{26}Mo_{10}O_{69}$ and $Bi_{26}Mo_6V_4O_{67}$. We agree with regard to their crystallographic structure determination but cannot agree with their conclusions on the basis of solid state chemistry and, in particular, on their chemical formulas which are not in agreement with their own structural data.

We have already shown that oxygen nonstoichiometry is not possible either for the $[Bi_{12}O_{14}E_{12}]_n$ columns or the (Mo, V)O_4 tetrahedra. In $Bi_{26}Mo_6V_4O_{67}$, the ratio Mo:V within the tetrahedra has been refined from crystallographic data; such a ratio however must be difficult to establish with high reliability in such crystals, which are strongly affected by high absorption coefficients. In any event, if electrostatic charge balance is respected, there is still one oxygen missing and there is no reasonable explanation on the basis of crystal and structural chemistry.

Similar comments can be made concerning overstoichiometry for $Bi_{26}Mo_{10}O_{69}$: where can we insert the extra oxygen? The proposed formulations $Bi_{26}Mo_6O_\delta$ and $Bi_{26}Mo_6V_4O_\delta$ are confusing, δ not being explained. Within the Bi_2O_3–MoO_3 system they also suggest a solid solution between 1.29 Bi_2O_3:1 MoO_3 and 1.39 Bi_2O_3:1 MoO_3. Such a solid solution is extended toward $Bi_{26}Mo_6V_4O_{67}$ in the Bi_2O_3–MoO_3–V_2O_5 system.

We note that such compositions and conclusions are outside the limits we have found from strict crystal chemical rules. We note also that the results of Erman *et al.* (14) indicate a phase with a solid solubility corresponding to 1.40 Bi_2O_3:1 MoO_3, much closer to our lower limit ($x = 1 \Rightarrow 1.43$ Bi_2O_3: 1 MoO_3). Miyazawa *et al.* (10), as well as Egashira *et al.* (15) and Chen *et al.* (16), have also found phases around the ratio 1.50 Bi_2O_3:1 MoO_3, below our upper limit ($x = 0 \Rightarrow 1.75$ Bi_2O_3:1 MoO_3).

Finally, we cannot exclude the hypothesis that these authors, making their synthesis in alumina crucibles, have stabilized phases via aluminium for molybdenum substitution in some MO_4 tetrahedra.

CONCLUSION

In the Bi_2O_3–MoO_3–V_2O_5 system we have clearly established, by solid state chemistry and X-ray single crystal

TABLE 4
Cell Parameters of Single Crystals Obtained from Different Starting Compositions

Starting composition	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	Ref.	
$1.625Bi_2O_3$:$1MoO_3$:$0.25V_2O_5$	11.652(7)	5.7923(8)	24.420(9)	101.38(6)	1616(1)	[a]	$Bi_{13}Mo_4V_2O_{34}$
$4Bi_2O_3$:$1MoO_3$:$1.5V_2O_5$	11.633(7)	5.795(3)	24.39(2)	101.35(5)	1612	(9)	$Bi_{26}Mo_6V_4O_{67}$
$1.3Bi_2O_3$:$1MoO_3$	11.799(3)	5.804(1)	24.723(3)	102.75(2)	1651.7(4)	(16)	
$1.3Bi_2O_3$:$1MoO_3$	11.776(6)	5.798(2)	24.681(9)	102.67(5)	1644(1)	[a]	
$1.39Bi_2O_3$:$1MoO_3$:$0.035Al_2O_3$	11.718(7)	5.788(2)	24.751(8)	102.70(5)	1638(1)	[a]	$Bi_{13}Mo_{4.66}Al_{0.33}O_{34}$
$1.43Bi_2O_3$:$1MoO_3$	11.743(4)	5.793(1)	24.764(7)	103.00(3)	1641.6(8)	[a]	point B (Fig. 1)
$1.5Bi_2O_3$:$1MoO_3$	11.742(8)	5.800(7)	24.77(5)	102.94(6)	1644	(9)	$Bi_{26}Mo_{10}O_{69}$
$1.5Bi_2O_3$:$1MoO_3$	2 × 11.764	5.805	24.786	102.93	2 × 1650	(10)	[b]
$1.7Bi_2O_3$:$1MoO_3$	11.720(3)	5.778(3)	24.738(9)	102.63(5)	1635(1)	[a]	
$1.75Bi_2O_3$:$1MoO_3$	11.720(5)	5.784(2)	24.739(8)	102.96(7)	1634(1)	[a]	point A (Fig. 1)
$1.9Bi_2O_3$:$1MoO_3$	11.702(6)	5.786(2)	24.710(9)	102.50(1)	1633(1)	[a]	

[a] This work.

[b] Crystal analysis $1.32Bi_2O_3$:$1MoO_3$.

structure determination, the existence of the phase $Bi_{13}Mo_4VO_{34}$ or $\{BiE[Bi_{12}O_{14}E_{12}][(Mo_{4/5}, V_{1/5})O_4]_5\}_2$ on the two component line $Bi_6Mo_2O_{15}$–$BiVO_4$ of the ternary diagram.

From the analysis of the crystal structure of this phase, we have demonstrated:

– Structural relationships with the structures of Vannier's *et al.* but not followed their conclusions on the chemistry. Their crystallographic refinement of the Mo:V ratio leads to a substoichiometric composition $Bi_{26}Mo_6V_4O_{67}$ and an over-stoichiometry for the phase $Bi_{26}Mo_{10}O_{69}$.

– The probable stabilization by alumina substituting molybdenum in the preceding work concerning such phases, established by the synthesis and crystal structure of $Bi_{26}Mo_{9.33}Al_{0.66}O_{68}$, may have occurred. In a forthcoming paper we shall demonstrate that Si, Ge, Mg, Li can play the same role as Al to stabilize such crystal structure.

We have also developed a hypothesis to explain the presence of the same structure in the pure Bi_2O_3–MoO_3 system by suggesting the possible substitution of $[BiO_3E]$ tetrahedra or $[BiO_4E]$ trigonal bipyramid to MoO_4 tetrahedra. These hypotheses induce at the level of chemistry the possibility to find this structure for two extreme limits: 1.43 Bi_2O_3:1 MoO_3 and 1.75 Bi_2O_3:1 MoO_3 and their possible solid solution

$$[BiE][Bi_{12}O_{14}E_{12}][MoO_4]_{4+0.67x}[BiO_3E]_{1-x} \times [BiO_4E]_{0.33x}.$$

Finally, if we had only pure MoO_4 tetrahedra we should diminish the positive charges of the network, and, if we keep the columns $[Bi_{12}O_{14}E_{12}]$, a metal with a +2 charge should be substituted to the single bismuth, $M^{2+}[Bi_{12}O_{14}E_{12}]^{8+}[MoO_4]_5^{2-}$. Such a possibility has been achieved with Pb^{2+}; its synthesis and crystal structure is presented in a companion paper (17).

To conclude, we must underline that the solid state chemistry with such heavy metals as bismuth or lead is very difficult to control owing their ability to attack crucibles and/or to sublime. The starting compositions are then not always followed by the metal/oxygen ratios in the resulting single crystals. More syntheses need to be performed in the Bi_2O_3–MoO_3 system, in particular to elucidate with a better precision the Bi_2O_3-rich part of the system.

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