ELSEVIER

Journal of Alloys and Compounds 320 (2001) 1–6

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Electronic structure of hexagonal tungsten trioxide: XPS, XES, and XAS studies

O.Yu. Khyzhun*, Yu.M. Solonin, V.D. Dobrovolsky

I.M. Frantsevych Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Krzhyzhanovsky str., UA-03142 Kiev, Ukraine

Received 29 August 2000; accepted 13 November 2000

Abstract

X-Ray photoelectron (XPS), emission (XES) and absorption (XAS) spectroscopy methods were used to study the electronic structure of hexagonal tungsten trioxide, h-WO_3. Its precursor, hexagonal hydrogen tungsten bronze, H_xWO_3, and the monoclinic form of tungsten trioxide, m-WO_3, were also studied. For the mentioned compounds, both the XPS valence-band and core-level spectra, as well as the O Kα emission bands and the W L_{III} absorption edges were derived. It was established that, binding energies of both the W 4f and O 1s core-level electrons do not change when going from the tungsten trioxides to H_xWO_3. A high-energy shift of the inflection point of the XAS W L_{III} spectrum of the H_xWO_3 bronze, with respect to its position on the spectrum of pure metallic tungsten, was found to be close to those of the spectra of the two WO_3 forms studied. Half-widths of both the XPS valence-band spectra and the O Kα bands increase somewhat in the sequence m-WO_3→h-WO_3→H_xWO_3. The formation of a near-Fermi sub-band, which is absent for both the modifications of WO_3, was observed on the XPS valence-band spectrum of hexagonal H_xWO_3. The energy positions of the centers of gravity of the O Kα band remain constant for all the compounds studied. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxide materials; Photoelectron spectroscopy; Electronic band structure

1. Introduction

Since Gerand et al. [1] first obtained the hexagonal modification of tungsten trioxide, h-WO_3, due to dehydration of $WO_3\cdot1/3\cdot H_2O$ hydrate, there has been considerable interest in development of alternative routes for synthesis of h-WO_3 and in studying some properties of the compound. The hexagonal modification of tungsten trioxide is synthesized using the following substances as precursors: $(NH_4OH)_x\cdot WO_3$ [2,3], $(NH_4)_{0.30}\cdot WO_3$ [4], H_xWO_3 [5], $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 10H_2O$ [6,7], $WO_3\cdot yH_2O$ ($y=0.8-1.1$) [8]. Some of the above synthetic routes for obtaining hexagonal WO_3 have been reviewed recently by Han et al. [7]. Hexagonal tungsten trioxide is of great interest in technology in particular because of its possibility to serve as an intercalation host of lithium. As a result, lithium tungsten bronzes, Li_xWO_3, are synthesized. The bronzes are found to be a useful cathode material for rechargeable lithium batteries [9]. Recent electrochemical measurements made by Han et al. [10] reveal discharge–charge curves with remarkable hysteresis. In the latter work, it was also observed that very large polarization occurs abruptly at a certain stage of the charging process near its end point.

The electronic structure of the monoclinic form of tungsten trioxide, m-WO_3, was studied either by experimental methods or by theoretical band calculations. X-ray photoelectron valence-band spectra of the compound were studied in Refs. [11,12]. The valence-band for m-WO_3 were investigated by Bringans et al. [13] using ultraviolet photoemission spectroscopy; different photon energies (16.85, 21.22 and 40.82 eV) were used for the excitation of the spectra. The W L_{III} absorption spectra for the mentioned modification of tungsten trioxide were studied in Refs. [14,15], but the O 2p-like emission band for m-WO_3 was obtained by Nemoshkalenko et al. [16]. A complex experimental study (using X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) methods) of the monoclinic form of WO_3, as well as of some substoichiometric compounds WO_x over the range $2\leq x\leq 2.77$, has been carried out very recently in Ref. [17]. The electronic structure of WO_3 in the oversimplified cubic perovskite-type structure was calculated by Kopp et al. [18] using a

---

*Corresponding author.
E-mail address: khyzhun@ipms.kiev.ua (O.Yu. Khyzhun).

