

Study of the Electronic Structure of Rhenium and Tungsten Oxides on the O K-Edge

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Abstract. Oxygen K-edge x-ray absorption spectra were studied on the electrochromic amorphous thin film a-WO₃ in the comparison with crystalline oxides having variable electronic (d⁰, d¹, d²) and atomic structure: monoclinic m-WO₃ (insulator - d⁰), cubic Na_{0.6}WO₃ (metal - d¹), cubic ReO₃ (metal - d¹), layered-type hexagonal h-WO₃, WO₃·H₂O and with intercalated H_xReO₃ (metal - d²), H_xWO₃ oxides having a metal-insulating transition. The changes in the XANES range 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) on the nearest atoms. The intensity of the feature at 550-560 eV is attributed for the first time to the value of the metal-oxygen-metal bond angle.

1. Introduction

X-ray absorption spectroscopy (XAS) studies on the O K-edge have been intensively conducted during the last years on 3d transition metal (TM) oxides and perovskites [1, 2]. However, there are only few contributions related to the O K-edge in 5d TM oxide compounds (Na_xWO₃ [3] and WO₃ [4, 5], which were performed using electron energy loss spectroscopy (EELS). Here we present the XAS results on the O K-edge in 5d perovskite-type compounds (ReO₃, H_xReO₃, m-WO₃, H_xWO₃ and Na_{0.6}WO₃), layered-type compounds (hex-WO₃ and WO₃·H₂O), and evaporated electrochromic amorphous thin film a-WO₃. The results are obtained with high-resolution using synchrotron radiation. The first group of studied compounds (ReO₃, H_xReO₃, m-WO₃, H_xWO₃ and Na_{0.6}WO₃) belong 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. In monoclinic m-WO₃ tungsten trioxide, the WO₆ octahedra are distorted (R(W-O) = 1.73-2.19 Å) with tungsten ions being displaced off-centre. Upon formation of hydrogen bronze, it is believed that the hydrogen ions form the O-H bonds and modify the host structure. These modifications lead to the local symmetry lowering in H_xReO₃ due to a tilting of the ReO₆ octahedra (the value

of the Re-O-Re angle decreases from 180 to 170 degree). On the opposite, an increase of the crystal symmetry occurs in H_xWO₃ due to the WO₆ octahedra symmetrization and an increase of the W-O-W angle. At x > 0.5, the H_xWO₃ structure becomes cubic. The sodium tungsten bronze Na_{0.6}WO₃ has cubic structure with R(W-O) = 1.919 Å and W-O-W angle equal to 180 degree as in ReO₃.

The second group of studied compounds (hex-WO₃ and WO₃·H₂O) has 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 hex-WO₃ are built up of WO₆ octahedra sharing their corners arranged in six-member rings in layers normal to the hexagonal c-axis [6]. In c-axis direction of hex-WO₃ the WO₆ octahedra sharing their corners arranged in the chain parallel to c-axis, therefore hex-WO₃ has two type of oxygens. It is supposed that tungsten ions are in the center of the WO₆ octahedra with four equivalent bonds W-O₁ in the hexagonal layer R = 1.89 Å (intralayer bonds) and two W-O₂ bounds R = 1.95 Å between the layers with the linear W-O-W₂ chain and possible disorder within the set of (001) planes. The WO₃·H₂O compound has three types of oxygen: intra- (O₁) and interlayer (O₂)

oxygens and oxygen (O_3) of interlayer water molecule. They have four different distances W-O in the first coordination shell. The tungstyl oxygen O_2 has very short distance 1.68 Å, the intralayer oxygen has two medium distances (1.82 Å and 1.93 Å), and the interlayer water oxygen has long site (2.33 Å). On the other hand, only one value (about 160 degree) of the tilting angle exists between four neighbouring octahedra within the layer.

From previous structural data (EXAFS) obtained by us for the a- WO_3 thin films [7, 8], one can separate three groups of distances which are well observed on RDFs as three peaks of different height and width. In crystalline m- WO_3 and hex- WO_3 , the peaks are well defined even at long distances (~ 2.15 Å) and are splitted into three main groups: sharp peak from 1.7 to 1.8 Å, broad peak 1.8 to 2.0 Å, and broad peak from 2.0 to 2.4 Å. In amorphous thin films, the shape of the distribution differs essentially from the crystalline case: the longest bonds have greater Debye-Waller factor values; therefore the last peak is very broadened and the center of the distribution is shifted to the region of smaller distances. The average tungsten-oxygen distances, calculated by the relationship $\langle R \rangle = (\sum_i R_i N_i) / (\sum_i N_i)$, are equal to 1.929 Å (m- WO_3) and 1.881 Å (a- WO_3). Moreover, from XRD data it is suggested the nanocrystalline hexagonal model of a- WO_3 with the WO octahedra sharing their corners arranged in six-member rings in layers.

