X-ray absorption study of the electronic structure of tungsten and molybdenum oxides on the O K-edge

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Abstract

Magnetron sputtered amorphous thin films a-WO₃, a-MoO₃ and doped a-WO₃:Ir have been studied by X-ray absorption spectroscopy on the oxygen K-edge in comparison with crystalline oxides as monoclinic m-WO₃, orthorhombic α-MoO₃, cubic Na₀.₆WO₃, layered-type hexagonal h-WO₃ and WO₃·H₂O, having variable electronic and atomic structure. The changes in the XANES ranging 10–15 eV above the absorption edge are interpreted based on the known band-structure calculations. The high-energy features are related to the multiple-scattering processes (EXAFS) at the nearest atoms. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: WO₃; MoO₃; Electrochromic thin films; X-Ray absorption spectroscopy; O K-edge

1. Introduction

X-Ray absorption spectroscopy (XAS) studies on the O K-edge have been intensively conducted on 3d transition metal oxides (TMO) in the past [1,2]. However, there are only a few works related to the O K-edge in 5d TMO compounds (Na₀.₆WO₃ [3] and WO₃ [4–6]) which were performed using electron energy loss spectroscopy (EELS). Recently we have reported the results of high-resolution O K-edge XAS experiments using synchrotron radiation [7,8] in 5d perovskite-type (ReO₃, H₂ReO₄, m-WO₃, H₃WO₄ and Na₀.₆WO₃) and layered-type (hexagonal h-WO₃ and WO₃·H₂O) crystalline compounds and in thermally evaporated amorphous thin films (labelled further as a-WO₃ (e)). The complementary study at the W, Re, Ir L₁ and L₃ edges were published by us previously [9].

The first group of crystalline compounds (ReO₃, m-WO₃, WO₃·H₂O and Na₀.₆WO₃) belongs to the perovskite-type structure with a general formula ABO₃. Cubic rhenium trioxide is composed of regular ReO₆ octahedra (R(Re–O) = 1.875 Å) joined by vertices with the A places being vacant. The sodium tungsten bronze Na₀.₆WO₃ has also a cubic structure with R(W–O) = 1.919 Å and a W-O-W angle equal to 180° as in ReO₃. In monoclinic m-WO₃ tungsten trioxide, the [WO₃] octahedra are distorted (R(W–O) = 1.73–2.19 Å) with tungsten ions being displaced off-centre.

The second group of crystalline compounds (h-WO₃, WO₃·H₂O and α-MoO₃) have a layered-type structure. Two-dimensional (2D) perovskite-like layers of distorted [WO₆] octahedra joined by vertices exist in hydrate, whereas the 2D-layers in h-WO₃ are built up of [WO₃] octahedra sharing their corners arranged in six-member rings in layers normal to the hexagonal c-axis [10,11]. In the c-axis direction of h-WO₃, the [WO₃] octahedra sharing their corners arranged in the chain parallel to the c-axis, therefore h-WO₃ has two types of oxygen atoms. It is supposed that tungsten ions are at the centre of the [WO₆] octahedra with four equivalent bonds W–O₁ in the hexagonal layer R = 1.89 Å (in-
and one atom $O_3$ of interlayer water molecule at 2.33 Å. The value of the W–O–W angle within the layer is about 160°. Finally, the 2D layers in $\alpha$-MoO$_3$ are built up of double chains of edge-sharing [MoO$_3$] octahedra connected through vertices [12,13]. The molybdenum oxide has strongly distorted the first shell; there, three groups of the Mo–O distances can be defined, centred at 1.7, 2.0 and 2.3 Å.

In this work, we report on the O K-edge XAS study of magnetron sputtered electrochromic a-WO$_3$, a-WO$_3$:Ir and a-MoO$_3$ thin films in comparison with several crystalline compounds.