PII: S0925-8388(00)01454-7

non-self-consistent and non-relativistic version of the Korringa–Kohn–Rostoker (KKR) method, by Bullett [19] using a self-consistent and non-relativistic version of the atomic-orbital-based method, and by Hjelm et al. [20] using a self-consistent and relativistic version of a full-potential linear muffin-tin orbital (FP-LMTO) method. Results of the calculations [18–20] concerning the occupation as well as the energy position of the main peculiarities of both the valence and conduction bands of cubic tungsten trioxide, are in agreement. Bullett [19] has studied also the electronic structure of both the monoclinic and orthorhombic modifications of WO_3. As shown in Ref. [19], the cubic→full monoclinic distortion of WO_3 increases by 0.8 eV the size of the semiconducting energy gap and leads to increasing the W d-orbital occupation. Hjelm et al. [20] also used the FP-LMTO method to calculate the band structure of the hexagonal form of tungsten trioxide, as well as those of two cubic hydrogen tungsten bronzes, HWO_3 and H_2WO_3. To our knowledge, the electronic structure of the hexagonal H_xWO_3 compounds were not studied either by theoretical band-structure calculations or by experimental methods.

The purpose of the present work was to investigate the XPS valence-band spectra and the XES O 2p-like emissions bands of the two different forms, hexagonal and monoclinic, of WO_3, as well as of hexagonal hydrogen tungsten bronze, H_xWO_3, which was a precursor for obtaining the hexagonal form of tungsten trioxide. The purpose was also to compare charge states of the atoms for the studied compounds using data of the XPS core-level and XAS measurements.

2. Experimental

The techniques of the present experimental investigation of the electronic structure of the two modifications of WO_3 and the hexagonal hydrogen tungsten bronze, H_xWO_3, were analogous to those described elsewhere [17]. Therefore, in this paper only the main details of the experiment are reported.

The fluorescent X-ray emission O Kα bands ($K \rightarrow L_{II,III}$ transition), reflecting the energy distribution of filled valence states of p-symmetry of oxygen, in the studied compounds were obtained using a SARF-1 spectrometer. The energy resolution, ΔE_{min}, of the SARF-1 spectrometer in the range corresponding to the energy of the O Kα band was found to be about 0.15 eV. An RbAP crystal (2d=26.136 Å) with a radius of curvature of $R \approx 500$ mm was used. An X-ray tube with a chromium anode was used as the source of primary radiation. The operating conditions of the X-ray tube were the following: accelerating voltage, $U_a = 6$ kV; anode current, $I_a = 400$ mA. The O Kα bands were recorded in a spectrometer chamber having a base pressure less than 1×10^{-6} Pa. The detector was a gas-flow argon-methane counter.

Table 1
Lattice parameters of the compounds studied

Compound	*a*, nm	*b*, nm	*c*, nm	β, °	Ref.
H_xWO_3	0.7356	–	0.7612	–	[5]
h-WO_3	0.7276	–	0.7800	–	[5]
m-WO_3	0.7297	0.7539	0.7688	90.91	[19]

The W L_{III} absorption spectra, which reflect the energy distribution of the empty W d-like states were obtained using the spectrometer with scintillation recording of the X-ray radiation intensity. The spectra were measured using the method of ‘a variable_field of absorption’ [21,22]. A quartz crystal with the (1340) reflecting plane and a radius of curvature of $R \approx 500$ mm was used. The method for preparing the absorber and selection of its optimum thickness was analogous to that used earlier [17]. A BHV-23 X-ray tube with a tungsten anode operating at $U_a = 14$ kV and $I_a = 40$ mA was used as the source of primary excitation. In the determination of $\ln(I_0/I)$ at each point of the area of energies beyond the absorption edge, the number of pulses reflecting the X-ray quanta which passed through the absorber was not less than 5×10^5. The number of pulses reflecting the X-ray quanta which passed through the second half of the holder free of the absorber was $(2-7) \times 10^6$. The quantum yield of the X-ray photoeffect in the area of the oxygen K absorption edge in tungsten trioxides and hydrogen tungsten bronze could not be studied, probably as a result of the strong screening of the oxygen atoms by the tungsten atoms [15].

