Molecular Structure of Molybdenum Oxide in Bismuth Molybdates by Raman Spectroscopy

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The $\text{Bi}_2\text{O}_3$-$\text{MoO}_3$ system was examined using Raman spectroscopy and a recently developed method for deriving oxygen coordinations and metal-oxygen bond lengths of metal oxide species from their Raman spectra. Many of the compositions examined ($\text{Bi} : \text{Mo} = 2.3$-$14.1$) are multiphasic, consisting of two or more bismuth molybdate phases, as well as a few bismuth oxide phases. The bismuth molybdate phases that occur were found to depend on the $\text{Bi} : \text{Mo}$ ratio. The following seven bismuth molybdate phases were identified in the $\text{Bi} : \text{Mo}$ stoichiometric range from 2.3 to 14.1: $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, $\text{Bi}_2\text{Mo}_2\text{O}_9$, $\gamma'\text{Bi}_2\text{Mo}_3\text{O}_9$, $\gamma'\text{Bi}_2\text{Mo}_3\text{O}_9$ (high-temperature form), $\text{Bi}_2\text{Mo}_2\text{O}_{13}$, $\text{Bi}_2\text{Mo}_2\text{O}_{13}$, and a sillenite phase at the 14.1 composition. The complete crystal structures of $\alpha\text{Bi}_2\text{Mo}_3\text{O}_{12}$, $\beta\text{Bi}_2\text{Mo}_2\text{O}_9$, and $\gamma\text{Bi}_2\text{Mo}_3\text{O}_9$ have already been reported in the literature, and the structures of their molybdate species are known. In the present study, the molybdenum coordinations and $\text{Mo} - \text{O}$ bond lengths are determined for the molybdate species in $\gamma'\text{Bi}_2\text{Mo}_3\text{O}_9$, $\text{Bi}_2\text{Mo}_2\text{O}_{13}$, and the sillenite phase. In addition, the bismuth oxide phases are identified for each of the stoichiometries.

I. Introduction

The bismuth molybdates fall into an unusual class of compounds, the ternary bismuth oxide system $\text{Bi}-\text{M}-\text{O}$ (where $\text{M} = \text{Mo, W, V, Nb, and Ta}$), which exhibit a variety of interesting physical properties. For example, the tetragonal phases of thin-film bismuth-derived vanadates, niobates, and tantalates are efficient photoconductors. Thin-film bismuth molybdates have been noted to be effective gas sensors for alcohols and ketones and may be potentially useful as breathalyzer devices. Some of the ternary bismuth oxides show tremendous promise as heterogeneous catalysts. The bismuth molybdates, in fact, are heterogeneous catalysts in commercially important selective oxidations and ammoxidations (the Sohio process): for example, propylene ($\text{C}_3\text{H}_6$) to acrolein ($\text{C}_3\text{H}_4\text{O}$) by oxidation or to acrylonitrile ($\text{C}_3\text{H}_3\text{N}$) by ammoxidation. In spite of the remarkable properties demonstrated by these systems, the molecular structures of many of the phases constituting these important systems are not completely known because of the difficulties encountered in determining the location of the oxygen atoms surrounding the metal sites by diffraction techniques. In light of the importance of these systems, structural studies are currently in progress using a wide assortment of techniques.

Conclusions

From our measurements it is clear that pressure can play a significant role on the phase behavior of water + oil + nonionic surfactant systems. Furthermore, its influence on the three-phase region can be well understood by the pressure-composition phase prism which we suggested in our earlier work. Vice versa the experimental results found in this study clearly support the suggested phase prism. The most important features of the phase prism are phase transitions of the type 2-3-2 at constant temperature and increasing pressure. The surfactant-rich middle phase moves with respect to its composition from the oil-rich side of the phase prism to the water-rich side indicating that the surfactant becomes more hydrophilic with increasing pressure. A new experimental setup that enables one to sample the coexisting liquid phase at constant temperature and (elevated) pressure has been used.

Acknowledgment. We are indebted to Mr. K. van der Schoor for technical assistance. We thank Mr. J. H. F. Grondel and Mr. A. van der Plas in assisting us with the design and construction of the equipment. We also thank the "Koninklijke/Shell Exploratie en Produktie Laboratorium", Rijswijk, The Netherlands, for stimulating discussions and financial support.

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of structural probes including electron diffraction, high-resolution electron microscopy (HREM), X-ray absorption near-edge structure (XANES), and Raman spectroscopy. The present study uses Raman spectroscopy to investigate the compositional dependence of the bismuth molybdate and bismuth oxide phases in the stoichiometric range Bi:Mo = 2.3-14.1. The molecular structures of the molybdate species in each of the identified bismuth molybdate phases are determined using a systematic method derived from Raman stretching frequency/bond length/bond strength empirical correlations.

Raman spectroscopy has recently proven to be a very effective tool in the characterization of the structures of transition-metal oxides as bulk phases and two-dimensional surface phases. The basic idea behind the conventional method of evaluating Raman spectra is that different molecular structures are expected to have different types of bonds and this, in turn, leads to a different set of Raman spectral features. Used in this way, Raman spectroscopy is an effective structural tool because it can be used to discriminate or “fingerprint” between alternate structures proposed for a chemical species.

