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Low thermal gradient Czochralski growth of large CdWO$_4$ crystals and electronic properties of (010) cleaved surface

V.V. Atuchin$^{1,2,3}$, E.N. Galashov$^4$, O.Y. Khyzhun$^5$, V.L. Bekenev$^5$, L.D. Pokrovsky$^1$, Yu.A. Borovlev$^6$, V.N. Zhdankov$^7$

$^1$Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 90, 630090, Russia
$^2$Functional Electronics Laboratory, Tomsk State University, Tomsk 634050, Russia
$^3$Laboratory of Semiconductor and Dielectric Materials, Novosibirsk State University, Novosibirsk 630090, Russia
$^4$Department of of Applied Physics, Novosibirsk State University, Novosibirsk 630090, Russia
$^5$Frantsevich Institute for Problems of Materials Science, NAS of Ukraine, 3 Krzhyzhanivsky Street, UA-03142, Ukraine
$^6$Laboratory of Crystal Growth, Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk 90, 630090, Russia
$^7$CML Ltd, 3 Lavrentiev Aven., Novosibirsk 90, 630090, Russia
Abstract

The crystal growth of large high-quality inclusion-free CdWO$_4$ crystals, 115 mm in diameter and mass up to 20 kg, has been carried out by the Low Thermal Gradient Czochralski (LTG Cz) technique. The high-purity CdWO$_4$(010) surface has been prepared by cleavage and high structural quality of the surface has been verified by RHEED, revealing a system of Kikuchi lines. The chemical state and electronic structure of the surface have been studied using X-ray photoelectron spectroscopy (XPS) and X-ray emission spectroscopy (XES). The total and partial densities of states of the CdWO$_4$ tungstate were calculated employing the first-principles full potential linearized augmented plane wave (FP-LAPW) method. The results indicate that the principal contributors to the valence band of CdWO$_4$ are the Cd 4d, W 5d and O 2p states which contribute mainly at the bottom, in the central portion and at the top of the valence band, respectively, with also significant contributions of the mentioned states throughout the whole CdWO$_4$ valence-band region. With respect to the occupation of the O 2p states, the results of the FP-LAPW calculations are confirmed by comparison on a common energy scale of the XPS valence-band spectrum and the XES band representing the energy distribution of the O 2p states in this compound. Additionally, the FP-LAPW data allow us to conclude that the CdWO$_4$ tungstate is a non-direct semiconductor.

**Keywords:** A2.Low Thermal Gradient Czochralski Technique, B1.Tungstates, B2.Scintillator materials

**PACS:** 42.70.-a; 61.05.jh; 68.47.Gh; 81.10.Fq; 82.80.Pv
1. Introduction

Cadmium tungstate, CdWO$_4$, belongs to a fascinating family of A$^{2+}$WO$_4$ compounds which crystallize in the wolframite-type structure with space group $P2/c$ at ionic radius $r_{A^{2+}} < 77$ pm. The A$^{2+}$WO$_4$ tungstates are chemically stable and several compounds are spread in nature as minerals. The tungstates can be synthesized by different chemical routes and can be grown as high-quality big-sized single crystals [1-8]. They demonstrate highly promising technological applications in many areas, e.g. humidity sensor materials, optical fibers, phase-change optical recording devices, laser hosts. In addition, wolframite-type tungstates are widely used in nanotechnologies [1,4,9], photocatalysis [3,10], electronics [4], laser techniques [11,12] and as efficient scintillator materials [13-16].

CdWO$_4$ crystallizes in the monoclinic wolframite-type structure (space group $P2/c$) with the following unit-cell parameters: $a = 5.0289$ Å, $b = 5.8596$ Å, $c = 5.0715$ Å, $\beta = 91.519^\circ$ [17]. The CdWO$_4$ cell contains two formula units. The crystal structure of CdWO$_4$ is shown in Fig. 1. For the structure of CdWO$_4$, two non-equivalent positions of oxygen atoms (labelled as O1 and O2 in Fig. 1) are characteristic. In the nearest arrangement of the O1 atoms, there are two cadmium atoms at the Cd–O1 distances of 2.273 Å and 2.414 Å, and one tungsten atom at the W–O1 distance of 1.785 Å. While two tungsten atoms with W–O2 bond lengths 1.910 Å and 2.145 Å and one cadmium atom with Cd–O2 bond length 2.198 Å are the nearest neighbours of O2 atoms [17]. Further, each cadmium and tungsten atom is surrounded by six oxygen atoms.