Measurements of the XPS valence-band and core-level spectra of the WO_3 and H_xWO_3 samples were carried out in an ion-pumped chamber of an ES-2401 spectrometer. The chamber was evacuated to $(1-2) \times 10^{-7}$ Pa. The Mg $K\alpha_{1,2}$ ($E = 1253.6$ eV) excitation was used as the source of X-ray radiation. The impurity carbon 1s line (285.0 eV) was taken as reference.

The hexagonal hydrogen tungsten bronze studied in the present work, was obtained from a hexagonal $CuWO_3$ phase by hydrogen reduction to copper and hexagonal H_xWO_3; copper was separated by dissolving in HNO_3, and during this separation a brown–blue sediment, hexagonal H_xWO_3, remained as the precipitate [5,23]. Hexagonal tungsten trioxide, h-WO_3, was obtained by the following heating of the hexagonal H_xWO_3 phase up to 400°C as described in Refs. [5,24]. The method of synthesis of the specimens and the X-ray diffraction analysis data for the investigated WO_3 and H_xWO_3 samples were reported in Refs. [5,23,24]. The content of hydrogen atoms, *x*, in the H_xWO_3 specimen investigated in the present work was found to be 0.24 [25]. The lattice parameters of the samples are listed in Table 1. All the studied compounds were single-phase materials.

3. Results and discussion

As is known (see, for example, monographs [26,27]), in tungsten oxides the X-ray Mg (or Al) K$\alpha_{3,4}$ satellite excitation of W $4f_{7/2,5/2}$ electrons overlaps the structure of the XPS valence-band spectra owing to photoemission from the O 2s-like states located in the energy region near 22.5 eV binding energies (BEs) with respect to the Fermi energy, E_F. The subtraction of the W $4f_{7/2,5/2}$ core-level spectra, excited by the radiation of the Mg (Al) Kα satellites, from the XPS spectra is a rather difficult problem [26,27]. Therefore, as in Ref. [17], in the present work the XPS spectra of the tungsten trioxides and hydrogen tungsten bronze were recorded within the continuous energy range up to 46 eV with respect to E_F, and then the Mg Kα satellite excitation of the W $4f_{7/2,5/2}$ core-level spectra were subtracted using the method earlier successfully applied for XPS studies of substoichiometric tantalum carbides [28,29]. This gives the possibility of obtaining the XPS valence-band spectra including photoemission from the O 2s-like states. As an example, Fig. 1 shows the XPS spectrum of hydrogen tungsten bronze, H_xWO_3, which was a precursor for obtaining the hexagonal form of tungsten trioxide, without any corrections (solid curve 1) and after the subtraction (dashed curve 2) of the XPS W 4f core-level spectra excited by the radiation of the Mg Kα', α_{3-6} satellites. The XPS spectra shown in Fig. 2 were obtained for the studied compounds using the mentioned procedure. The spectra have been normalized to one and the same integral intensity of the XPS W $4f_{7/2,5/2}$ core-level spectra of the corresponding compound. The results of such normalization indicate that the peak intensity of the XPS valence-band spectra remains constant within the experimental error for all the compounds studied. The relative intensities of the O 2s-like sub-band (with respect to the intensity of the XPS valence-band spectrum of the corresponding compound) almost do not change in the sequence m-WO_3→h-WO_3→H_xWO_3. The broad structures representing the XPS O 2s-like sub-band do not allow us to detect any tendency of a shift of the sub-band maximum in the mentioned sequence of compounds. Therefore, as can be seen from Table 2, BEs of the sub-band maxima remain constant within ±0.1 eV for all the compounds investigated.