Recently, a new, systematic approach has been developed for interpreting the Raman spectra of transition-metal oxides. This approach regards each metal-oxygen bond in a molecular species or crystalline lattice as vibrationally independent of its surroundings so that a direct relationship may be formulated between its metal-oxygen Raman stretching frequencies and bond lengths. Naturally, this approach does not lead to a vibrational mode analysis because it neglects nearest-neighbor interactions and, consequently, bending/wagging and external modes. Furthermore, this approach fails to distinguish between symmetric and asymmetric stretching modes. Within the limits of experimental error afforded by crystallographic bond length determinations, however, this approach is justified and may be used to determine metal-oxygen bond lengths from Raman stretching frequencies because the effect of the interaction force constants on the bond lengths is smaller than the uncertainty associated with most crystallographic bond length determinations. Applying this reasoning, empirical relations have been established between molybdenum-, vanadium-, niobium-, tungsten-, and bismuth-oxygen bond lengths and observed Raman stretching frequencies for reference metal oxide compounds. In the present study, Raman spectroscopy was used to characterize the molybdenum environments in the bismuth molybdates of compositional range Bi:Mo = 2.3-14.1. The molybdate coordinations and Mo-O bond lengths are determined from the observed Raman stretching frequencies using the stretching frequency/bond length/bond strength empirical relations. In addition, the coexisting bismuth oxide phases are identified by their characteristic Raman bands.

II. Experimental Section

The bismuth molybdates were provided by D. J. Buttry, D. A. Jefferson, and J. M. Thomas. The bismuth molybdates were prepared by mixing stoichiometric amounts of α-Bi₂O₃ with MoO₃ (both of 99.9% purity), grinding with molar and pestal in a slurry of acetone, followed by drying in air, and finally heating in flowing oxygen at 840 °C. The Raman spectra were collected by using 10-40 mW of the 514.5-nm line of a Spectra-Physics argon ion laser (Model 171) for excitation. The laser beam power was measured at the sample. The diffusely scattered radiation from the sample was collected in a 90° scattering geometry and directed into a Spex Triplet Spectrometer (Model 1877) coupled to an intensified photodiode array detector (880 intensified array elements) and optical multichannel analyzer (OMA III: Princeton Applied Research, Model 1463). The detector was thermoelectrically cooled to -35 °C. The Raman spectra were collected and recorded with an OMA III (PAR) dedicated computer and software. The spectral resolution and reproducibility were experimentally determined to be better than 2 cm⁻¹. About 100-200 mg of each bismuth molybdate sample was pressed onto a thin layer of KBr to provide mechanical support and pressed into a thin wafer of about 1-mm thickness. The pressed sample was then mounted onto a sample holder capable of spinning at 2000 rpm to avoid local heating effects caused by the concentrated laser beam. Further details concerning the optical arrangement and sample handling procedure used in the Raman experiments can be found elsewhere. A quick basic computer program was written to systematically determine every possible combination of Mo-O bond strengths, in valence units, that add to the formal oxidation state of the molybdenum cation according to the valence sum rule. The user-input parameters include the formal oxidation state of the molybdenum species, which is 6.0 v.u. for the fully oxidized cation, the tolerance on the oxidation state (determined to be 0.12 v.u. from a previous study), and the observed Raman frequencies greater than about 400 cm⁻¹. The program converts all Raman frequencies to bond strengths, in valence units, and bond lengths in angstroms. The output consists of all possible combinations of bond strengths consistent with the user-input formal oxidation state of the molybdenum cation. Each combination of bond strengths represents a possible molybdate structure, with coordination and bond strengths also provided as output. The “best” molybdate structure is chosen from the list of possible structures according to the following guidelines: (1) The highest occurring Raman stretching frequency must be used, as this represents the shortest Mo-O bond present in the compound. (2) The number of frequencies used must be maximized. After the first two guidelines are followed, (3) the structure(s) with the most consistent valence is chosen, (4) reference structures and information from other structural techniques are used, if possible, and, finally, (5) a hybrid “best” structure is formed from all possible structures not eliminated by using guidelines 1-4. The output of the computer program is covered in the text. This method of determining the structures of metal oxides from their Raman spectra, which is used in the present study to determine molybdate structures in the bismuth molybdates, has recently been exhaustively covered for several vanadate reference compounds.

III. Theory

The interpretation of the Raman spectra of a transition-metal oxide species in the solid state is facilitated by imposing two levels of approximation. First, the internal and external modes of the crystal are assumed to be independent of one another. The internal modes of metal oxide molecules within the unit cell of a crystal occur in the medium- and high-frequency regions (>400 cm⁻¹). The external modes, in contrast, occur in the medium- and high-frequency regions (>400 cm⁻¹). The internal modes of metal oxide molecules within the unit cell of a crystal occur in the medium- and high-frequency regions (>400 cm⁻¹). The external modes include translational and librational modes of the molybdenum(VI) oxide species while the external modes, including translational and librational modes, occur at lower frequencies (<400 cm⁻¹). Second, the site symmetry approximation, or correlation method, may be imposed by assigning a high degree of structural degeneracy.
of symmetry to each atom, or site, within the unit cell. Although the site symmetry approach leads to the total number and types of infrared- and Raman-active modes expected from the crystal, a detailed knowledge of the crystal structure is first required in order to perform the vibrational mode analysis. The site symmetry approach, however, does allow the internal modes of a molecular species confined to a crystalline lattice to be directly compared with those of a similar molecule in solution or the gas phase. Consequently, the site symmetry approach forms the basis of the “fingerprint” method of identifying molecular geometries. For metal oxides with distorted molecular geometries, however, the fingerprint approach cannot be reliably used because of inconsistent matches between spectra due to a virtually infinite number of geometric irregularities possible for a distorted metal oxide species. Clearly, there is a demonstrated need for a systematic way of determining molecular structures from Raman spectra that does not rely on the subjectivity and uncertainty involved with fingerprinting characteristic vibrational bands. Furthermore, the desired systematic method would be generally applicable and capable of yielding detailed structural information not only for ideally symmetric geometries but also for distorted metal oxide species as well.