2. Experimental Details

Pure ReO_3 and $Na_{0.6}WO_3$ oxides were commercially available polycrystalline powders for which single-phase structure was confirmed by XRD. Green m- WO_3 monocrystal and yellow $WO_3 \cdot H_2O$ powder were prepared (ISSP), and its single phase structure was confirmed by XRD and Raman spectroscopy. The hex- WO_3 is obtained by dehydration of hydrate precursors [6]. The H_xReO_3 and H_xWO_3 bronzes were prepared in-situ in vacuum chamber by hydrogen intercalation into platinized oxide ReO_3 and m- WO_3 powders during 4 hours. The amorphous tungsten trioxide (a- WO_3) thin films were prepared by thermal evaporation of WO_3 powder in medium vacuum on a glass substrate at 200 °C.

X-ray absorption experiments at the O K-edge were carried out at room temperature 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.

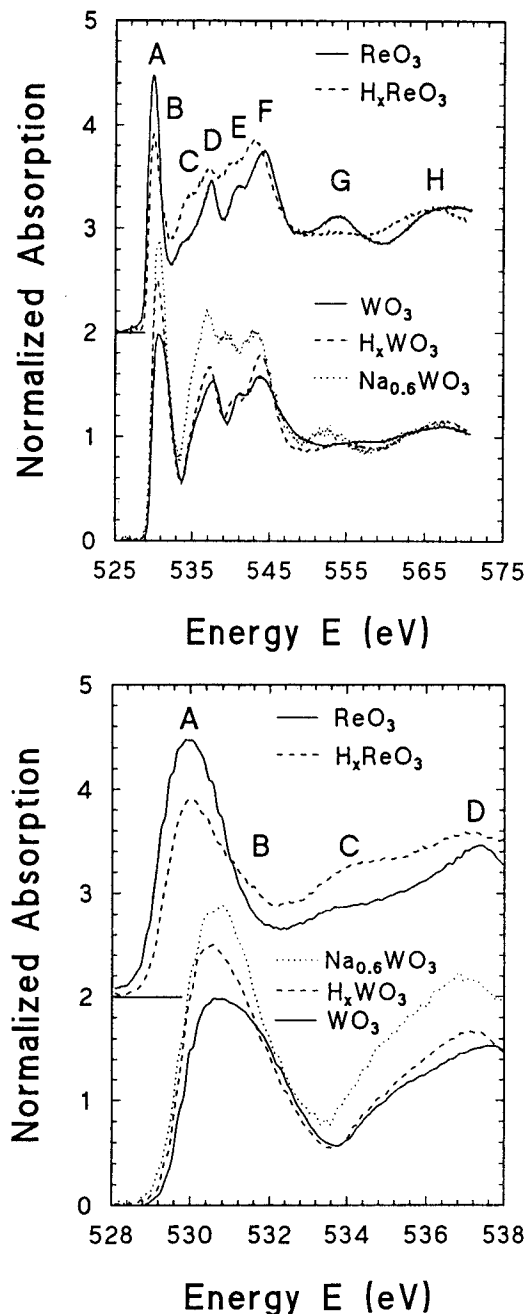


Fig. 1a). Oxygen K-edge full (XANES+EXAFS) x-ray absorption spectra in pure oxides ReO_3 and m- WO_3 , sodium tungsten bronze $Na_{0.6}WO_3$ and hydrogen intercalated H_xReO_3 and H_xWO_3 . All spectra are normalized to the absorption edge jump. The spectra for ReO_3 and H_xReO_3 are vertically shifted for clarity; b). XANES part of oxygen K-edge x-ray absorption spectra in pure oxides ReO_3 and m- WO_3 , sodium tungsten bronze $Na_{0.6}WO_3$ and hydrogen intercalated H_xReO_3 and H_xWO_3 . The spectra for ReO_3 and H_xReO_3 are vertically shifted for clarity.