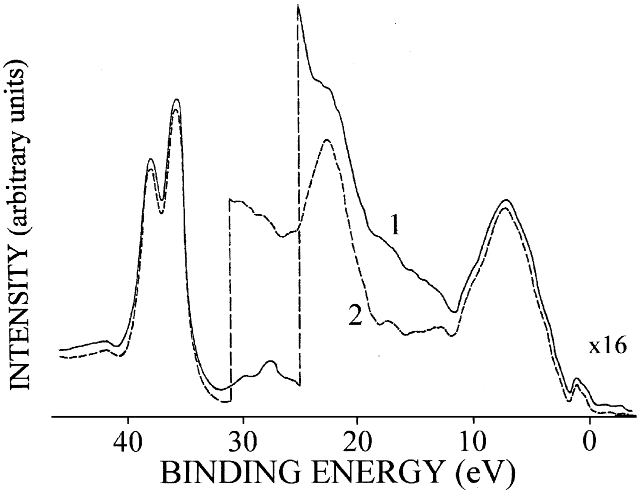

Fig. 1. XPS spectra of hexagonal hydrogen tungsten bronze, H_xWO_3, without any correction (solid curve 1) and after subtraction of the XPS W $4f_{7/2,5/2}$ core-level spectra excited by the X-ray Mg Kα', α_{3-6} satellites (dashed curve 2).

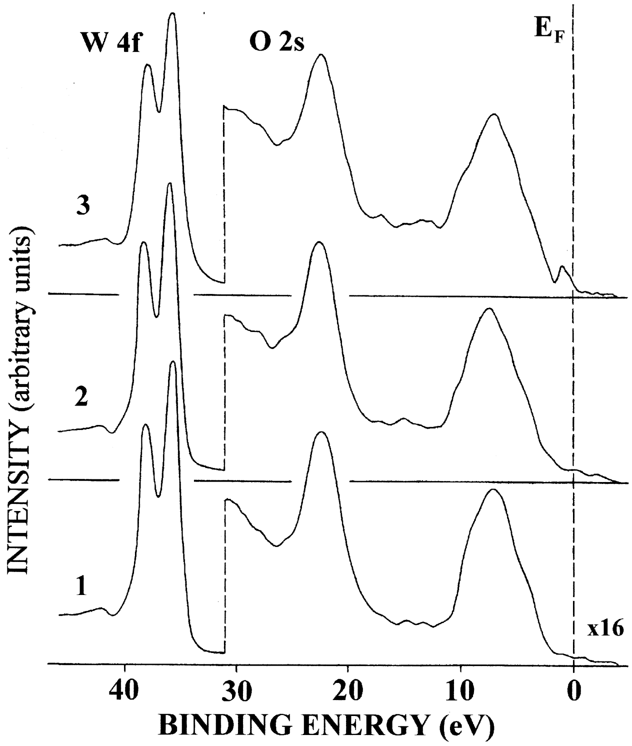

Fig. 2. XPS spectra normalized to one and the same integral intensity of the W $4f_{7/2,5/2}$ core-level spectra for (1) m-WO_3, (2) h-WO_3, and (3) H_xWO_3.

Fig. 3 shows the O Kα emission bands for all the compounds studied. The relative intensities of the O Kα spectra were not measured because there was not a standard X-ray line within the range of energies corresponding to the energy of the O Kα band [30,31]. This is why all the O Kα bands shown in Fig. 3 are normalized so that the integral intensities of the spectra are equal. As can be seen from Fig. 3, the half-width of the O Kα band is somewhat broader (by about 0.3 eV, see Table 3) in the hexagonal form of WO_3 than in the monoclinic form. As is shown in Refs. [1,10], two types of oxygen atoms can be distinguished in the structure of h-WO_3: the atoms belonging to the hexagonal planes and the atoms between the

Table 2
Some characteristics (in eV) of the XPS spectra for the compounds studied

Compound	BE and a half-width[a] of the XPS O 1s core-level spectrum	BE and a half-width[a] of the XPS W 4f core-level spectrum	BE of the maximum of the XPS O 2s-like sub-band	Half-width of the XPS valence-band spectrum
H_xWO_3	530.84 (2.16)	36.05 (3.90)	22.5	6.56
h-WO_3	530.86 (1.83)	36.02 (3.66)	22.6	6.03
m-WO_3	530.78 (1.96)	35.95 (3.63)	22.5	5.52
Uncertainty	±0.05 (±0.08)	±0.05 (±0.05)	±0.1	±0.08

[a] Half-widths are given in parentheses.