Recently, empirical relations have been found between the metal–oxygen Raman stretching frequencies and metal–oxygen bond lengths for several transition-metal oxide systems including molybdenum–, vanadium–, niobium–, tungsten–, titanium–, and bismuth–oxygen bonds. In each case, the empirical Raman stretching frequency/bond length relationship was found to follow a simple exponential form. For the present purpose of investigating Mo–O Raman stretching frequencies, the following empirical stretching frequency/bond length relation is used:

\[ R_{\text{MoO}} = 0.48239 \ln \left( \frac{32 \, 895}{\nu} \right) \] (1)

where \( \nu \) is the Raman stretching frequency in wavenumbers and \( R \) is the metal–oxygen bond length in angstroms. Equation 1 yields a standard deviation of \( \sigma = 0.016 \, \text{Å} \) for a Mo–O bond length.

The Pauling bond strengths of metal–oxygen bonds, in valence units, also referred to as bond orders or bond valences, are useful for discussing the plausibility of proposed metal oxide structures. The Pauling bond strength reflects the relative distribution of available valence electrons throughout the covalent bonds of a metal oxide species. Furthermore, according to the valence sum rule, there is a conservation of valence associated with the metal cation, and this allows the valence sum rule to serve as a bookkeeping device for the number of valence electrons in that structure. Hence, the calculated valence state of the metal cation in a proposed metal oxide structure, arrived at by simply adding the individual metal–oxygen bond valences, may be compared to the formal oxidation state of the metal cation as a simple test for the plausibility of that structure. The empirical expression of Brown and Wu \(^{10} \) for relating Mo–0 bond lengths \( R \) to their Pauling bond strengths \( s \) is given by

\[ s = (R / 1.882)^{-0.0} \] (2)

By combining eqs 1 and 2, a relation between the Pauling strength and the empirical stretching frequency/bond length relation is used for a Mo–O bond in valence units and its Raman stretching frequency in wavenumbers is expressed as

\[ s_{\text{MoO}} = (0.256 \ln \left( \frac{32 \, 895}{\nu} \right))^{-0.0} \] (3)

IV. Results

The Raman spectra for the \( \beta \)-MoO\(_3\) samples, ranging in composition from 2:3 to 14:1, are presented in Figures 1–6. Most of the bismuth molybdates studied are multiphasic, and this is shown in Table I, which lists the observed Raman bands of the various Bi:Mo compositions with corresponding band positions for each of the identified phases. These phases are briefly summarized in this section.

The molecular structures of the molybdate species in the \( \alpha \)-Bi\(_2\)Mo\(_3\)O\(_8\), \( \beta \)-Bi\(_2\)Mo\(_2\)O\(_9\), and \( \gamma \)-Bi\(_2\)Mo\(_6\)O\(_9\) phases have been previously determined by diffraction methods. \(^{24-26} \) In this section, the crystallographically determined Mo–O bond lengths of these...

\[ (25) \text{Chen, H.; Sleight, A. W. J. Solid State Chem. 1986, 63, 70.} \]
of the method. In the Discussion, the same method will be
used to determine the Mo-O bond lengths of the molybdate species in remaining bismuth molybdate phases having undetermined structures and detected for Bi:Mo compositions of 2:3, 3:1, 4:1.

molybdate species are assigned to Raman stretching frequencies by directly comparing their reported bond lengths with their corresponding stretching frequencies. As an exercise, the method of determining the coordinations and Mo–O bond lengths of the molybdate species in these three compounds is first demonstrated on the known structures to illustrate the simplicity and effectiveness of the method. In the Discussion, the same method will be used to determine the coordinations and Mo–O bond lengths of the molybdate species in remaining bismuth molybdate phases having undetermined structures and detected for Bi:Mo compositions of 2:3, 3:1, 4:1.

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TABLE III: α-Bi₂Mo₆O₁₉ Structure Determination of Molybdate Species 1 by Raman Spectroscopy

<table>
<thead>
<tr>
<th>Mo-O bond type</th>
<th>ν</th>
<th>s (vu)</th>
<th>R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>992</td>
<td>1.914</td>
<td>1.689</td>
</tr>
<tr>
<td>B</td>
<td>838</td>
<td>1.443</td>
<td>1.770</td>
</tr>
<tr>
<td>C</td>
<td>720</td>
<td>1.132</td>
<td>1.844</td>
</tr>
<tr>
<td>D</td>
<td>685</td>
<td>1.047</td>
<td>1.867</td>
</tr>
</tbody>
</table>

Best struct = a, Raman (Å), lit.²⁴ (Å)

Table III outlines the systematic procedure for determining the coordination and Mo-O bond lengths of molybdate species 1 (see Table II) in α-Bi₂Mo₆O₁₉. The assigned Raman stretching frequencies for the four shortest bonds of the Mo₆O₁₉ unit (the fifth bond length, 2.37 Å), is assumed at 992, 838, 720, and 685 cm⁻¹. As shown in a previous study, each Raman band in the high-frequency region for a molybdate species is assumed to represent a unique Mo-O bond length. Thus, four different bond lengths, labeled A–D in Table III, are initially assumed for molybdate species 1. The QUICKBASIC computer program described in the Experimental Section converts the four Raman stretching frequencies to Pauling bond strengths and bond lengths and then proceeds to find every combination of bond strengths that add to the working valence (see previous paragraph) of 5.486 vu (tolerance σ = 0.12 vu) for the Mo₆⁺ cation. As Table III shows, only seven molybdate structures are possible, labeled a–g, and these are presented along with the coordination, bond types, and calculated Mo₆⁺ valence for each structure. Of the possible structures, only structure a uses all four Raman stretching frequencies, while all other possibilities use less than four frequencies. Thus, as shown at the bottom of Table III, the best structure is (a) with Mo-O bond lengths 1 × A, 1 × B, 1 × C, and 1 × D, or 1 × 1.689 (16), 1 × 1.770 (16), 1 × 1.844 (16), and 1 × 1.868 (16) Å; the fifth Mo-O bond was given as 2.37 (1) Å. Within experimental error, the Mo-O bond lengths are identical to the literature values, also shown at the bottom of Table III.

