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Electronic structure of $CuWO_4$: XPS, XES and NEXAFS studies

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Abstract

X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES) and near-edge X-ray absorption fine structure (NEXAFS) methods were applied to study the electronic structure of copper tungstate, $CuWO_4$. For the compound, XP valence-band spectra with different energies of excitation were studied, as well as the XE O Kα band and the NEXAFS O 1s spectrum were derived. The binding energies of the XP core-level electrons of the constituting elements of $CuWO_4$ were measured. For comparison, some spectra of the hexagonal form of tungsten trioxide, h-WO_3, were investigated. It was found that the half-width of the O Kα band decreases somewhat but that of the XP valence-band spectrum increases when going from h-WO_3 to $CuWO_4$, however the energy positions of the maxima and of the centres of gravity of the O Kα band remain constant for the above compounds. Measurements of the XP O 1s core-level binding energies and of the energy positions of the inflection point of the NEXAFS O 1s spectra reveal that the effective negative charge of oxygen atoms in $CuWO_4$ is close to that in h-WO_3, while XPS W 4f core-level measurements reveal that the positive effective charge of tungsten atoms decreases somewhat in the sequence h-WO_3 → $CuWO_4$.

Keywords: Copper tungstate; Tungsten oxide; Electronic structure; XPS; XES; NEXAFS

1. Introduction

The hexagonal form of tungsten trioxide, h-WO_3, was first synthesized by Gerand et al. [1] due to dry heating of the $WO_3{\cdot}1/3{\cdot}H_2O$ hydrate. In the structure of h-WO_3, every six [$W-O_6$] octahedra linked by corner sharing form hexagonal channels oriented along the *c*-axis [1–3] and the channels were found to be a very prospective intercalation host of lithium for obtaining Li_xWO_3 bronzes, a remarkable cathode material of rechargeable lithium batteries [4,5]. Therefore, a number of alternative routes for synthesis of h-WO_3 were developed since the beginning of 1980s. A review of the alternative routes (using as precursors the $WO_3{\cdot}xH_2O$ ($x = 0.8-1.1$), $(NH_4)_{0.30}{\cdot}WO_3$, $(NH_4)_{10}[H_2W_{12}O_{42}]{\cdot}10H_2O$ and $(NH_4OH)_x{\cdot}WO_3$ substances) was made comparatively recently by Han et al. [6]. As shown in Refs. [7,8], copper tungstate, $CuWO_4$, is also a very prospective precursor for synthesis of the hexagonal form of tungsten trioxide. A product derived during reduction of $CuWO_4$ in flowing hydrogen at 300 °C with following treatment by concentrated HNO_3 upto the full desolving of copper leads to the formation of a brown-blue hexagonal hydrogen tungsten bronze, H_xWO_3, with $x = 0.24$ [9]. The oxidation of $H_{0.24}WO_3$ in air at 400–450 °C leads to the synthesis of pure h-WO_3 with unit-cell parameters $a = 0.7276$ nm and $c = 0.7800$ nm [7], which are very close to those ($a = 0.7298$ nm and $c = 0.7798$ nm) obtained by Gerand et al. [1].

The crystal structure of $CuWO_4$ belongs to a triclinic (space group $P\bar{1}$) distorted wolframite type, with unit-cell parameters $a = 0.47026$ nm, $b = 0.58389$ nm, $c = 0.48784$ nm, $\alpha = 91.677^\circ$, $\beta = 92.489^\circ$, $\gamma = 82.805^\circ$ [10]. As established by Kihlborg and Gebert [10], in the structure of $CuWO_4$ every metal atom is surrounded by six oxygen atoms: the ranges of the six M–O distances are within 0.1961–0.2450 nm for

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the [Cu–O_6] octahedra and within 0.1760–0.2208 nm for the [W–O_6] octahedra. The crystal structure of $CuWO_4$ can be described within a framework of oxygen atoms in an approximately hexagonal close-packing with copper and tungsten atoms occupying half of the octahedral sites [10,11]. In the structure of $CuWO_4$, copper and tungsten atoms form alternating sequence of layers laying between the oxygen sheets: infinite zigzag chains are formed by edge-sharing alternating [W–O_6] and [Cu–O_6] octahedra [10].

As shown in Ref. [12], hexagonal close packing of oxygen atoms does not remain after termination of the $CuWO_4$ → h-WO_3 transformation. While the value of average volume per oxygen atom is ca. 0.01659 nm^3 for the structure of $CuWO_4$, the average volume per oxygen atom is ca. 0.0197 nm^3 in the case of h-WO_3 [12]. Therefore, the value of average volume per oxygen atom in the hexagonal form of tungsten trioxide is far away from the value of ca. 0.015 nm^3 for the ideal anionic close packing [7,12]. Electron diffraction analysis [12] has revealed that an ideal correlation for reciprocal orientation of the initial lattices are characteristic of $CuWO_4$ and h-WO_3:

$$(0\,0\,0\,1)\text{h-WO}_3 \parallel (1\,\bar{1}\,\bar{1})\text{CuWO}_4$$

$$\text{the normal to } (1\,\bar{2}\,1\,0)\text{h-WO}_3 \parallel [0\,1\,\bar{1}]\text{CuWO}_4.$$