2. Experimental

Tungsten oxide WO$_3$ and molybdenum oxide MoO$_3$ thin films were produced from W(Mo) metallic targets by dc reactive magnetron sputtering. Mixed amorphous thin films WO$_3$:Ir (80% W–20% Ir) and IrO$_2$:Ti (95% Ir–5% Ti) were produced from W, Ir and Ti metallic targets by simultaneous magnetron sputtering. A gas mixture of argon (80%) and oxygen (20%) was used as the sputter atmosphere. The sputter deposition was performed during 60–90 min at the total gas pressure 6–6.7 Pa. Pure Si substrates were mounted about 8 cm above the target and were not intentionally heated. The films had a thickness of 0.5–1.2 μm. The as-deposited amorphous a-WO$_3$ and a-MoO$_3$ films were nearly transparent, but mixed a-WO$_3$:Ir and a-IrO$_2$:Ti films were grey coloured.

XAS experiments on the O K-edge were carried out at room temperature (r.t.) in the total electron yield (TEY) mode on the SA22 beam line at the LURE Super-ACO storage ring (Orsay, France), which operated at the energy 800 MeV with the current from 215 to 407 mA. The samples were measured at the magic angle to average polarisation effects. The energy scale was calibrated by setting the position of the first peak for polycrystalline NiO to 531.7 eV. The energy resolution was 0.2 eV.

3. Results and discussion

The normalised XAS spectra are shown in Figs. 1–3, and the energy positions of the main features are given in Table 1. According to the dipole selection rule, the O K-edge spectra are due to transitions from atomic-like 1s state to unoccupied bound and free states with $p$-character, which experience some relaxation in the presence of the 1s core-hole positive charge. The O K-edge spectra reflect also the shape of the density of metal d-states, due to a hybridisation between the metal d and oxygen 2p orbitals. No shift in the position of the absorption edge was observed for tungsten oxide crys-
The first intense peak at 530 eV has a shape consisting of the main peak A and the shoulder B. This peak reflects the oxygen 2p-states in the d(\(t_{2g}\)) conduction band formed by 5d tungsten (4d molybdenum) and 2p oxygen orbitals. The shoulder B is related to the anisotropy of the d(\(t_{2g}\))-band, caused by non-equivalent oxygen atoms of the first coordination shell. The spectra of sputtered a-WO₃ and evaporated a-WO₃ (e) as well as of mixed a-WO₃:Ir have a very sharp peak A and shoulder B, similar to the ones found in layered tungsten oxides (Figs. 1 and 2).

The peaks A and B intensity depends on the number of the 2p(O) empty states, which are determined by the occupancy of the conduction band, and by a degree of the Me–O bond covalency (or the value of the oxygen-to-metal back-charge transfer) [1]. Therefore, it is expected that the first peak should have higher intensity in more covalent tungsten and molybdenum oxides, since the formal valence state (and thus the number of the d electrons) is 6+ in all cases. At the same time, the full width at half maximum (FWHM) of the peak is related to the width of the d(\(t_{2g}\)) band.

