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ELECTRONIC STRUCTURE OF BISMUTH MOLYBDENUM OXIDE SINGLE CRYSTAL $Bi_{0.19}MoO_3$*

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Single crystal $Bi_{0.19}MoO_3$ has been grown by fused salt electrolytic technique. X-ray powder diffraction shows that the unit cell parameters are: a=1.9985nm, b=0.4085nm and c=1.4437nm. The temperature dependence of resistivity demonstrates a semiconductor characteristic. X-ray photoemission spectroscopy studies provide that the valence band of $Bi_{0.19}MoO_3$ are made up of oxygen p_π and the π^*, π and σ bonding bands formed by orbital combination. The shoulder at 0.4 eV near the top of valence band may be formed from the non-bonding d_{xy} orbitals of some Mo atoms. The O1s core-electron spectrum reveals the presence of two inequivalent bonds of oxygen ions in $Bi_{0.19}MoO_3$. Bi4f core-level spectrum shows two bonding characters of Bi atoms in bismuth molybdenum oxide single crystals. Mo3d core-level spectrum could be decomposed into two kinds of valence states of molybdenum(Mo^{+5} and Mo^{+6}).

Keywords: bismuth molybdenum oxide single crystal, X-ray photoemission spectroscopy, electronic structure, core-level structure

PACC: 7125T, 6110M, 7280G

I. INTRODUCTION

Ternary molybdenum oxides, which exhibit a wealth of structural complexity and a variety of physical phenomena, are of interest. Molybdenum phases A_xMoO_y, where A is a monovalent (K, Rb, Tl, Na)[1−3] or a divalent (Ba, Sr, Ca)[4−6] cation, have been studied in considerable detail. Molybdenum bronzes with a trivalent cation were first synthesized by Parmentier *et al.*[7] They studied two ternary molybdenum oxides: $Sb_4Mo_{20}O_{62}$ and $Sb_8Mo_{20}O_{62}$. The first bismuth molybdenum oxides were formed by Conan and Schneemeyer *et al.*[8,9] subsequently. All these compounds are purple with high reflectivity and show semiconducting behavior. All are orthorhombic with space groups $Pmma$ or $Pmc2$. The crystal structure of these ternary molybdenum oxides may be described as a framework of corner-sharing MoO_6 octahedra. The pseudohexagonal channels are fully occupied by A_2O chains. Two covalent bonds are "formed" between the trivalent atom A and two oxygen atoms of the framework MoO_3, and a third covalent bond is "formed" between A atom and the oxygen in the hexagonal channel.[7−10]

Up to now, investigations mainly focus on the semiconducting properties and the crystal structure of trivalent cation molybdenum bronzes. Limited information about the electronic structure and the core-level structures of these compounds are available. In this paper, single crystal $Bi_{0.19}MoO_3$ has been grown by fused salt electrolytic method. The resistivity and crystal structure of single crystal $Bi_{0.19}MoO_3$ were reported. For the first time, the electronic structure and the core - level structures were investigated by means of X-ray photoemission spectra.

II. EXPERIMENTAL

Single crystals of bismuth molybdenum oxide bronze were grown by the electrolytic reduction of a melt of Bi_2O_3-MoO_3 with molar ratio of Bi_2O_3:MoO_3=1:5.5. The temperature (700±2°C), melt composition and current density (40mA) controlled the product phase. The resulting crystals are purple platelets of a typical size 3cm×4cm×0.2cm and have the composition of $Bi_{0.19}MoO_3$.

X-ray powder diffraction data were collected on a Dmax-rA diffractometer using Cu$K\alpha$ radiation. The working voltage V and current I and time constant τ were 40kV and 50mA and 0.2 s, respectively. Lattice parameters were refined from a least squares fit using at least fifteen reflections with 2θ <80°. The results of lattice parameters were also verified by four-circle single crystal diffraction technique.

The electrical resistivities were measured along the easy growth axis by a conventional four-probe con-

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figuration. The electric contacts were made by evaporating Au film on the two terminals of the sample; Au wires were attached to the Au-film areas by Ag paint. The distance between the two voltage contacts was about 0.5mm. The sample was mounted in the vacuum chamber of a refrigerator, and the temperature could be changed in the range of 100–300K.