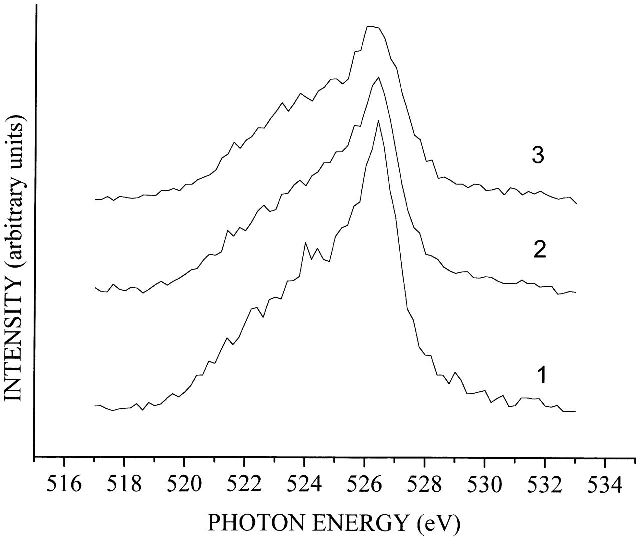

Fig. 3. O Kα emission bands of (1) m-WO_3, (2) h-WO_3, and (3) H_xWO_3.

planes. When calculating the electronic structure of h-WO_3, Hjelm et al. [20] showed that the O 2p-like states originating from the atoms in the hexagonal planes dominate in the low-energy part of the oxygen p-like band, while the states originating from the atoms between the planes dominate the top of the band. As a result, the width of the O 2p-like band should be somewhat broader in the hexagonal form of tungsten trioxide than in the cubic form (or in the monoclinic form, because the cubic→monoclinic distortion of WO_3 seems to cause only an increase in both the W d-orbital occupation and the value of the semiconducting gap [19]). The data of the theoretical FP-LMTO band structure calculations [20] are in agreement with the present experimental results as mentioned. Furthermore, while the valence bands of both the m-WO_3 and h-WO_3 modifications are dominated by the O 2p-like states [19,20], the changes of the XPS valence-band spectra, reflecting the energy distribution of total density of states, should be similar to those observed for the O Kα bands. In fact, as can be seen from Fig. 2, a half-width of the XPS valence-band spectrum increases by about 0.5 eV (Table 2) when going from m-WO_3 to h-WO_3.

As Hjelm et al. [20] noted, insertion of hydrogen atoms into the lattice of cubic WO_3 should broaden the valence band due to the oxygen states in the OH pair. It is believed that this should be true for the hexagonal WO_3 and H_xWO_3 phases as well. Therefore, one could expect broadening the O Kα band as well as the XPS valence-band spectrum when going from h-WO_3 to the hexagonal H_xWO_3 compound. As can be seen from Figs. 2 and 3, half-widths of both the XPS valence-band spectrum and the O Kα band broaden significantly in the sequence h-WO_3→H_xWO_3 (by about 0.5 and 0.8 eV, respectively; cf. Tables 2 and 3). As a whole, both the spectra broaden somewhat when going from m-WO_3 to h-WO_3 and than to H_xWO_3. Nevertheless, for all the compounds studied, the energy positions of the centers of gravity of the O Kα emission bands remain constant within ±0.1 eV (Table 3).

As can be seen from Fig. 2 (curve 3), the formation of an additional sub-band at E_F is characteristic for the XPS valence-band spectrum of the hexagonal tungsten bronze, H_xWO_3. The sub-band is absent on the XPS valence-band spectra of both the forms of WO_3 (Fig. 2, curves 1 and 2).