Previously, electronic parameters of several complex tungstates were obtained by the X-ray photoelectron spectroscopy (XPS) method [4,18,19]. It is well known that the energy position of element core level is an indicator of ionicity of the chemical bonds between cations and anions in the crystal lattice. This study is meant to find the relation of the binding energy (BE) values of W 4f$_{7/2}$ and O 1s core levels with mean chemical bond length $L$(W-O) in complex tungstates accounting recent XPS measurements for wolframite-type tungstates. In the present study, we intend to calculate the energy distribution peculiarities of the electronic states of different
symmetries of the atoms constituting cadmium tungstate. For this purpose, we use the possibilities of the full potential linearized augmented plane wave (FP-LAPW) method as incorporated in the WIEN97 code [20] in order to study total density of states (DOS), partial densities of states and electronic bands along selected symmetry paths within the first Brillouin zone of CdWO₄ tungstate.

2. Experimental data/results

3.1. Single crystals growth and their characterization

High-quality inclusion-free CdWO₄ crystals were grown by the Low Thermal Gradient Czochralski Technique (LTG Cz) in NIIC SB RAS [7,8]. Originally, the LNG Cz set up was elaborated for the growth of large Bi₄Ge₃O₁₂ and ZnWO₄ crystals, and the optical quality crystals of a mass up to ~50 and 8 kg, respectively, were grown [19,21,22]. In this method, the thermal gradient at the crystallization front is confined to be not above 1°C/cm. At the Bi₄Ge₃O₁₂ crystal growth, the charge use factor, reached as high as ~95 %, and the grown crystals were of excellent structural and optical quality. The low thermal gradient provides high homogeneity of the physical parameters over the crystal bulk. Now, the LTG Cz technique is developed for the growth of high-quality crystals of congruently-melting ZnMoO₄ and several compounds from the wolframite family [14,19,23-25].

In the CdWO₄ growth experiment, the laboratory puller HX-620 with precise weight monitoring and computer process control was used. The resolution of the weighing sensor was ±20 mg for the load of 10 kg. A three-zone furnace with resistive heating elements was used as the thermal unit. The temperature fluctuations during the growth process were not exceeding ±0.1°C. Growing was performed in the air from a platinum crucible of 100 mm in diameter and 250 mm high. To reduce the WO₃ loss due to evaporation, the crucible was covered with a cap equipped with a pipe through which the pulling rod with a seed was introduced into the crystallization zone. The crystal remains inside the crucible during the entire growth process. The starting materials for charge preparation were pure oxides WO₃ (99.999%) made in the NIIC SB RAS [26] and CdO manufactured by Toho...
Zinc Co., Ltd (Japan). The solid-phase synthesis was carried out directly into the crystal growth system at temperature $T = 1000^\circ$C during $t = 12$ h. The crystals were grown along the [010] direction. The crystallization rate varied from 0.5 to 1.0 mm/h and the rotation rate was 15 rpm. After the growth, the crystal was cooled to room temperature at the rate of 150$^\circ$C/h. As a result, the CdWO$_4$ crystal of 90 mm in diameter and the mass of 8 kg was grown. Currently, CML Ltd developed the puller and the LTG CZ technique of the CdWO$_4$ growth. As a result, the test growth of CdWO$_4$ crystals up to 20 kg has been performed. We do not see essential difficulties in a further increase of the crystal size. The large CdWO$_4$ crystal grown by the LTG Cz technique is shown in Fig. 2. The increase of the CdWO$_4$ crystals size does not decrease their quality. Stabilization of a slightly convex crystallization front along the whole length of the cylindrical part of a large crystal is easier than that for small crystals. For this reason, the area of the layer-by-layer growth mechanism expands up to 80-90% of the total crystallization front area. The smooth transition between the zones of flat and rounded shapes on the slightly convex crystallization front greatly decreases the probability of defect formation at the zone boundaries. Besides, during large crystal growth, the pulling rate can be increased up to 2 mm/h.

The parallelepiped-shaped sample was cut with the edges directed along the basic crystallographic axes. The substrates of CdWO$_4$(010) with dimensions $13 \times 0.9 \times 13$ mm$^3$ optimal for the electronic structure evaluation were prepared by cleavage in the air. The structural quality of the cleaved surface was tested by RHEED by the technique described elsewhere [27-29]. The results of RHEED measurements are presented in Fig. 3. As one can see from the pattern, a system of Kikuchi lines is characteristic of the surface under study. These RHEED data indicate the highest crystallographic quality of the cleaved CdWO$_4$(010) surface.