The angle-integrated X-ray photoemission spectroscopy(XPS) measurements were performed at room temperature in an XSAM-800 spectrometer. Clean surfaces were cleaved immediately before measurements were undertaken. X-ray photo energy was 1468.6eV from Al$K\alpha$ with total resolution of 0.9eV, which was determined by full width at half maximum (FWHM) of the $Ag3d_{5/2}$ line. The linearization of energy scale was adjusted through three lines of $Au4f_{7/2}$, $Ag3d_{5/2}$ and $Cu2p_{3/2}$ with the energies of 84.0, 368.2 and 932.6eV, respectively. The spectra encompassing the valence band and Bi4f and Mo3d and O1s corelevels were investigated at an operating pressure of 4×10^{-7}Pa.

Ⅲ. RESULTS AND DISCUSSION

X-ray powder diffraction (XRD) data of the measured and calculated were listed in Table 1. The unit cell parameters of $Bi_{0.19}MoO_3$, along with those of trivalent cation molybdenum bronzes reported in Ref.[9], are summarized in Table 2. It is significant to see that the lattice parameter of b axis is nearly not changed, while in a and c axis, a $2a$ and $2c$ changing of lattice parameter is observed. The unit cell parameter in a axis of $Bi_{0.19}MoO_3$ in our experiment is twice as large as that of $Bi_{0.135}MoO_{2.5}$, and in c axis twice that of $Bi_{0.11}MoO_{2.5}$. This crystalline superstructure for trivalent cation molybdenum bronzes has also been observed by Schneemeyer and Conan *et al.*[8,9] It may be explained by the higher binding energy of Bi cation, leading to a less ordered structure for the Bi_2O chains.

Table 1. X-ray powder diffraction data of $Bi_{0.19}MoO_3$.

$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	hkl	I/I_0
8.845	8.842	10.003	10.003	200	23
12.254	12.251	7.2191	7.2191	020	15
15.124	15.129	5.8594	5.8594	220	6
21.780	21.738	4.0804	4.0878	001	100
22.620	22.620	3.9308	3.9308	011	3
23.420	23.508	3.7983	3.7855	201	5
24.650	24.646	3.6100	3.6129	040	10
25.030	25.026	3.5561	3.5589	021	7
25.420	25.426	3.5038	3.5038	121	13
26.234	26.231	3.3961	3.3961	240	8
26.750	26.743	3.3313	3.3337	600	70
28.460	28.433	3.1361	3.1382	321	2
30.520	30.530	2.9289	2.9270	440	4
30.850	30.843	2.8974	2.8993	421	3

Table 2. Lattice parameters of A_xMoO_y (A=Bi or Sb).

	a/nm	b/nm	c/nm	c/a	$\alpha\beta\gamma$
$Bi_{0.11}MoO_{2.5}$	1.9996	0.4169	0.7209	0.361	90
$Bi_{0.135}MoO_{2.5}$	1.0002	0.4079	1.4443	1.444	90
$Bi_{0.19}MoO_3$	1.9985	0.4085	1.4437	0.732	90
$Sb_{0.235}MoO_{2.5}$	2.0058	0.4135	0.7349	0.376	90

Figure 1 shows the temperature dependence of electrical resistivity ρ of $Bi_{0.19}MoO_3$ single crystal in the range of 300–100K. It is seen that the electrical resistivity ρ increases drastically with the decrease of temperature. Figure 2 gives the logarithmic value of ρ versus the reverse value of temperature. Obviously a quasi-linear dependence is clearly observed in this temperature range. The relation between the resistivity and temperature can be approximately described by the simple thermal activation law, typical formula for semiconductor,

$$\rho = \rho_0 \exp(\Delta/2k_{\mathrm{B}}T),$$

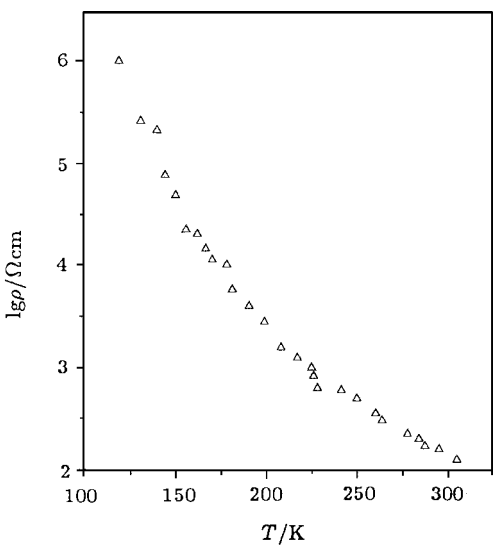


Fig.1. Temperature dependence of electrical resistivity ρ of $Bi_{0.19}MoO_3$.

