

XANES studies of MeO_{3-x} (Me = W, Re, Ir) crystalline and amorphous oxides

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X-ray absorption near-edge spectroscopy (XANES) of the L_1 - and L_3 -edges of transition metals (W, Re, Ir) oxides has been studied in the "ADONE" synchrotron source. The distortion of oxygen polyhedra and the metal valence state correlate with the amplitude of the pre-edge peak in L_1 -spectra and the "white line" in L_3 -spectra.

1. Introduction

X-ray absorption near-edge spectroscopy has recently found increasing application [1] in the probing of the local structure and electronic properties of a large variety of materials through both experimental and theoretical advances. In this paper a systematic study of the L-edge absorption of the transition metal (W, Re, Ir) oxides is presented. The applicability of L_1 - and L_3 -edge spectra for probing the local distortion of oxygen polyhedra and the metal valence state in these systems is discussed.

The feature in which we are interested for the L_3 -edge is the "white line" (WL), whose amplitude should reflect the local density of the d-state and the number of unoccupied 5d states. For the L_1 -edge we are interested in the pre-edge feature arising from the $2s \rightarrow 5d(\text{Me}) + 2p(\text{O})$ transition determined by the site symmetry of the transition metal.

The obtained results for crystalline compounds are the basis for an investigation of electrochromic amorphous $a\text{-WO}_3$ thin films prepared by different methods – thermal evaporation, high frequency sputtering, chemical deposition, etc.

2. Experimental

Transmission XANES spectra were taken on W, Re, Ir L_1 - and L_3 -edges using the EXAFS station (for L_1 – Si[220] and for L_3 – Si[111] channel-cut crystal monochromators) of one of the wiggler beam lines (BX-1, "PWA" ADONE LNF INFN). The "ADONE" storage ring was operated at 20–50 mA and 1.5 GeV with a

wiggler current of 4000 A. The amplitudes of the lines were normalized to the absorption jump. The thickness effects were estimated by different measurements for some samples [2].

The thin films were obtained by slow $a\text{-WO}_3$ (no. 1) and fast (no. 2) rate thermal evaporation in middle and low vacuum on a polyimide substrate at $T_s = 200^\circ\text{C}$. The amorphous $a\text{-WO}_3$ (no. 3) and polycrystalline $c\text{-IrO}_2$ thin films were prepared by reactive radio frequency (rf) and magnetron sputtering of metals in O_2 and Ar atmospheres on a polyimide substrate at room temperature. The powders $c\text{-WO}_{3-x}$ [3], $c\text{-ReO}_3$ and $c\text{-CaWO}_4$ were taken as reference compounds.

3. Experimental results and discussion

Fig. 1 shows the L_3 -edge region in the crystalline compounds ReO_3 , WO_3 , IrO_2 and CaWO_4 . The most striking difference between the XANES spectra for these compounds is in the amplitude and the width of the WL and that a post-edge peak is seen only in the spectrum of CaWO_4 , at about 12 eV higher energy than the WL. The structures of the first three compounds consist of oxygen octahedra connected by corners (ReO_3 , WO_3) or by the edge (IrO_2 – the rutile type), but the structure of the last compound (CaWO_4) consists of oxygen tetrahedra, and this is why the post-edge peak exists.

In tungsten compounds WO_{3-x} with a different valence state of tungsten (from W^{4+} to W^{6+}), we have observed a drastic change of the WL amplitude but in general the shape of the spectra is practically close to the WO_3 spectrum. The amplitudes of the WL are presented in table 1 (column C). In these compounds

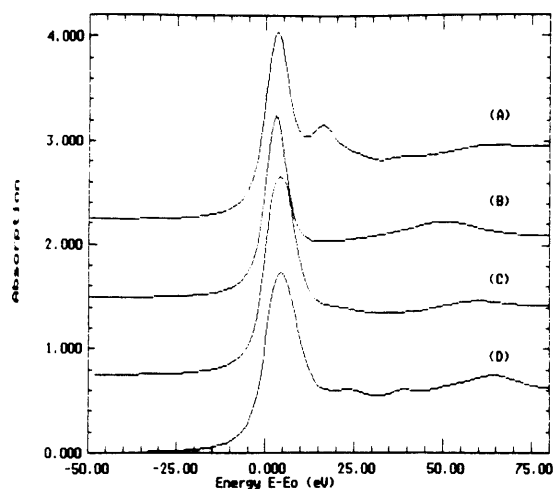


Fig. 1. The L_3 -edge of W in $CaWO_4$ (A) and WO_3 (C), Ir in IrO_2 (B), and Re in ReO_3 (D).

the average W–O distance increases monotonically with a reduction of tungsten from W^{6+} (WO_3) to W^{4+} (WO_2), and also with decreasing distortion of the WO_6 octahedra [4]. In the EXAFS spectra we have also observed a drastic change of the average W–O distance calculated in a one-sphere approximation (fig. 2). We believe that the increase of WL intensity in the compounds WO_3 , $WO_{2.96}$, $WO_{2.90}$ and $WO_{2.72}$ is due to the increase of distortion of WO_6 octahedra, and the decrease of the WL amplitude in the last compound WO_2 originates from the filling of an unoccupied 5d level.