The samples were measured at the magic angle to average polarization effects. The energy scale was calibrated by setting the position of the first peak for polycrystalline NiO to 531.7 eV [1]. The energy resolution was 0.2 eV.

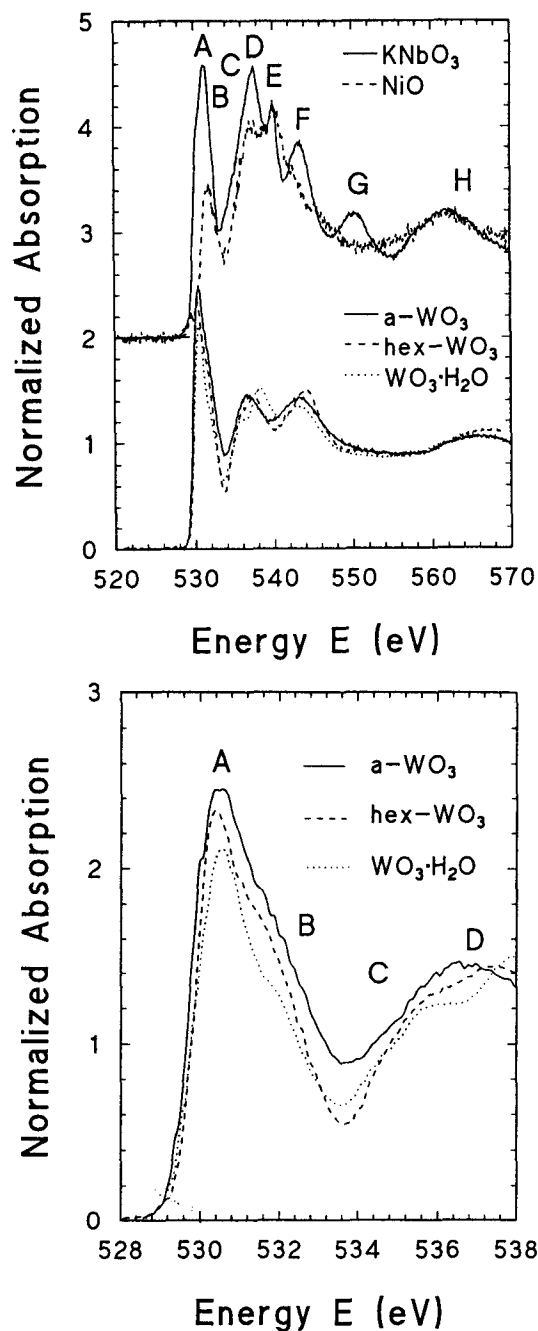


Fig. 2a). Oxygen K-edge full (XANES+EXAFS) x-ray absorption spectra in the layered crystalline oxides hex-WO_3 and $\text{WO}_3 \cdot \text{H}_2\text{O}$, evaporated amorphous thin film a-WO_3 . The spectra of reference crystalline compounds KNbO_3 and NiO_3 are also shown and are vertically shifted for clarity. All spectra are normalized to the absorption edge jump; b). XANES part of oxygen K-edge x-ray absorption spectra in the layered crystalline oxides hex-WO_3 and $\text{WO}_3 \cdot \text{H}_2\text{O}$, evaporated amorphous thin film a-WO_3 .

3. Results and Discussion

The normalised XAS spectra are shown in Figs 1 and 2, and the energy positions of the main features are given in