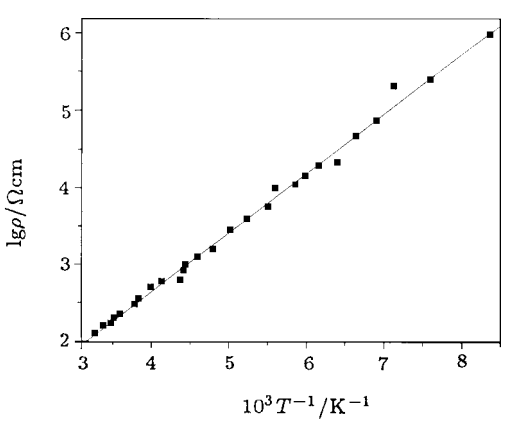


Fig.2. The logarithmic value of ρ versus the reverse value of temperature.

where Δ presents the single particle active energy gap, and k_{B} is the Boltzmann constant. The fitted data gives Δ approximate to 0.30eV. This value is very close to 0.36 and 0.32eV of polycrystal $Bi_4Mo_{20}O_{62}$ and $Sb_4Mo_{20}O_{62}$ reported by Conan[8] and Bonnet,[10] and smaller than 0.75eV reported by Dickens *et al.* in $K_{0.33}MoO_3$,[11] much larger than 0.15eV for $K_{0.3}MoO_3$ reported by Travaglini *et al.*[12]

An XPS spectrum of the valence-band region is shown in Fig.3. The structure of the spectrum is mainly characterized by the shape of two peaks. One of them with a weak intensity is located at 1.4eV below Fermi level (E_{F}) and with a shoulder near 0.4eV. The other being a broad peak consists of two peaks at 7.8 and 6.7eV, and with two shoulders at 8.6 and 4.9eV below Fermi surface. The shape of the valence band is much similar to that reported for MoO_3[13] and $K_{0.33}MoO_3$,[14] and is characteristic of edge - sharing MoO_6 octahedra presented by Travaglini from optical reflection measurement.[12] While there are some differences derived from the fact that the Bi_2O chains occupy the pseudohexagonal channels in the framework of corner-sharing MoO_6 octahedra, the electronic structures of molybdenum bronzes can be derived from the elementary MoO_6 octahedron as described previously.[11–14] In a MoO_6 octahedron, the Mo5p, 5s and 4d (e_{g}) cationic orbitals combine with the 2s and the three $2p_\sigma$ anionic orbitals to form three occupied bonding σ and three empty anti-bonding σ^* molecular orbitals with significant d(e_{g}) character. The Mo4d ($t_{2\mathrm{g}}$) cationic orbitals combine with three $2p_\pi$ anionic orbitals to give the bonding π valence band and an anti-bonding π^* band. Three oxygen $2p_\pi$ orbitals per octahedron remain as nonbonding levels because they are of the wrong symmetry for combining with any of the Mo orbitals. While σ and π bonding bands and p_π oxygen nonbonding levels form the fully filled valence band, π^* and σ^* bands can form the conduction or the outermost valence bands. Because of the octahedral crystal-field and the strong d-character, the π^* bands and σ^* empty bands are separated from each other. From Fig.3, the fully filled valence bands of $Bi_{0.19}MoO_3$ are made up of π^*, oxygen p_π , π and σ bonding bands, while the empty conduction bands consist of σ^* bands dominated by the Mo4d orbitals. Since the photoelectric cross-section of the Mo4d states at Al$K\alpha$ energy is 16 times greater than that of the O2p states, the valence band spectrum obtained by XPS is largely representative of the Mo4d admixture into the valence band. The top of the band, where the O2p character is the strongest, is significantly attenuated. So that only a weak shoulder at 4.9 eV due to O2p_π nonbonding levels is ob-

served. The peak at 7.8eV and the other shoulder at 8.6eV are related to π and σ bonding bands respectively. The top of the valence band with the weak peak at 1.4 eV corresponds to the π^* band consisting dominantly of Mo4dt_{2g} states with only a weak O2p$_\pi$ admixture presented above, while for $K_{0.3}MoO_3$ it corresponds to the occupied conduction band. It is worth noting that the spectrum exhibited in Fig.3 is slightly different from that of monovalent molybdenum bronzes. The shoulder at 0.4eV near the top of the valence band and the peak at 6.7eV of the valence band are not observed in $K_{0.3}MoO_3$,[14−16] $K_{0.33}MoO_3$[14,17] and KMo_6O_{17}.[14,18]