3.2. **XPS and XES measurements**

Electronic properties of the CdWO$_4$(010) surface were characterized by X-ray photoelectron spectroscopy (XPS). The XPS valence-band and core-level spectra of CdWO$_4$ were measured using
the UHV-Analysis-System assembled by SPECS (Germany). The system is equipped with a PHOIBOS 150 hemispherical analyzer. When measuring the XPS spectra, a base pressure of a sublimation ion-pumped chamber of the System was below $8 \times 10^{-10}$ mbar. As a source of XPS spectra excitation, Mg Kα radiation ($E = 1253.6$ eV) was used. The XPS spectra were recorded at the constant pass energy of 30 eV. The energy scale of the spectrometer was calibrated setting the measured Au 4f$_{7/2}$ and Cu 2p$_{3/2}$ binding energies of pure reference metals to $84.00 \pm 0.05$ eV and $932.66 \pm 0.05$ eV, respectively, with respect to the Fermi energy, $E_F$. The energy drift due to charging effects was accounted taking the C 1s (284.6 eV) core-level spectrum of adventitious hydrocarbons as it was previously suggested for dielectric wolframite-type tungstates [30-32]. To remove surface contaminations, the Ar$^+$ ion bombardment of the crystal surface was implemented at the ion energy of 3.0 keV and current density of 17 µA/cm$^2$ during 5 min.

The X-ray emission O Kα ($K \rightarrow L_{II,III}$ transition) band, representing the energy distribution of the O 2p states, was measured for the CdWO$_4$(010) surface using an RSM-500 spectrometer which is equipped with a diffraction grating (600 grooves/mm, curvature radius - $R = 6026$ mm). A secondary electron multiplier VEU-6 with a CsI photocathode was used as a detector. The operating conditions of a spectrometer electron gun in the present experiments were as follows: accelerating voltage, $U_a = 5.4$ kV; anode current, $I_a = 3.2$ mA. No XES band shape changes were observed during spectral acquisition. The spectrometer energy resolution was about 0.2 eV in the energy region corresponding to the position of the XES O Kα band.

3. Computational details

The electronic structure of CdWO$_4$ is calculated using the first-principles FP-LAPW method as incorporated in the WIEN97 package [20]. In the calculations, lattice parameters ($a = 5.0289$, $b = 5.8596$, $c = 5.0715$ Å, $\beta = 91.519^\circ$) and positions of the atoms constituting CdWO$_4$ listed in Table 1 are used in accordance with the crystallography data reported for cadmium tungstate in Ref. [18]. In the calculations, the muffin-tin (MT) sphere radii of the atoms constituting CdWO$_4$ are assumed to
be 2.2 a.u. for Cd, 1.75 a.u. for W, and 1.60 a.u. for O (1 a.u. = 0.529177 Å). The parameter, where $R_{\text{MT}}$ denotes the smallest MT sphere radius and $k_{\text{max}}$ determines the value of the largest $k$ vector in the plane wave expansion, is equal to 7.0 (the charge density is Fourier expanded up to the value $G_{\text{max}} = 15$). In the potential decomposition, the valence wavefunctions inside the MT spheres are expanded up to $l_{\text{max}} = 6$. For the exchange-correlation potential calculations, the generalized gradient approximation (GGA) proposed by Perdew et al. [33] is used, while, for integration through the Brillouin zone (BZ), the tetrahedron method by Blöchl et al. [34] is adopted. The Brillouin zone sampling is made using 250 $k$-points within the irreducible part of the zone. In order to calculate the densities of states, an additional sampling is made using 1232 $k$-points within the irreducible BZ wedge. The basis function consists of the atomic orbitals of Cd, W, and O, as reported in Table 2. In the present FP-LAPW calculations, the total number of semi-core and valence electrons (in addition to core electrons) per CdWO$_4$ unit cell is equal to 144. The iteration process has been verified taking into account the changes of integral charge difference $q = \int |\rho_n - \rho_{n-1}| dr$, where $\rho_{n-1}(r)$ and $\rho_n(r)$ are input and output charge densities, respectively. The calculations were interrupted in the case of $q \leq 0.0001$.