The identical procedure used in determining the structure of molybdate species 1 in α-Bi₂Mo₆O₁₉ is also used to determine the structures of molybdate species 2 and 3, and the results are shown in Tables IV and V. For molybdate species 2, the assigned Raman bands occur at 954, 899, 814, and 648 cm⁻¹, and these four Raman bands give rise to only three possible molybdate structures having a calculated valence of 5.647 vu, within a tolerance of σ = 0.12 vu, while for molybdate species 3, shown in Table V, eight structures are possible having a calculated valence of 5.421 vu. Clearly, only structure a, for molybdate species 2, and structure c, for molybdate species 3, use the maximum number of four frequencies and are therefore considered to be best represent molybdate species 2 and 3, respectively. Both Tables IV and V show that the Raman results compare very well to those of the reported bond strengths determined by diffraction methods. Furthermore, Tables III–V show that Raman spectroscopy is expected to be very effective in the elucidation of coordinations and bond lengths of molybdate species having unknown molecular structures.

The remaining Raman bands above 400 cm⁻¹ for α-Bi₂Mo₆O₁₉ may be assigned to Bi-O stretches and medium-range order. Although the Raman bands above 600 cm⁻¹ for α-Bi₂Mo₆O₁₉ are accounted for as Mo-O stretches, and those below 400 cm⁻¹ are
The peaks at frequencies/bond length relation, the shortest Bi-O bonds in the dioxo linkages connecting pairs of the MoO₆ tetrahedra to form MoO₆ structural units. For example, Griffith Assignment of the Raman Bands of \( \gamma^\prime \)-Bi₂MoO₆. The Raman spectrum of the 2:1 composition is shown in Figure 3. The 2:1 composition is biphasic and consists of \( \alpha \)-Bi₂MoO₆₋ₓ, which is the minor component and for which the Raman spectrum is shown as a dotted line in Figure 3, and \( \gamma^\prime \)-Bi₂MoO₆, which is the major component. The structure of \( \gamma^\prime \)-Bi₂MoO₆ has been studied by X-ray diffraction and powder neutron diffraction and found to consist of alternating layers of Bi₂O₂SO₄ and Bi₂O₂SI₄, and corner-sharing, distorted MoO₆ octahedra (that is, an Aurivillius layered oxide structure). There is one type of MoO₆ octahedron present in this structure, and the observed Raman bands at 846, 793, 712, 596 (very weak), and 398 cm⁻¹ are assigned as Mo-O stretching frequencies of the MoO₆ octahedron.

Table VII shows the structure determination of the molybdate species in \( \gamma^\prime \)-Bi₂MoO₆ by Raman spectroscopy. There are 23 molybdate structures possible from the 5 observed Raman stretching frequencies, yielding a calculated valence of 6.0 vu (within 0.12 vu), and these are labeled a–w. Only structure n uses all five of the stretching frequencies and is therefore considered to represent the best structure. The bond lengths of this MoO₆ octahedron are 1 x 1.4, 1 x 2, 1 x 2, and 1 x 1.7. As shown at the bottom of Table VIII, this structure is comparable to that determined by diffraction.

Raman Spectra of \( \gamma^\prime \)-Bi₂MoO₆ (High-Temperature Form), \( \beta^\prime \)-Bi₂MoO₆₋ₓ, \( \beta^\prime \)-Bi₂MoO₆₋ₓ and Sillenite. The Raman spectrum of the high-temperature modification of the 2:1 composition is presented in Figure 4. The Raman band assignments in Table I show that this sample is multiphasic. The major component is \( \gamma^\prime \)-Bi₂MoO₆, which has been investigated by high-resolution electron diffraction and high-resolution transmission electron microscopy (HRTEM). The oxygen coordination to the Mo and Bi cations in \( \gamma^\prime \)-Bi₂MoO₆, however, has not been reported. In addition to the \( \gamma^\prime \)-Bi₂MoO₆ phase at the high-temperature 2:1 composition, three additional phases are present as minor components: the sillenite phase, which has the \( \gamma^\prime \)-Bi₂MoO₆ structure and for which the Raman spectrum is shown in Figure 4 as a dotted line, and two polymorphs of bismuth oxide, \( \beta^\prime \)-Bi₂O₃ and

\[ \text{TABLE VI: } \alpha \text{-Bi₂MoO₆ Structure Determination by Raman Spectroscopy} \]

<table>
<thead>
<tr>
<th>Mo-O bond type</th>
<th>( \nu ) (cm⁻¹)</th>
<th>s (vu)</th>
<th>R (Å)</th>
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<tr>
<td>D</td>
<td>669</td>
<td>1.009</td>
<td>1.879</td>
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\[ \text{TABLE VII: } \beta^\prime \text{-Bi₂MoO₆ Structure Determination by Raman Spectroscopy} \]

<table>
<thead>
<tr>
<th>Mo-O bond type</th>
<th>( \nu ) (cm⁻¹)</th>
<th>s (vu)</th>
<th>R (Å)</th>
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<tr>
<td>A</td>
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<td>1.745</td>
</tr>
<tr>
<td>B</td>
<td>765</td>
<td>1.246</td>
<td>1.814</td>
</tr>
<tr>
<td>C</td>
<td>753</td>
<td>1.215</td>
<td>1.822</td>
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\[ \text{TABLE VIII: } \beta^\prime \text{-Bi₂MoO₆ Structure Determination by Raman Spectroscopy} \]