The WL amplitudes (fig. 3) in water-containing layered compounds $WO_3 \cdot nH_2O$ are much higher than in $c-WO_3$, which is due to the presence of a very short

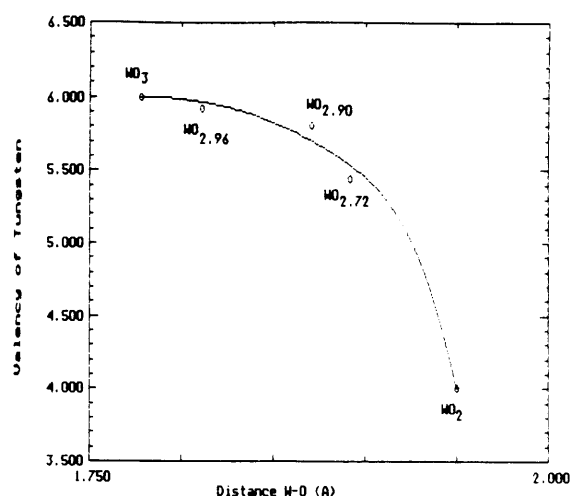


Fig. 2. The dependence of the tungsten valency on the W–O distance calculated in the one-sphere approximation.

terminal W=O bond opposite to the water molecule site. From the EXAFS spectra in practically all crystalline compounds and amorphous thin films with a 6 + tungsten valence state, we have obtained by the one-sphere approximation an average distance equal to 1.78–1.80 Å.

In amorphous chemically stable thin films of $a-WO_3$ (no. 1) the WL amplitude is smaller than in $a-WO_3$ (no. 2) films, which are chemically not as stable. The WL amplitude in rf prepared film (no. 3) is close to that in $a-WO_3$ (no. 1).

Figs. 4, 5 and 6 show the L_1 -edge region in crystals and $a-WO_3$ thin films. The intensity of the pre-edge peak corresponds to the $2s \rightarrow 5d(W) + 2p(O)$ transition and can be used to determine the distortion of an

Table 1
The relative amplitudes of the XANES features in L_1 and L_3 absorption spectra

Compound	L_1 -XAS		L_3 -XAS
	A	B	C
c- ReO_3	0.22 ± 0.02	1.07 ± 0.15	2.6 ± 0.1
c- $CaWO_4$	0.71	1.00	2.2
c- WO_3	0.42	1.21	2.5
c- $WO_{2.96}$	0.31	1.11	2.8
c- $WO_{2.90}$	0.25	1.18	2.9
c- $WO_{2.72}$	0.22	1.24	3.0
c- $WO_{2.00}$	0.25	1.24	2.7
c- $WO_3 \cdot \frac{1}{3}H_2O$	–	–	3.1
c- $WO_3 \cdot H_2O$	0.50	1.23	3.0
c- $WO_3 \cdot 2H_2O$	–	–	3.2
a- WO_3 no. 1	0.51	1.26	2.9
a- WO_2 no. 2	–	–	3.7
WO_3 rf no. 3	0.46	1.37	3.1
IrO_2	–	–	2.4

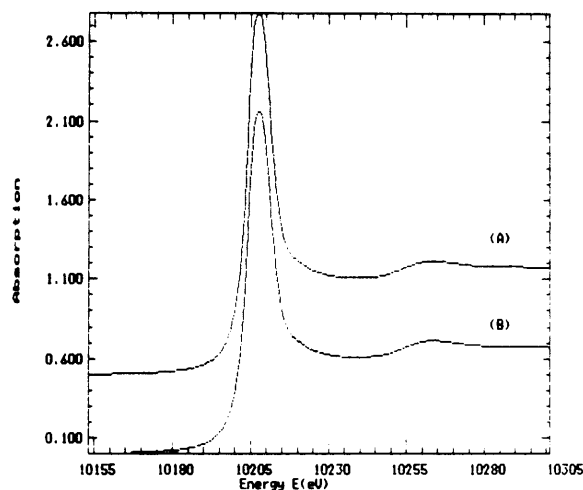


Fig. 3. The L_3 -edge of tungsten in $a-WO_3$ (A) and $c-WO_3 \cdot H_2O$ (B).