4. Results and discussion

The survey XPS spectra recorded from the cleaved CdWO$_4$(010) surface are shown in Fig. 4. It is apparent that all the spectral features, except the C 1s level observed at the pristine surface, are attributed to the core-levels or Auger lines of the atoms constituting cadmium tungstate. It is worth mentioning that the presence of the C 1s line in the survey XPS spectrum of the pristine cleaved CdWO$_4$(010) surface appeared evidently due to the hydrocarbons adsorbed from the laboratory air. However, as one can see from the survey XPS spectrum (Fig. 4, curve 1), the intensity of the C 1s core-level line is rather low for the untreated cleaved CdWO$_4$(010) surface and the 3.0 keV Ar$^+$-ion bombardment over 5 min causes almost complete vanishing of the C 1s core-level line in the survey XPS spectrum, as shown in Fig. 4, curve 2. The total set of binding energies (BE) of the core levels
and Auger lines measured for the CdWO$_4$(010) surface, both pristine and Ar$^+$-ion bombarded, is listed in Table 3. The main XPS core-level spectra associated with cadmium and tungsten atoms of the CdWO$_4$(010) surface are presented in Figs. 5 and 6, respectively. The XPS O 1s core level is shown in Fig. 7. From Figs. 5a and 6a, it is apparent that the XPS Cd 3d and W 4f core-level spectra of the pristine cleaved CdWO$_4$(010) surface are simple spin-orbit doublets. The BE(Cd 3d$_{5/2}$) and BE(W 4f$_{7/2}$), as obtained by XPS, correspond to those of cadmium and tungsten in the formal valence states of 2+ and 6+, respectively [17,19,28,30,35,36].

The 3.0 keV Ar$^+$-ion bombardment does not change significantly the chemical composition of CdWO$_4$(010) surface. As can be seen from Fig. 6a, the above treatment of the CdWO$_4$(010) surface causes partial tungsten ion transformation from W$^{6+}$ to lower valence states (mainly W$^0$ [35]). From the survey XPS spectra presented in Fig. 4, one can see that a significant loss of oxygen from the CdWO$_4$(010) surface does not take place at such Ar$^+$-ion bombardment and this treatment causes only an insignificant loss of oxygen atoms which are in the nearest surrounding of tungsten atoms (WO$_6$ octahedrons). This partial removal of oxygen atoms belonging to WO$_6$ octahedra due to the Ar$^+$-ion bombardment induces only a little shift of tungsten core-level spectra towards lower binding energies, as indicated in Table 3. Further, no partial loss of oxygen atoms belonging to CdO$_6$ octahedra is detected after the 3.0 keV Ar$^+$-ion bombardment of the CdWO$_4$(010) surface because cadmium atoms remain exclusively in the formal valence state of 2+ (Fig. 5). The Ar$^+$-ion bombardment of the cleaved CdWO$_4$(010) surface does not cause changes of the BE(O 1s) value, as well as the positions of the maxima of Auger lines of oxygen and cadmium atoms remain unchanged (Table 3). Besides, the 3.0 keV Ar$^+$-ion bombardment does not induce detectable changes of the electronic states energy distribution over the valence-band region, as revealed in Fig. 8. The above XPS data indicate high stability of the cleaved CdWO$_4$(010) surface with respect to the Ar$^+$-ion irradiation.

Core level photoelectron spectroscopy is among direct methods applicable for the characterization of chemical bonding in complex oxides. On the oxide bond formation, the valence
electrons are shifted from metal to oxygen that results in great variation of electrical inner shell screening accompanied by the variation of inner electron BE values. This effect can be detected as a core level BE variation in XPS spectra. Evidently, it is interesting to consider W-O chemical bonding in CdWO₄ in comparison to that in other tungstates using the BE values measured for O 1s and W 4f½ lines. Mean chemical bond length L(W-O) calculated using the structural data is taken as a structure related parameter. The BE difference Δ(O-W) = BE(O 1s) – BE(W 4f½) is applied as a key parameter for chemical bonding characterization because BE difference is a more robust parameter insensitive to BE scale shifts due to the dielectric surface charging typical of oxides [19,27-29,37-40]. The collection of available tungstate structural and electronic parameters is shown in Table 1S. The diagram with these tungstates and CdWO₄ based on the present XPS measurement results and those reported in the literature, is shown in Fig. 1S. The tungstates show the Δ(O-W) values dominantly in the range of 494.9-495.5 eV with two unclear exceptions of NiWO₄ and SrWO₄. It should be noted that the monoclinic, m-WO₃, and hexagonal, h-WO₃, tungsten oxide modifications possess a very similar value of Δ(O-W) = 494.8 eV, as it was earlier found [71,72]. Generally, there is no strong dependence of (W-O) bond ionicity on the coordination of W⁶⁺ ions by oxygens. As it is evident from Fig. 1S, the point related to CdWO₄ is settled into the tight tungstates cluster with octahedral W⁶⁺ ions coordination.