<table>
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<tr>
<th>Mo-O bond type</th>
<th>( \nu ) (cm⁻¹)</th>
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<td>765</td>
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<tr>
<td>C</td>
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<td>1.822</td>
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\[ \text{(29) Buttery, D. J.; Jefferson, D. A.; Thomas, J. M. Philos. Mag. A 1986, } 55, 897. \]
TABLE VII: γ-Bi$_2$MoO$_6$ Structure Determination by Raman Spectroscopy

<table>
<thead>
<tr>
<th>obd Raman bands (cm$^{-1}$)</th>
<th>Mo-O str</th>
<th>846, 793, 712, 596, 398</th>
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<tr>
<td><strong>Mo-O bond type</strong></td>
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<tr>
<td></td>
<td>1 × B</td>
<td>1 × 1.797 (16)</td>
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<tr>
<td></td>
<td>1 × C</td>
<td>1 × 1.849 (16)</td>
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<tr>
<td></td>
<td>2 × D</td>
<td>2 × 1.935 (16)</td>
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<tr>
<td></td>
<td>4 × E</td>
<td>4 × 2.130 (16)</td>
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</tbody>
</table>

δ-Bi$_2$O$_3$. β-Bi$_2$O$_3$ is metastable but may be observed in its pure form at 650 °C upon cooling from the δ-Bi$_2$O$_3$ phase (high-temperature phase) or may be stabilized to room temperature by the addition of small amounts of a metal cation impurity. This phase has been identified by Raman spectroscopy in Ta- and Nb-stabilized phases at a Bi:M = 60:1 composition and has sharper bands characteristic of 4:1 composition; the only difference is that the bands of 3:1, 4:1, and 38:7 are shown in Figure 5. These compositions have been investigated by electron diffraction, but the oxygen coordination around the Mo and Bi cations was not determined. As Table I shows, the 3:1 composition contains a new phase with the stoichiometry Bi$_3$MoO$_9$, as the major component and γ' Bi$_2$MoO$_6$ as a trace component. As the Bi:Mo ratio is increased to the 4:1 composition, also shown in Figure 5, a new phase of reported stoichiometry Bi$_4$Mo$_2$O$_9$ is present as the major component. The Bi$_4$Mo$_2$O$_9$ phase is most defined at the 38:7 composition, which has a Raman spectrum that is nearly identical to that of the 4:1 composition; the only difference is that the bands are much sharper for the 38:7 composition, indicating a more ordered system. The β and δ phases of Bi$_2$O$_3$ are present at all three of the Bi:Mo compositions, as shown in Table I.

The Raman spectrum of the sample having a Bi:Mo ratio of 1:4:1 is shown in Figure 6. This composition is found to contain two phases: The major component is a sillenite phase, and the minor component is the α-Bi$_2$O$_3$ phase for which the Raman spectrum is shown in Figure 6 as a dotted line. The α-Bi$_2$O$_3$ phase, which possesses a monoclinic lattice, was used as the starting material in the preparation of the bismuth molybdate samples.

V. Discussion

Here, the details of the molybdenum coordination that can be inferred from the interpretation of the Raman data for γ'-Bi$_2$MoO$_6$, Bi$_4$Mo$_2$O$_9$, Bi$_3$MoO$_9$, and the distorted sillenite phase are discussed. The molybdenum coordination in these bismuth molybdate phases has previously not been determined.

Structure Determination of γ'-Bi$_2$MoO$_6$ (High-Temperature Form) by Raman Spectroscopy. The perovskite γ'-Bi$_2$MoO$_6$ transforms to γ'-Bi$_2$MoO$_6$ when heated to 645 °C. As noted before, the structure of γ'-Bi$_2$MoO$_6$ has been investigated by high-resolution transmission electron microscopy. These studies showed a structural relationship between fluorite and γ'-Bi$_2$MoO$_6$. The space group of γ'-Bi$_2$MoO$_6$ was determined to be P2$_1$/c, with lattice parameters a = 17.244 Å, b = 22.420 Å, c = 5.857 Å, and β = 90.486°, with 16 formula units per unit cell. Previous investigations have resulted in a number of proposed structures for the molybdenum and bismuth oxide polyhedra in the γ'-Bi$_2$MoO$_6$ phase. Electron diffraction work led by Buttery, (33) Betsy, R. J.; White, W. B. Spectrochim. Acta 1973, 26, 505. (34) Malmos, G. Acta Chem. Scand. 1970, 24, 384.

(33) Betsy, R. J.; White, W. B. Spectrochim. Acta 1973, 26, 505.
suggested a structure similar to that of β-Bi2MoO6 where columns of isolated MoO4 tetrahedra form square tunnels enclosing a single column of Bi5+ sites. These square tunnels are arranged in pairs and are further linked by additional MoO4 tetrahedra. Watanabe proposed that each Mo5+ cation is surrounded by four oxygen atoms at an angle of 90° with the possible presence of a Mo-Mo bond. Matsura found the Raman spectrum of γ'-Bi2MoO4 to be similar to that of α-Bi2MoO4 and consequently proposed the presence of at least three different MoO4 configurations in γ'-Bi2MoO4, because of the three types of molybdate species present in the α-Bi2MoO4 structure.