The amplitude of the first peak at 530 eV increases significantly from m-WO₃ to Na₀.₆WO₃, while the broadening of the peak (and thus the 5d band width) decreases due to the crystal symmetry increase from monoclinic in m-WO₃ to cubic in Na₀.₆WO₃. The combination of two effects leads to a slight increase of the intensity of the first peak in Na₀.₆WO₃. In the series from m-WO₃ to WO₃·H₂O, h-WO₃, a-WO₃:Ir and a-WO₃ (a-WO₃ (e)), the intensity of the peak at 530 eV increases, but its shape is nearly unchanged: the two peaks A and B are separated by about 1.0–1.5 eV (Table 1). Finally, the intensity of the first peak decreases drastically from a-WO₃ to a-IrO₂:Ti presumably due to an increase of the number of d electrons in iridium oxide.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Edge</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-WO₃</td>
<td>529.8</td>
<td>530.7</td>
<td>531.7</td>
<td>535.4</td>
<td>537.6</td>
<td>541.1</td>
<td>543.8</td>
<td>556.1</td>
<td>567.2</td>
</tr>
<tr>
<td>WO₃·H₂O</td>
<td>529.7</td>
<td>530.5</td>
<td>531.9</td>
<td>536.1</td>
<td>538.2</td>
<td>541.9</td>
<td>543.0</td>
<td>551.6</td>
<td>567.2</td>
</tr>
<tr>
<td>a-WO₃ (e)</td>
<td>529.7</td>
<td>530.5</td>
<td>531.8</td>
<td>536.7</td>
<td>536.7</td>
<td>543.3</td>
<td>565.6</td>
<td>576.9</td>
<td>565.6</td>
</tr>
<tr>
<td>a-WO₃:Ir</td>
<td>530.0</td>
<td>530.7</td>
<td>532.0</td>
<td>536.9</td>
<td>535.2</td>
<td>542.4</td>
<td>560.0</td>
<td>566.0</td>
<td>563.0</td>
</tr>
<tr>
<td>a-MoO₃</td>
<td>529.3</td>
<td>530.0</td>
<td>533.0</td>
<td>534.7</td>
<td>535.3</td>
<td>540.5</td>
<td>542.8</td>
<td>552.5</td>
<td>564.0</td>
</tr>
<tr>
<td>a-IrO₂:Ti</td>
<td>529.3</td>
<td>529.8</td>
<td>532.8</td>
<td></td>
<td></td>
<td></td>
<td>540.7</td>
<td></td>
<td>564.0</td>
</tr>
</tbody>
</table>
The W–O bond covalency is the main factor influencing the area of the first peak in tungsten oxides, and, therefore, cubic Na$_{0.6}$WO$_3$ is considered to have the most covalent W–O bonds. The FWHM of the first peak in Na$_{0.6}$WO$_3$, being about 3.5 eV, is determined by the experimental resolution (0.2 eV), the natural 1s(O) core-hole level width (0.22 eV), the 5d spin-orbit splitting (1.5 eV) and the 5d($t_{2g}$)-band width (3 eV). It is comparable to the one estimated from theoretical calculations [14,15] and equal to 3–4 eV. On the other hand, in distorted perovskite (m-WO$_3$) and in layered compounds (h-WO$_3$ and WO$_3$:H$_2$O), as well as in amorphous a-WO$_3$, the broadening or splitting of the first peak (A) is due to several non-equivalent oxygen atoms present in these structures. In layered compounds h-WO$_3$ and WO$_3$:H$_2$O, there are two main contributions from the intralayer and interlayer oxygen atoms, giving the origin of the two peaks A and B, respectively (Fig. 1). In molybdenum oxide α-MoO$_3$, there are three groups of the Mo–O distances [12,13], leading to large splitting of the first peak into A, B and C components (Fig. 3).

The peaks C and D are due to 5d($e_g$)(W)-2p(O) hybridisation, influenced strongly by distortion of [WO$_6$] octahedra. An increase of the C and D peak intensity suggests a partially covalent interaction between oxygen and metal ions. The amplitude of the peaks increases with increasing the symmetry of [WO$_6$] octahedra and is the largest in cubic perovskite Na$_{0.6}$WO$_3$. In mixed a-WO$_3$:Ir thin film, the amplitude of the peak C decreases with an addition of iridium. In molybdenum oxide, having very distorted first shell [MoO$_6$] octahedra, the amplitude of the peaks C and D is the smallest. One can also roughly estimate the splitting between the $t_{2g}$ and $e_g$ sub-bands in tungsten oxides from the difference between A and C peaks: it is about 4.7 eV, compared to the theoretical estimate 5.5 eV for cubic NaWO$_3$ [14,15].

By analogy with the oxygen K-edge XAS in 3d perovskites [16], we attribute the peaks E and F to 6sp(W)-2p(O) (5sp(Mo)-2p(O)) interaction: their variation has behaviour similar to that of the peaks C and D. The next features G and H are identified to scattering resonances at the nearest atoms. Our multiple-scattering calculations suggest that the peak H is due to single-scattering processes on the nearest oxygen atoms at about 2.7 Å. The intensity of the feature G is attributed to the value of the W–O–W angle: it is higher for the structures having near-linear atomic chain as Na$_{0.6}$WO$_3$, WO$_2$:90 and α-MoO$_3$. The peak G is not visible in amorphous thin films (Figs. 2 and 3) due to the presence of strong static disorder.

4. Conclusions

Our results show that the O K-edge absorption spectra in 5d metal oxides can serve as a sensitive probe of highly detailed information on the chemical bonding and peculiarities of the local electronic and atomic structure of electrochromic oxides.

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References