Table 3
Some characteristics (in eV) of the O Kα emission band for the compounds studied

Compound	Energy position of the band maximum	Energy position of the center of gravity of the band	Half-width of the band
H_xWO_3	526.2	525.1	4.43
h-WO_3	526.4	525.0	3.61
m-WO_3	526.4	525.1	3.34
Uncertainty	±0.1	±0.1	±0.06

The formation of the similar near-Fermi sub-band was observed earlier during XPS studies of the sodium tungsten bronzes, Na_xWO_3 [32]. Höchst et al. [32] observed a non-linear increase of the relative intensity of the sub-band with increasing x in the Na_xWO_3 bronzes. According to the results of Refs. [19,32], the formation of the near-Fermi sub-band on the XPS valence-band spectra of the sodium tungsten bronzes, Na_xWO_3, can be explained by that, the extra sodium electrons in Na_xWO_3 enter the t_{2g}-like band, which is empty in tungsten trioxide. As Hjelm et al. [20] noted, for the HWO_3, $LiWO_3$, and $NaWO_3$ compounds, the physical properties should not be too different regardless of whether hydrogen or alkali ions are intercalated into the WO_3 host. Therefore, it may well be true that the formation of the small near-Fermi sub-band on the XPS valence-band spectrum of H_xWO_3 (Fig. 2, curve 3) is due to the extra hydrogen electrons filling the t_{2g}-like band.

It should be noted that, as can be seen from Fig. 3 (curve 3), the formation of additional fine-structure features was not detected on the high-energy slope of the O Kα emission band of the hexagonal hydrogen tungsten bronze studied in the present work. The above fact indicates that the O 2p-like states do not take part in the formation of the mentioned sub-band on the XPS valence-band spectrum of hexagonal H_xWO_3. As earlier [17], in the present work we have made attempts studying the fluorescent W $L\beta_5$ band ($L_{III}\rightarrow O_{IV,V}$ transition), reflecting primarily the occupied W 5d-like states, in the hexagonal H_xWO_3 tungsten bronze. Nevertheless, our attempts were unsuccessful. After accumulation times of about 190 h, the intensity of the W $L\beta_5$ band for the hexagonal H_xWO_3 specimen, studied in the present work was too small to be able to discuss its fine-structure features. The method was analogous to those used previously to study the W 5d-like emission bands of tungsten carbides and germanides [33,34].

As can be seen from Table 2, half-widths of both the XPS W 4f and O 1s core-level spectra remain constant for the two WO_3 forms studied. Half-widths of the spectra increase slightly when going from the tungsten trioxides to hexagonal tungsten bronze, H_xWO_3 (Table 2).

Fig. 4 shows the W L_{III} absorption spectra of the compounds studied. For comparison, the spectrum of pure metallic tungsten is also presented. The spectra are normalized so that intensities of their 'white' lines are equal. As can be seen from Fig. 4, the inflection point of the XAS W L_{III} spectra for all the studied compounds undergo a high-energy shift (from 2.9 to 3.3 eV) with respect to its position on the spectrum of pure metallic tungsten. This indicates the displacement of the electron density from the tungsten atoms in the WO_3 and H_xWO_3 compounds studied in the present work. This fact is confirmed by the XPS core-level measurements. As one can see from Table 2, in the studied compounds the XPS W $4f_{7/2}$ core-level BEs increase by about 4.6 eV in comparison with the W $4f_{7/2}$ core-level BE of pure metallic tungsten (for pure W_{met}, BE(W $4f_{7/2}$)=31.4 eV [34]).