The presence of an isolated MoO4 tetrahedron in γ'-Bi2MoO4 is indicated by the absence of Mo-O stretching bands in the 730-540 cm⁻¹ region of the spectrum in Figure 4. This is because MoO4 octahedra and bridged structures (that is, having Mo-O-Mo linkages) possess Mo-O bonds of about unit valency and the Mo-O stretching frequencies associated with these bonds occur in the 730-540 cm⁻¹ region. For example, compounds having distorted MoO4 units display bands in this region as shown: CoMoO4, 943, 694 cm⁻¹; NiMoO4, 966, 914, 701 cm⁻¹; MoO3, 997, 820, 660 cm⁻¹; (NH4)2MoO4-H2O, 934, 893, 888, 633, 625, 570, 543 cm⁻¹; (NH2)6Mo7O20, 910, 843, 694 cm⁻¹.15 By comparison, γ'-Bi2MoO4 has a more regular MoO4 octahedron with Raman bands at 846, 792, and 712 cm⁻¹ (see Table I). In short, the absence of Raman bands in the 730-540 cm⁻¹ region argues against MoO6 as well as bridged MoO5 and MoO4 species. This lack of evidence for Mo-O-Mo linkages provides strong evidence for the presence of isolated MoO4 tetrahedra in the γ'-Bi2MoO4 structure. Further evidence is provided by the characteristic position of the highest frequency band at 897 cm⁻¹ which is consistent with that of a slightly distorted, isolated MoO4 tetrahedron. For example, Na2MoO4·2H2O and Bi2(FeO4)3·(MoO4)3 have both slightly distorted MoO4 tetrahedra and show a Raman Mo-O stretching band at 897 cm⁻¹.16 From these combined observations it is concluded that the γ'-Bi2MoO4 structure contains slightly distorted and isolated MoO4 tetrahedra. This conclusion is in agreement with recent findings using X-ray absorption near-edge structure spectroscopy.16

The structure determination of the molybdate species in γ'-Bi2MoO4 is shown in Table VIII. Six Mo-O stretching frequencies are observed at 897, 865, 829, 822, 788, and 771 cm⁻¹, and these give rise to 20 possible molybdate structures, labeled a–t; note that all structural possibilities are MoO4 tetrahedra. There must be more than one type of MoO4 tetrahedron in the γ'-Bi2MoO4 structure because there are more than four distinct Raman Mo-O stretching frequencies and, consequently, more than four different bond types. If there are distinct MoO4 tetrahedra present, then the bond lengths of MoO4 in each structure would exhibit a unique highest occurring stretching frequency that would occur above 858 cm⁻¹ (which is the Raman stretching frequency estimated for a perfect MoO4 tetrahedron).15 Accordingly, the very sharp Raman band observed at 865 cm⁻¹ (see Figure 4) is assigned to the shortest Mo–O bond of the second MoO4 tetrahedron in the γ'-Bi2MoO4 structure. The best combination of structural possibilities consistent with the presence of two unique MoO4 tetrahedra is a hybrid of structures a and f representing the first tetrahedron and structure t representing the second tetrahedron. Thus, the first MoO4 tetrahedron in γ'-Bi2MoO4 has bond lengths of 2×1.738(16) and 1×1.780(16), and the second MoO4 tetrahedron in γ'-Bi2MoO4 is very regular with bond lengths of 3×1.755(16) and 1×1.776(16) Å. These results are summarized in Table VIII.

The structures of the molybdate species in γ'-Bi2MoO4, as determined in the present Raman study, may be compared to previously proposed models. Matsura12 compared the Raman spectrum of γ'-Bi2MoO4 to that of α-Bi2MoO4 and subsequently proposed at least three different MoO4 configurations in γ'-Bi2MoO4. A visual inspection of the Raman spectra of α- Bi2MoO4 and γ'-Bi2MoO4 in Figures 1 and 4, however, shows that the Raman features of these two phases are dramatically different: α-Bi2MoO4 has Raman bands as high as 953 cm⁻¹ for nonbridging Mo-O bonds and several bands in the 500-750 cm⁻¹ region due to bridging Mo-O bonds, whereas γ'-Bi2MoO4 exhibits stretching modes only in the 900-770 cm⁻¹ region. In fact, the Raman features of γ'-Bi2MoO4 are more closely resemble those of β-Bi2MoO4, which has Mo-O stretching modes in the 884-753 cm⁻¹ region (see Tables I and VI). Watanabe's proposal of MoO4 units with Mo-O bond lengths at 1.9 Å (calculated Mo6+ valence of 3.8 v Lu2 indicating erroneous bond lengths) is similar to the present study except that in the present study the tetrahedra were found to have bond lengths ranging from 1.74 to 1.80 Å in one tetrahedron and 1.76 to 1.78 Å in the other tetrahedron. The model that is perhaps most consistent with the results of the present study is from the electron diffraction work of Buttry which in which two types of MoO4 tetrahedra were proposed: isolated MoO4 tetrahedra forming square tunnels and a single column of Bi5+ sites and a second type of MoO4 tetrahedron linking pairs of these tunnels.

**Structure Determination of Bi2MoO7 and Bi3Mo3O12 by Raman Spectroscopy.** The Bi2MoO7 phase, which is present only at the 3:1 composition, was determined to have a defect fluorite structure and a space group of P2₁c. The lattice parameters were determined to be a = 24.786 Å, b = 5.805 Å, c = 23.527 Å, and β = 102.93° with 9 formula units per unit cell. The structure of the molybdate species was not determined. The Raman spectrum of the Bi2MoO7 phase (Figure 5) shows bands at 880 and 800 cm⁻¹, which are assigned to the Mo-O stretching vibrations of a MoO4 tetrahedron because of the very close similarity of its Raman features to those of β-Bi2MoO4 (Figure 2) and γ'-Bi2MoO4 (Figure 4).

The Bi3Mo3O12 phase dominates at both the 4:1 and 38:7 compositions. The structure of Bi3Mo3O12 was determined by X-ray microanalysis and electron and X-ray powder diffraction to have a 3×5×3 fluorite superlattice. Its orthorhombic space group is Pmca, with lattice parameters a = 16.818 Å, b = 28.658 Å, and c = 16.903 Å, with 4 formula units per unit cell. The structure of the molybdate species was not determined. The Raman spectrum of the Bi3Mo3O12 phase closely resembles that of the Bi2MoO7 phase; the only difference is that the highest frequency band at 880 cm⁻¹ for Bi2MoO7 is shifted down by 10 cm⁻¹ to 870 cm⁻¹ for Bi3Mo3O12, indicating a slightly more regular MoO4 tetrahedron for the Bi3Mo3O12 phase.