In $Bi_{0.19}MoO_3$, there are six different Mo atom sites, and deep π levels may be formed from d_{xz}, d_{yz} orbitals of all the Mo atoms, while d_{xy} orbitals of some Mo atoms may lead to another bonding π bands lying above them. For the same reason, the top of the valence band consists of two π^* levels due to the existence of six different Mo atom sites. These two π^* bands have been assumed to be the donor and acceptor levels and located in the gap by Conan and Bonnet.[8,10]

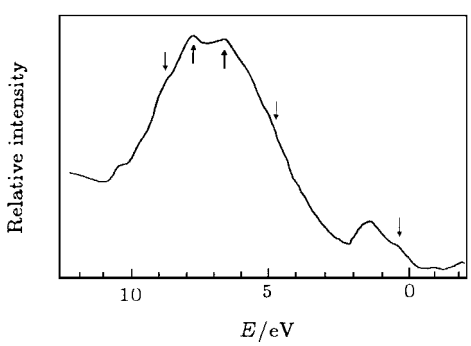


Fig.3. X-ray photoemission spectrum of the valence-band region.

The O1s core-electron spectrum of $Bi_{0.19}MoO_3$ shown in Fig.4 is different from that of the monovalent molybdenum bronzes. It has an asymmetric shape with the broadened maximum around 529.8eV binding energy and a broadened shoulder at 531.3eV binding energy. This spectrum apparently reveals the presence of two nonequivalent bonds of oxygen ions in $Bi_{0.19}MoO_3$. The maximum peak at 529.8eV is due to the unresolved contributions from the many nonequivalent Mo—O bonding in the crystal structure. The broadened shoulder is due to the contributions from three different Bi—O bonding in the crystal structure. That is, two covalent bonds are formed between the Bi atom and the oxygen atoms in the framework MoO_3, and a third bond between the Bi atom and the oxygen in the hexagonal channel. The absence of the long, monotonically decaying tail produced by the conduction-electron screening in metals[19,20] is consistent with the semiconducting property of the bismuth molybdenum oxide crystal. The asymmetric line shape is actually due to the unresolved contributions from the nonequivalent oxygen sites in this crystal structure. Distinct oxygen core-electron binding energies are expected for atoms at corners shared by different numbers of octahedra, i.e., with different numbers of metal-atom neighbors. However, individual contributions to the spectrum are difficult to isolate because the line has only two points of inflection.

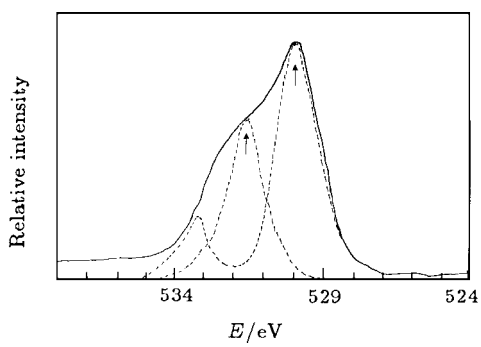


Fig.4. The O1s core level spectrum.

Figure 5 is the Bi4f core-level spectrum. Obviously, this spectrum demonstrates the presence of two bonding characters of Bi atoms in bismuth molybdenum oxide single crystal. The corresponding binding energies are located at 158.5 and 159.2eV, all have the +3 valence characters, which may be due to the Bi—O bonding of Bi atoms with the O atoms in the framework MoO_6 and the Bi—O bonding in the hexagonal channel, respectively.

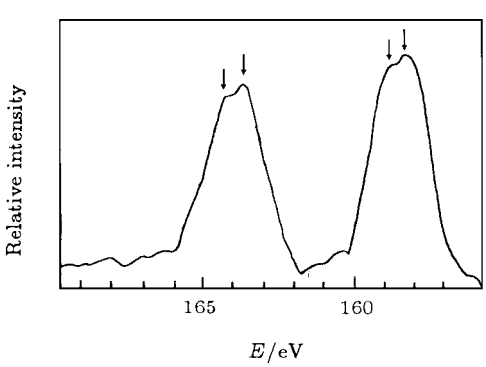


Fig.5. Bi4f core level spectrum.