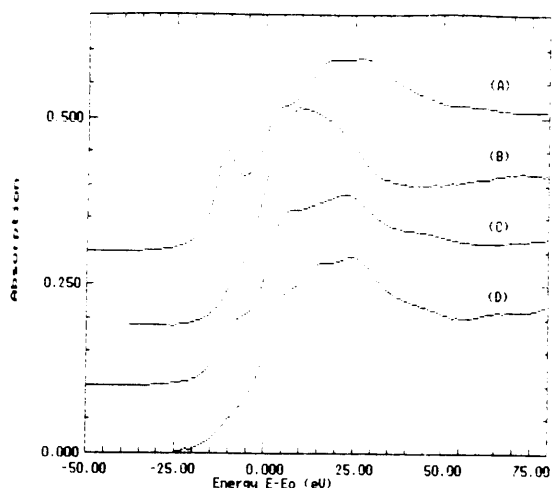


Fig. 4. The L_1 -edge of W in $CaWO_4$ (A) and WO_3 (C), Ir in IrO_2 (B), and Re in ReO_3 (D).

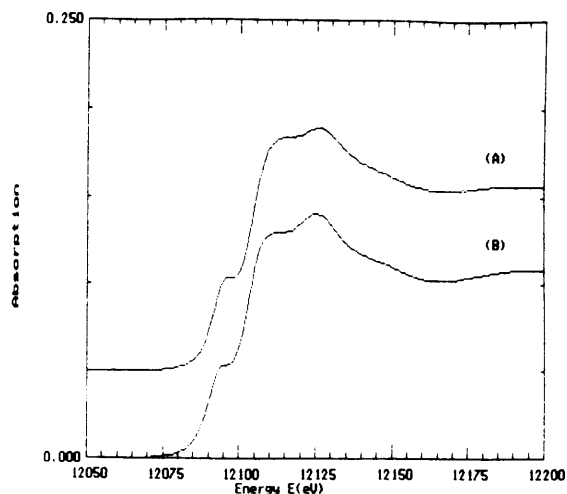


Fig. 6. The L_1 -edge of tungsten in $a-WO_3$ (A) and $WO_3 \cdot H_2O$ (B).

octahedral complex [5]. Its amplitude (column A in table 1) is too small for perfect (ReO_3) or near-perfect (WO_2 , IrO_2) WO_6 octahedra, but it is too large for highly distorted octahedra (WO_3 , $WO_3 \cdot nH_2O$) and it is highest for WO_4 tetrahedra ($CaWO_4$). The distortion of the octahedra facilitates d-p orbital mixing, thereby enhancing the pre-edge peak amplitude [6]. There is a

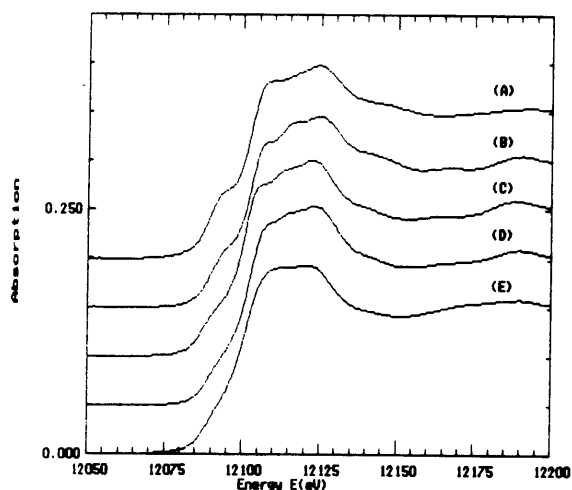


Fig. 5. The L_1 -edge of tungsten in crystalline tungsten oxides: WO_3 (A), $WO_{2.96}$ (B), $WO_{2.90}$ (C), $WO_{2.72}$ (D) and $WO_{2.0}$ (E).

very good anticorrelation between the amplitude of the pre-edge peak and the WL (table 1).

The amplitudes of the pre-edge peak and the WL in amorphous thin films (no. 1, no. 3) are close to those of water-containing crystals of $WO_3 \cdot H_2O$ with W=O terminal bonds.

The amplitude of the first main peak (column B in table 1) in the L_1 -edge is assigned to the $2s \rightarrow 6p(W) + 2p(O)$ transition and the next peaks are also visible in the main absorption ramp.

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