The structure determination of the molybdate species in Bi2MoO7 and Bi3Mo3O12 by Raman spectroscopy is shown in Table IX. Each phase exhibits only two Mo-O stretching modes: 880 and 800 cm⁻¹ for Bi2MoO7 and 870 cm⁻¹ for Bi3Mo3O12. As Table IX shows, only one structure is possible for each set of bands. The resulting bond lengths for the MoO4 tetrahedron in Bi2MoO7 are 3×1.77 and 1×1.78, whereas in Bi3Mo3O12 the bond lengths for the tetrahedron in Bi3Mo3O12 are 3×1.752(16) and 1×1.793(16) Å. Thus, the molybdate tetrahedra in both Bi2MoO7 and Bi3Mo3O12 are found to have identical bond lengths within experimental error.

**Structure of the Sillenite Phase by Raman Spectroscopy.** Buttry noted that no new phases are detected upon increasing the Bi:Mo ratio above 38:7, where the Bi3Mo3O12 phase dominates. He further noted that there may be a partial solubility between Bi2MoO7 and Bi3Mo3O12 (phase not specified) at higher Bi:Mo compositions. In contrast to these results, the Raman spectrum of the 14:1 composition, shown in Figure 6, does not show the presence of Bi3Mo3O12. Instead, Raman bands are observed for the α-Bi2MoO4 phase, which is used as the starting material in the preparations of the bismuth molybdates, and characteristic Raman bands are noted for the sillenite phase which is present as the major component at the 14:1 composition. The characteristic Raman bands for both of these phases are listed in Table I. A description of the sillenite structure is given in the following paragraph.
TABLE IX: Bi₉Mo₂O₁₅ and Bi₃₈Mo₂O₇₈ Structure Determination by Raman Spectroscopy

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<th>Bi₃₈Mo₂O₇₈</th>
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<td></td>
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<td>1 X B</td>
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</table>

which is metastable and forms at 639 °C by cooling from the high-temperature form of bismuth oxide, δ-Bi₂O₃. At lower temperatures, the γ-Bi₂O₃ structure is stabilized by a metal cation impurity, thereby yielding the sillenite structure. The most ideal sillenite structures are those containing quadrivalent metal cations such as Si⁴⁺ and Ge⁴⁺ to form Bi₁₂SiO₇₀ and Bi₁₂GeO₇₈. The metal cations themselves occupy nearly perfect tetrahedral sites in the sillenite structure, giving rise, for example, to nearly perfect SiO₆ or GeO₆ tetrahedra. The sillenite structure has also been stabilized by pentavalent cations such as P⁵⁺, As⁵⁺, V⁵⁺, and Bi⁵⁺ and the Raman spectra of these compounds have been reported.

The formation of the sillenite structure at the 14:1 composition in the Bi–Mo–O system is unexpected in view of the reports in the literature that hexavalent metal cations such as Mo⁶⁺ and W⁶⁺ do not stabilize the sillenite structure. Although the Raman spectrum of the 14:1 composition (Figure 6) clearly shows characteristic bands for the sillenite structure (see Table I for tabulation), the bands are slightly broader than those reported for quadrivalent- and pentavalent-stabilized sillenite structures such as Si⁴⁺ and Ge⁴⁺ to form Bi₁₂SiO₇₀ and Bi₁₂GeO₇₈. The metal cations themselves occupy nearly perfect tetrahedral sites in the sillenite structure, giving rise, for example, to nearly perfect SiO₆ or GeO₆ tetrahedra. Furthermore, the Raman Bi–O stretching frequencies of the Bi–Mo–O sillenite structure are shifted in wavenumber from those of the Bi–Si–O and Bi–V–O sillenite structures, indicating a slightly different set of Bi–O bond lengths. A comparison of the Raman frequencies of Bi₁₂SiO₇₀ with those of the 14:1 composition shows the following shifts for the Bi–O vibrational modes: 619 to 628 cm⁻¹, 530 to 539 cm⁻¹, 448 to 511 cm⁻¹, 321 to 352 cm⁻¹, and 267 to 270 cm⁻¹ for Bi₁₂SiO₇₀ and BiMo = 14:1, respectively. These Raman bands shift for the Bi–Mo–O sillenite structure, however, are commonly observed as the oxidation state of the stabilizing metal cation is altered from 4+ to 5+.

In contrast to the Raman bands of the bismuth oxide structure in Figure 6, the Raman bands of the MoO₄ tetrahedron in the sillenite structure are very sharp, indicating a very regular structure for this molybdate species. The perfect MoO₄ tetrahedron has been estimated to have an Mo–O Raman stretch at 858 cm⁻¹, with a precision of σ = 25 cm⁻¹, and the observed value of 877 cm⁻¹ for the tetrahedron in the 14:1 composition is consistent with this value within the reported experimental error of the Mo–O stretching frequency/bond length correlation. By analogy to molybdate reference compounds, the MoO₄ tetrahedron in the sillenite structure is comparable to that found in CaMoO₄, which has reported Mo–O bond lengths of 1.775 Å and Raman stretching modes at 879 (most intense), 848, and 794 cm⁻¹.