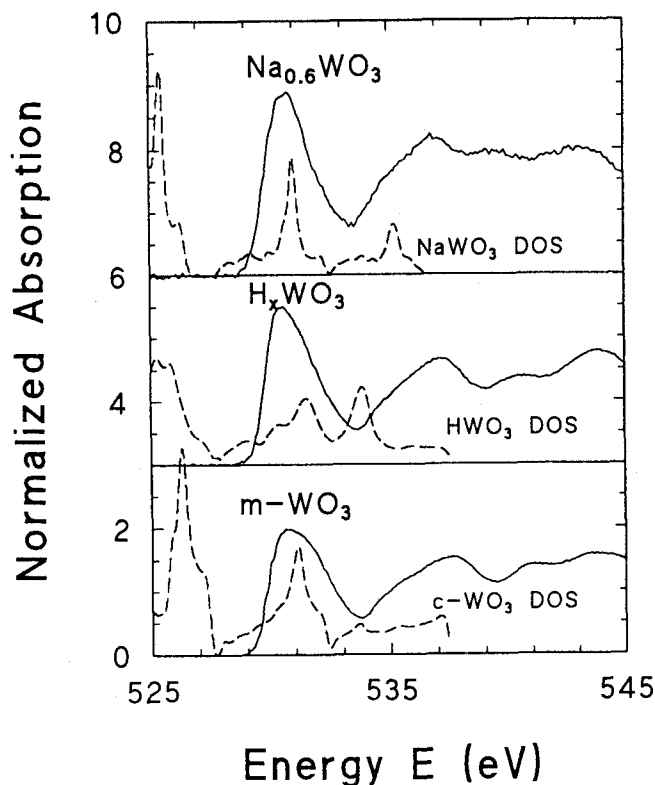


Fig. 3. Total density of state (dashed lines) for sodium tungsten bronze $\text{Na}_{0.6}\text{WO}_3$, hydrogen intercalated H_xWO_3 and ideal "cubic" c-WO_3 (from Hjelm et al. Phys. Rev. B **54**, 2436 (1996)) in comparison with the experimental O K-edge XANES spectra. The spectra for $\text{Na}_{0.6}\text{WO}_3$ and H_xWO_3 are vertically shifted for clarity.

Table 1. No shift in the position of the absorption edge was observed upon intercalation with hydrogen, but a small difference (about 0.7 eV) is present between rhenium and tungsten oxides. According to the dipole selection rule, the O K-edge spectra show transitions from O 1s to unoccupied states with p-character which are relaxed due to the 1s core-hole positive charge.

The first intense peak (A,B) at 530 eV has complex shape consisting of the main contribution A and shoulder B. The peak is related to oxygen 2p(O) states in the $5d(t_{2g})$ conduction band due to $5d(t_{2g})(\text{TM})-2p(\text{O})$ interaction. The shoulder B is related to the two type of oxiges and the anisotropy of the t_{2g} -band, presented in the non-cubic perovskites [9]. The peak intensity depends on the number of the 2p(O) empty states, which are defined by the occupancy of the conduction band and very strongly by the degree of the TM-O bond covalency (or the value of the oxygen-to-metal charge transfer) [1]. In particularly, this peak is absent for purely ionic bonds even for the empty d-band [1].

Table 1. XANES O K-edge structure energies for rhenium and tungsten oxides. I(A) is the intensity of the peak A (or A+B if B is present). The edge position was set at the half-height of the first peak A. The energy scale was determined using the known position of the peak A in NiO.

Compound	Edge	I(A)	A	B	C	D	E	F	G	H
ReO ₃	529.1	4.8	529.9		533.9	537.4	541.0	544.2	553.9	568.1
H _x ReO ₃	529.3	4.0	530.0		534.5	537.0	540.0	543.0	554.0	565.9
m-WO ₃	529.8	6.5	530.7	531.7	535.4	537.6	541.1	543.8	556.1	567.2
H _x WO ₃	529.7	6.5	530.5	531.7	535.0	537.1	540.6	543.8	553.9	567.3
Na _{0.6} WO ₃	529.7	7.2	530.7		535.4	537.6	541.1	543.8	556.1	567.2
a-WO ₃	529.7	6.9	530.5	531.8		536.7		543.3		565.6
hex-WO ₃	529.8	5.8	530.3	531.6	536.1	537.4	541.9	544.0	551.6	567.2
WO ₃ ·H ₂ O	529.7	5.3	530.5	531.9	536.1	538.2		543.0		565.6
KNbO ₃	529.9	6.5	531.1		535.4	537.5	539.9	543.3	550.3	561.9
NiO	530.8	3.2	531.7							