The fact that the packing of anions in h-WO_3 significantly differs from that in $CuWO_4$ indicates that reciprocal orientation of the $CuWO_4$ and h-WO_3 phases is defined by a heredity of the elements of their cationic sublattice. This phenomenon cannot be explained within the close-packing framework (within this framework cations should not play the main role [12]). The phenomenon seems to be similar to the effect of “stable cationic motives” suggested by Chichagov et al. [13] and by Borisov and Podberezskaya [14]. Analysis of the structures of a number of fluorides and oxides [13,14] has revealed an existence of a type of compounds with different arrangements of anionic sublattices but with very similar arrangements of atoms in the cationic sublattices. For example, comparison of the structures of $CdWO_4$ (wolframite $FeWO_4$-type) and $CdMoO_4$ (scheelite $CaWO_4$-type) reveals [13] that the stacking of anions significantly changes in the sequence $CdWO_4$ → $CdMoO_4$ (in the above sequence even the orientation of the close-packing layers changes dramatically), nevertheless the cationic motif remains unchanged for both compounds. Taking the same arguments, one can conclude that the main reason of formation of h-WO_3 (instead of the usual monoclinic form of tungsten trioxide, m-WO_3) during selective reduction of copper from $CuWO_4$ is smaller distortion of the cationic motif of $CuWO_4$ in the case of the $CuWO_4$ → h-WO_3 transformation as compared with that in the case of the $CuWO_4$ → m-WO_3 transformation. As shown very recently in Ref. [15], this was true in the case of formation of a new hexagonal $WO_{2.8}$ phase with the structure of UO_3-type during reduction of h-WO_3.

In addition to the ability to serve as a prospective precursor for synthesis of Li_xWO_3 bronzes, $CuWO_4$ was found to be a remarkable substance for synthesis of almost porousless W–Cu pseudoalloys containing 10–35 mol% of copper [16,17]. Since properties of solids can be well understood by considering their electronic structure, it is interesting to study the electronic structure of the mentioned copper tungstate. While the electronic structure of some relativevely close tungstates and molybdates ($CuMoO_4$, $CaMoO_4$, $CdMoO_4$, $PbMoO_4$, $CaWO_4$, $CdWO_4$, $PbWO_4$) was studied comparatively recently in a series of works [18–20], to the best of our knowledge, the electronic structure of $CuWO_4$ has not been studied yet either by theoretical band-structure calculations or by experimental methods.

It is also of interest to compare the electronic structure of $CuWO_4$ with that of h-WO_3. The band calculation of h-WO_3 was made by Hjelm et al. [21] using the ab initio relativistic full-potential linear muffin-tin orbital (FP-LMTO) procedure. As it was suggested by Hjelm et al. [21], because 2p-like states originating from the oxygen atoms in the hexagonal planes of h-WO_3 and those between the planes dominate in the low-energy part and the top of the O 2p-like band, respectively, one should expect broadening the valence band when going from the monoclinic (cubic) form of tungsten trioxide to h-WO_3. This conclusion was confirmed experimentally in Refs. [22,23].

The purpose of the present work was to carry out a complex investigation of the electronic structure of $CuWO_4$ using the X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES) and near-edge X-ray absorption fine structure (NEXAFS) methods. In this paper a comparison will be given of changes of the electronic structure when going from $CuWO_4$ to h-WO_3. Since the electronic structure of the hexagonal form of tungsten trioxide was investigated experimentally in [22,23], only new results for h-WO_3 will be reported in the present paper.

2. Experimental

Copper tungstate, $CuWO_4$, studied in the present paper was obtained by solid state reaction of CuO and the usual monoclinic form of tungsten trioxide, m-WO_3, according to the relation CuO + WO_3 = $CuWO_4$ [7,8]. The solid-state reaction was carried out on air at 800 °C [15]. After reduction of $CuWO_4$ in flowing hydrogen at 300 °C and following treatment by concentrated HNO_3 upto the full desolving of copper, the hexagonal phase of hydrogen tungsten bronze $H_{0.24}WO_3$ was obtained [22]. Pure h-WO_3 was derived during oxidation of $H_{0.24}WO_3$ in air at 400–450 °C as reported in Ref. [22]. The conventional X-ray diffraction analysis carried out on a DRON-3 diffractometer using Cu Kα radiation revealed [12,22] that unit-cell parameters of the $CuWO_4$ and h-WO_3 phases are in good agreement with the results of Kihlborg and Gebert [10] and Gerand et al. [1], respectively.

The method of studies of the XP valence-band spectra in $CuWO_4$ was analogous to that used in Ref. [24] for molybdenum oxides. Briefly, the experiments were made in a turbopumped ultrahigh vacuum (UHV) chamber (base pressure