The structure determination of the molybdate species in the sillenite phase by Raman spectroscopy is shown in Table X. Four stretching frequencies are identified in the high-frequency region at 877, 820, 815, and 800 cm⁻¹, and all are assigned as Mo–O stretching frequencies. As Table X shows, only five molybdate structures are possible from these stretching frequencies and all are MoO₄ tetrahedra. Structure e uses three frequencies while structures a–d each use only two frequencies. In order to use all four observed Raman stretching frequencies, however, a hybrid structure is formed from structures a and e. This results in Mo–O bond lengths of 2 X A, 1 X AB, and 1 X CD, or 2 X 1.748 (16), 1 X 1.765 (32), and 1 X 1.788 (20) Å, for the MoO₄ tetrahedron in the sillenite structure.

VI. Conclusions

The Bi₂O₃–MoO₃ system was examined with Raman spectroscopy. Seven distinct molybdenum-containing phases and four bismuth oxide phases were identified and the compositional regions of their existence established. In addition to detecting the phases present at each Bi:Mo composition, the Raman spectra permitted the structural determination of the molybdate species in these phases. The crystal structures of the α-Bi₉Mo₂O₁₅, β-Bi₃₈Mo₂O₇₈, and γ-Bi₂MoO₆ phases are known, and this allowed the assignment of their Mo–O bond lengths to their Raman stretching frequencies. In contrast, the molecular structures in the molybdate phases γ’-Bi₂MoO₆, Bi₅MoO₁₅, Bi₅MoO₂₇₄, and a Bi–Mo–O sillenite phase have not been reported. In the present study, the molecular structures of the molybdate species in these undetermined bismuth molybdate phases were determined by Raman spectroscopy using a new, systematic method that takes advantage of previously determined Raman stretching frequency/bond length/bond strength empirical correlations.

All four of the new bismuth molybdate phases investigated contain regular, isolated MoO₄ tetrahedra. At the Bi:Mo = 2:1 composition (treated at 645 °C), γ’-Bi₂MoO₆ is the major phase and was found to contain two types of MoO₄ tetrahedra: one slightly distorted with bond lengths of 2 X 1.738 (16), 1 X 1.780 (16), and 1 X 1.805 (21) Å and a very regular tetrahedron with bond lengths of 3 X 1.755 (16) and 1 X 1.776 (16) Å. At the

3:1 composition, Bi$_2$Mo$_2$O$_{13}$ predominates and has a MoO$_4$ tetrahedron with bond lengths of 3 $\times$ 1.747 (16) and 1 $\times$ 1.793 (16) Å. At the 4:1 and 38:7 compositions, the major phase is Bi$_{39}$-Mo$_{29}$O$_{13}$ and its MoO$_4$ tetrahedron is essentially identical to that in Bi$_2$Mo$_2$O$_{13}$, with bond lengths of 3 $\times$ 1.752 (16) and 1 $\times$ 1.793 (16) Å. At the 14:1 composition, the molybdenum-stabilized silicate structure is the major phase and its MoO$_4$ tetrahedron has bond lengths of 2 $\times$ 1.748 (16), 1 $\times$ 1.765 (32), and 1 $\times$ 1.788 (20) Å.

The systematic method used in the present study for interpreting the Raman spectra of molybdate species by using empirical Raman stretching frequency/bond length/bond strength relations is a very effective way of determining the coordinations and bond lengths of molybdate species from their Raman spectra. In cases where diffraction techniques fall short of providing the oxygen positions around cations in a metal oxide system, Raman spectroscopy may be used to generate this vital structural information. Used in this way, Raman spectroscopy becomes an important complementary technique to diffraction methods in structural investigations of transition-metal oxide systems.

**Acknowledgment.** We are indebted to D. A. Jefferson (University of Cambridge), D. A. Buttrey (University of Delaware), and J. M. Thomas (The Royal Institute) for supplying the bismuth molybdate samples. Financial support from the Texaco Philanthropic Foundation and the Sherman Fairchild Foundation is acknowledged by F.D.H.

**Registry No.** Bi$_2$O$_3$, 1304-76-3; MoO$_3$, 1313-27-5; α-Bi$_2$Mo$_2$O$_{13}$, 13595-85-2; β-Bi$_2$Mo$_2$O$_{13}$, 16229-40-6; γ-Bi$_2$Mo$_2$O$_{13}$, 13565-96-3; Bi$_2$Mo$_2$O$_{13}$, 51682-19-0; Bi$_2$Mo$_2$O$_{13}$, 103715-01-1.

Site Group Analysis of Normal Modes in Semiconductor Superlattices


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We present a site group analysis of normal modes in semiconductor superlattices which permits us to connect by symmetry the local atomic displacements and normal vibrational modes over the entire Brillouin zone. The arrangements of atoms over the Wannier positions for (GaAs), (AlAs), and (Si)$_m$(Ge)$_n$ superlattices oriented along [001] are determined for different sets of $m$ and $n$. We obtain the symmetry for $k \neq 0$ phonons using the theory of the band respresentations of space groups and derive selection rules for one- and two-phonon infrared absorption and for first- and second-order Raman scattering.

1. Introduction

New techniques allow the fabrication of rather complex crystals with a large number of atoms in the primitive cell. Success in growing (GaAs)$_m$(AlAs)$_n$ and (Si)$_m$(Ge)$_n$ superlattices (SL's) with varying primitive cell, consisting of $m$ and $n$ monolayers of GaAs and AlAs (Si and Ge), respectively, by molecular beam epitaxy as well as characterization by Raman scattering of these SL's has been demonstrated recently by several groups. Improvements in growth techniques and growth control give the ability to produce effective way of determining the coordinations and bond lengths of molybdate species from their Raman spectra. In cases where diffraction techniques fall short of providing the oxygen positions around cations in a metal oxide system, Raman spectroscopy may be used to generate this vital structural information. Used in this way, Raman spectroscopy becomes an important complementary technique to diffraction methods in structural investigations of transition-metal oxide systems.

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