The Mo3d core-level spectrum displayed in Fig.6 is particularly interesting. The components of the 3d spin-orbit doublet are relatively broad, compared to

those found in MoO_3,[13] and give an indication of some poorly resolved structure. Although there are many nonequivalent Mo sites in this structure, we attempt to resolve the data into two components representing different valences, following Refs.[13] and [21]. The assumption in the decomposing procedure is that the $3d_{5/2}$ and $3d_{3/2}$ have a spin-orbit split of 3.2 eV, and an intensity ratio $3d_{5/2}/3d_{3/2}$ of 1.5. In Fig.6, two overlapping spin-orbit doublets are marked by A and B, with $3d_{5/2}$ binding energies of 232.0 and 232.7 eV respectively. The approximation of fit with two doublets is satisfactory. The systematic deviations between the data and the fitted line are too small to detect. This indicates that the model function with two doublets is capable of reproducing the details of the data. Components with similar binding energies have been previously obtained for $K_{0.3}MoO_3$, MoO_3 and H_xMoO_3.[10,13] The value of 232.7eV agrees within the experimental error with that reported for stoichiometric MoO_3 (232.6 eV)[13] and for blue bronze $K_{0.3}MoO_3$(232.7 eV).[10] The binding energy of the other line falls about halfway between those of MoO_3 (232.6 eV) and MoO_2(229.4 eV), motivating the assignment of lines at this energy to a +5 initial state,[10,21] confirming the EPR spectroscopy.[8]

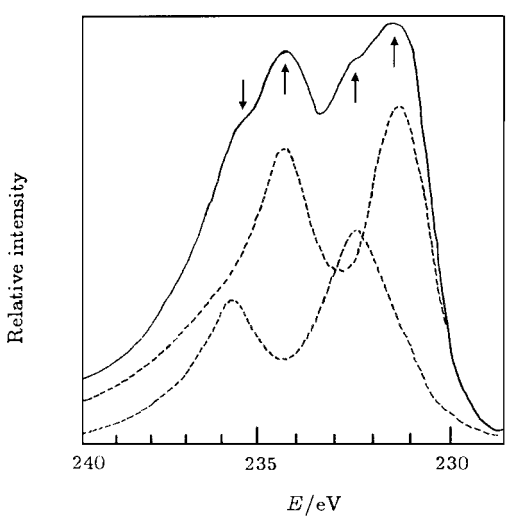


Fig.6. Mo3d core level spectrum.

It should be pointed out that it is consistent with the semiconductimg properties that no tail toward higher binding energy was observed in the spectrum of Mo3d.

IV. CONCLUSIONS

In conclusion, the measurement of the temperature dependence of electrical resistivity of the $Bi_{0.19}MoO_3$ single crystal demonstrates semiconductor characteristics. The crystalline superstructure for molybdenum bronzes was observed by X-ray powder diffraction. XPS Measurements presented in this article have provided much information about the electronic structure of bismuth molybdenum oxide single crystal. The structures of valence band are consistent with the model of Travaglini *et al.*, the fully filled valence bands of $Bi_{0.19}MoO_3$ are made up of π^*, oxygen p_π , π and σ bonding bands, while the empty conduction bands consist of σ^* bands. The shoulder at 0.4 eV of the top of valence may be formed from the non-bonding d_{xy} orbitals of some Mo atoms. The O1s core-electron spectrum has the asymmetric shape with a broadened maximum around 529.8eV binding energy and a broadened shoulder at 531.3eV due to the presence of two nonequivalent bonds of oxygen ions in $Bi_{0.19}MoO_3$. The shape of a symmetric and broadened line of O1s is also due to unresolved contributions from the many nonequivalent oxygen sites in this crystal structure. Bi4f core-level spectrum reveals the presence of two bonding characters of Bi atoms in bismuth molybdenum oxide single crystal. Mo3d core-level spectrum could be decomposed into two kinds of valence states of molybdenum(Mo^{+5} and Mo^{+6}). The calculated average valence state is about +5.6, which is consistent with the expectation value from the composition of this material.

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