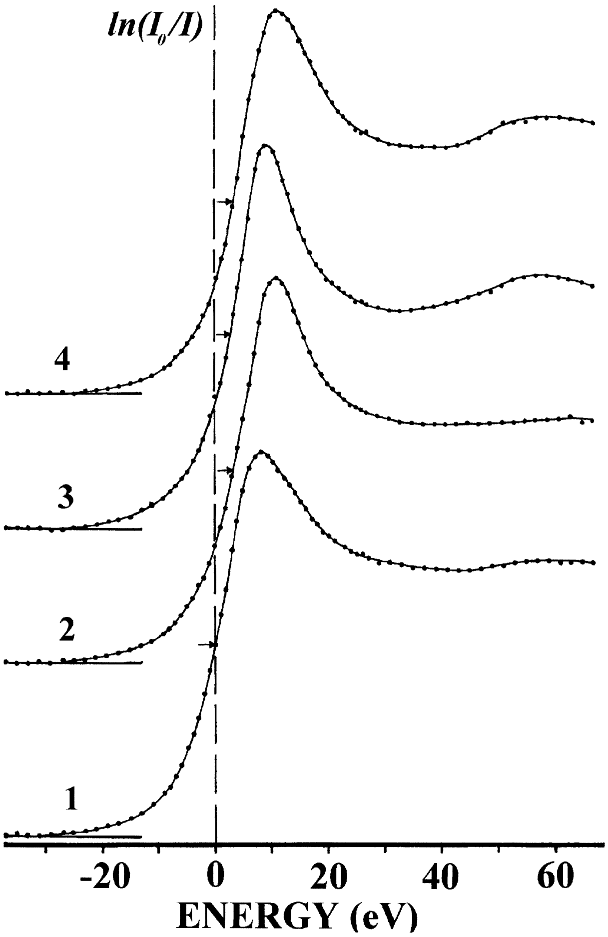

Fig. 4. W L_{III} absorption spectra of (1) W_{met}, (2) m-WO_3, (3) h-WO_3, and (4) H_xWO_3.

Positions of the inflection points of the W L_{III} absorption spectra, as well as BEs of both the W 4f and O 1s core-level spectra (Table 2), remain constant within experimental errors for all the compounds studied. These facts indicate that the charge states of both the tungsten and oxygen atoms do not change in the sequence m-$WO_3\rightarrow$h-$WO_3\rightarrow H_xWO_3$. Therefore, the intercalation of hydrogen into the WO_3 host does not change charge states of the W and O atoms. Charge state of the hydrogen atoms in hydrogen tungsten bronze could not be estimated because of the absence of XPS core-level spectra of hydrogen.

4. Conclusion

Measurements of binding energies of both the XPS W 4f and O 1s core-level electrons, as well as of high-energy shifts of the inflection points of the W L_{III} absorption spectra, indicate that the charge states of the tungsten and oxygen atoms in the monoclinic and hexagonal tungsten trioxides are close to those in hexagonal tungsten bronze, H_xWO_3. Half-widths of both the O Kα bands and the XPS valence-band spectra increase in the sequence monoclinic WO_3→hexagonal WO_3→hexagonal H_xWO_3. The formation of an additional near-Fermi sub-band, which is absent in the monoclinic and hexagonal modifications of tungsten trioxide, was observed on the XPS valence-band spectrum of the hexagonal tungsten bronze. The energy positions of the centers of gravity of the O Kα bands remain constant for all the compounds studied.

Acknowledgements

The authors would like to express their thanks to Professor Victor Uvarov (Institute of Metal Physics, NASU, Kiev, Ukraine) for his help in the XES studies.

References

[1] B. Gerand, G. Nowogrocki, J. Guenot, M. Figlarz, J. Solid State Chem. 29 (1979) 429.

[2] K.H. Cheng, A.J. Jacobson, M.S. Whittingham, Solid State Ionics 5 (1981) 355.

[3] A.M. Cruz, L.M. Torres-Martinez, G. Garcia-Alvarado, E. Moran, M.A. Alario-Franco, Solid State Ionics 84 (1996) 181.

[4] B. Schlasche, R. Schollhorn, Rev. Chim. Min. 19 (1982) 534.

[5] Yu.M. Solonin, Yu.G. Privalov, Dokl. AN UkrSSR, Ser. B, No. 1 (1985) 46 (in Russian).

[6] J. Oi, A. Kishimoto, T. Kudo, J. Solid State Chem. 96 (1992) 13.