The intensity of the first peak (A) significantly increases in the serie from m-WO₃, H_xWO₃ to Na_{0.6}WO₃, while the area under the peak increases only slightly (see table and Fig. 1). Well visible broadening of the peak is observed for monoclinic m-WO₃. In the series from m-WO₃, WO₃·H₂O to a-WO₃, the intensity of the peak (A)

increases and the area under the peak increases also. The form of the asymmetric peak practically not change and consists from well visible two asymmetric subpeaks separated about 1.2 eV. Finally, the intensity of the peak (A) decreases and the area under the peak decreases also from ReO₃ to H_xReO₃. These compounds correspond,

respectively, to the d⁰, d^x, d^{0.6}, d¹ and d^{1+x} TM ion formal configurations with an increasing number of d-electrons. Thus, no simple correlation is observed between the first peak intensity and the number of d-electrons. On the contrary, the TM-O bond covalency is the main factor influencing the area of the first peak, and, therefore, cubic Na_{0.6}WO₃ are considered to have the most covalent TM-O bonds. The full width (about 3.5 eV) of the first peak in the cubic perovskites is determined by the experimental resolution (0.2 eV), the natural 1s(O) core-hole level width (~ 0.22 eV), the 5d spin-orbit coupling (~ 1.5 eV) and the t_{2g}-band width (~ 3 eV). It is comparable to the

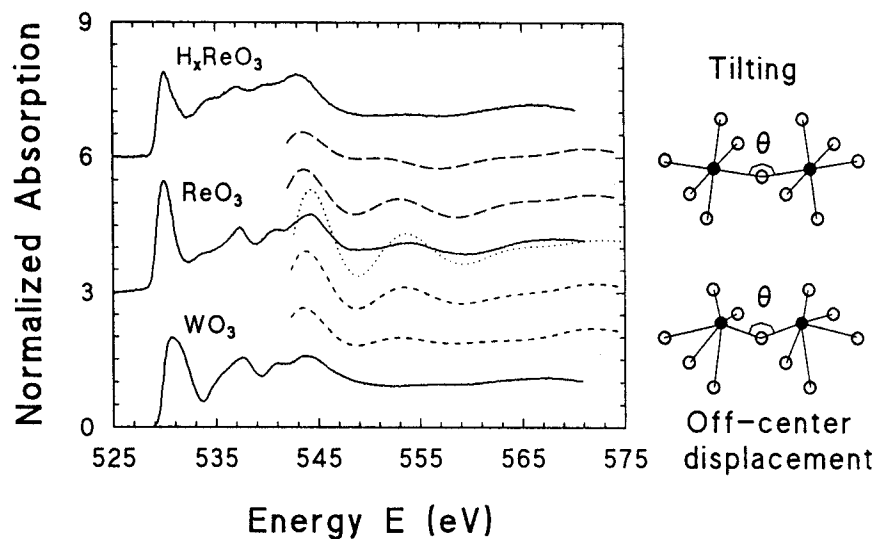


Fig. 4. Multiple-scattering calculations of the O K-edge EXAFS as a function of the tilting Me-O-Me angle (160, 170, 180 degree) and the metal ion off-center displacement (0.1, 0.2 Å) in comparison with experimental data for hydrogen intercalated H_xReO₃ (tilted), ReO₃ (ideal cubic) and monoclinic m-WO₃ (off-center displaced). The spectra are vertically shifted for clarity.

one (3 - 4 eV) estimated from theoretical calculations in [10]. On the other hand, in the distorted perovskites ($m\text{-WO}_3$) and in the layered compounds (hex- WO_3 and $\text{WO}_3\cdot\text{H}_2\text{O}$) as well as in amorphous $\alpha\text{-WO}_3$ the broadening or splitting of the first peak (A) is due to inequivalent oxygen sites in these structures. Particularly, layered compounds have two type (two intralayer and one interlayer) oxygens giving two subpeaks (A and B) with the ratio of about 2:1.

The peaks C and D are due to $5d(e_g)\text{(TM)}-2p(\text{O})$ hybridization, influenced strongly by competitive $2p(\text{O})-1s(\text{H})$ or $3s(\text{Na})$ interaction. An increase of the C and D peaks intensity suggests partially covalent interaction between oxygen and hydrogen/sodium ions. One can estimate the splitting between the t_{2g} and e_g subbands from the difference between A and C peaks: it is about 4 eV compared to the theoretical estimate 5.5 eV [10]. The peaks E and F are attributed to $6sp(\text{TM})-2p(\text{O})$ interaction: their variation has a behaviour similar to the C and D features. The next features G and H are identified as scattering resonances at the nearest atoms. Our multiple-scattering calculations show that the peak H is due to single-scattering process on 8 oxygen atoms at $\sim 2.7 \text{ \AA}$. The intensity of the feature G is attributed to the value of the TM-O-TM angle: it is higher for the linear atomic chain.

4. Conclusion

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 atomic structure.

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