[7] W. Han, M. Hibino, T. Kudo, Bull. Chem. Soc. Jpn. 71 (1998) 933.

[8] Naoaki Kumagai, Nabuko Kumagai, Y. Umetzu, K. Tanno, J.P. Pereira-Ramos, Solid State Ionics 86–88 (1996) 1443.

[9] W. Han, M. Hibino, T. Kudo, J. Electrochem. Soc. Jpn. 66 (1998) 1230.

[10] W. Han, M. Hibino, T. Kudo, Solid State Ionics 128 (2000) 25–32.

[11] R.J. Colton, J.W. Rabalais, Inorg. Chem. 15 (1976) 236.

[12] B.A. de Angelis, M. Schiavello, J. Solid State Chem. 21 (1977) 67.

[13] R.D. Bringans, H. Höchst, H.R. Shanks, Phys. Rev. B 24 (1981) 3481.

[14] B.Yu. Khelmer, V.F. Volkov, A.I. Platkov, Izv. SO AN SSSR, Ser. Khim. Nauk, 4 (9) (1975) 26 (in Russian).

[15] A. Meisel, G. Leonhardt, R. Szargan, X-Ray Spectra and Chemical Binding, Springer-Verlag, Berlin/Heidelberg, 1989.

[16] V.V. Nemoshkalenko, V.N. Uvarov, O.Ya. Yares'ko, Met. Phys. Adv. Tech. 17 (1998) 289.

[17] O.Yu. Khyzhun, J. Alloys Comp. 305 (2000) 1.

[18] L. Kopp, B.N. Harmon, S.H. Liu, Solid State Commun. 22 (1977) 677.

[19] D.W. Bullett, J. Phys. C: Solid State Phys. 16 (1983) 2197.

[20] A. Hjelm, C.G. Granqvist, J.M. Wills, Phys. Rev. B 54 (1996) 2436.

[21] Ya.V. Zaulychny, O.Yu. Khyzhun, E.A. Zhurakovsky, V.D. Dobrovolsky, Phys. Met. 10 (1991) 620.

[22] E.A. Zhurakovsky, O.Yu. Khyzhun, A.K. Sinelnichenko, V.A. Kolyagin, R.K. Chuzhko, V.D. Dobrovolsky, Phys. Met. 12 (1993) 444.

[23] M.V. Šušiæ, Yu.M. Solonin, J. Mater. Sci. 23 (1988) 267.

[24] Yu.M. Solonin, DSc. Thesis, Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kiev, 1990.

[25] O.Yu. Khyzhun, Yu.M. Solonin, Poroshkovaya Metallurgia, No. 5/6 (2000) 82 (in Russian).

[26] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindberg, B. Lindberg, ESCA-Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, Almqvist and Wiksells, Stockholm, 1967.

[27] V.I. Nefedov, Handbook on X-Ray Photoelectron Spectroscopy of Chemical Compounds, Khimia, Moscow, 1984 (in Russian).

[28] O.Yu. Khyzhun, E.A. Zhurakovsky, A.K. Sinelnichenko, V.A. Kolyagin, J. Electron Spectrosc. Relat. Phenom. 82 (1996) 179.

[29] O.Yu. Khyzhun, J. Alloys Comp. 259 (1997) 47.

[30] J.A. Bearden, X-Ray Wavelengths, Oak Ridge Atomic Energy Commission, Oak Ridge, TN, 1964.

[31] M.A. Blokhin, I.G. Shveitser, Handbook on X-Ray Spectra, Nauka, Moscow, 1982 (in Russian).

[32] H. Höchst, R.D. Bringans, H.R. Shanks, P. Steiner, Solid State Commun. 37 (1980) 41.

[33] O.Yu. Khyzhun, E.A. Zhurakovsky, Ya.V. Zaulychny, Sov. Powder Metal. Met. Ceram. 29 (1990) 732.

[34] O.Yu. Khyzhun, Ya.V. Zaulychny, E.A. Zhurakovsky, J. Alloys Comp. 244 (1996) 107.