The FP-LAPW band-structure calculations results of the total DOS for the CdWO₄ compound within a 115-eV range are presented in Fig. 2S. Energy zero was taken at the top of the last occupied band, as it is suggested for tungstate materials AWO₄ (A = Ca, Cd, Pb, Fe, Co) in ab initio band-structure calculations [17,31,32,36]. As evident from Fig. 2S, the upper core Cd 4s, W 5s, Cd 4p, W 5p and W 4f states generate rather narrow bands in CdWO₄, while the O 2s-like states, which are among the upper core states in the tungstate under consideration, generate a comparatively broad band with the width of about 2.0 eV ranging from –16.1 to –18.1 eV (Fig. 9). From comparison of Figs. 9 and 10, one can state that contributions into the O 2s band depend on the oxygen atoms positions in the CdWO₄ unit cell: the O2-type atoms are the dominant contributors to
the bottom and the top of the O 2s band, whereas contributions of the O1-type atoms - to the central part of this band - are somewhat bigger, as compared to contributions of the O2-type atoms. In accordance to our FP-LAPW data presented in Fig. 9, the valence band of CdWO₄ ranges from 0 to −6.7 eV and it consists of two sub-bands, namely A and B, which are separated by the narrow gap 0.2-eV wide. The main contributors to the valence band of the tungstate under consideration are the Cd 4d, W 5d and O 2p states (Figs. 9 and 10). The bottom of the valence band (sub-band B, Fig. 9) is dominated by the Cd 4d states contributions, while the O 2p states contributions dominate over the upper portion of the band (sub-band A). The main contributions of the W 5d occur in the central portion of the valence band with also significant contributions of these states throughout the whole region of the band.

From Fig. 9, it is apparent that two sub-bands (sub-band A* ranging from about 3.1 to about 5.1 eV and a broader upper sub-band B* above 5.1 eV) can be distinguished at the bottom of the conduction band of the CdWO₄ tungstate. In accordance with the present FP-LAPW results, the bottom of the conduction band (the sub-band A*) is composed mainly of the W 5d* states with smaller contributions of the O 2p* states. From the comparison of Figs. 10b and 10c, one can state that hybridization of the W 5d* and O 2p* states is characteristic within the energy region corresponding to the position of the sub-band A* of the conduction band of CdWO₄. It worth mentioning that similar hybridization of the W 5d* and O 2p* states at the bottom of the conduction band was observed previously when calculating electronic properties of other wolframite-type tungstates, namely ZnWO₄ [32] and CuWO₄ [36]. Furthermore, Fig. 10a reveals that contributions of the unoccupied electronic states associated with cadmium atoms are insignificant in the sub-band A* of the CdWO₄ conduction band. As one can see from Figs. 9 and 10, the main contributors for the upper sub-band B* of the conduction band are the W 5d* states combined with slightly smaller O 2p* states contributions.

The above FP-LAPW results, regarding the occupation of the valence band by the O 2p states in CdWO₄, are in agreement with the experimental XPS and XES results for this compound. The X-
ray emission O Kα band fitted on a common energy scale with the XPS valence-band spectrum carried out in the present work for CdWO₄(010) is presented in Fig. 11. The method of fitting the XES and XPS spectra of CdWO₄(010) on a common energy scale is analogous to that used previously when studying the electronic structure of other wolframite-type tungstates [32,36]. As can be seen from Figs. 10 and 11, in accordance with the present theoretical FP-LAPW data, the main contributions of the O 2p states should occur at the top of the CdWO₄ valence band. In Fig. 11, one can see that the fine-structure peculiarity A of the CdWO₄(010) XPS valence-band spectrum coincides with the maximum α of the XES O Kα band in this tungstate. Therefore, the contribution of the O 2p states dominate at the top of the CdWO₄ valence band. In addition, the fine-structure peculiarity b of the CdWO₄(010) XES O Kα band coincides with the sub-band B of the tungstate XPS valence-band spectrum.

The CdWO₄ band dispersions calculated for several symmetry directions of the monoclinic BZ are presented in Fig. 3S. We use the diagram of the monoclinic BZ, which is analogous to that reported previously in a monograph by Bradley and Cracknell [73]. As can be seen from Fig. 3S, the dispersions of the curves near the valence-band maxima and conduction-band minima are rather flat in CdWO₄. The conduction band minimum is located at point Z (k = (0.0; 0.0; 0.5)) and the valence-band maximum is found at k = (0.2903; 0.0; 0.2097). Our theoretical data allow us to conclude that CdWO₄ tungstate is an indirect-gap material with the band gap of \( E_g \approx 3.1 \) eV.

5. Conclusions

High-quality inclusion-free CdWO₄ crystals, up to 115 mm in diameter and mass up to 20 kg, have been successfully grown in the present work employing the LTG Cz technique. The high-purity CdWO₄(010) surface verified by the RHEED method has been studied by the XPS and XES methods to explore its electronic structure. It has been established that the 3.0 keV Ar⁺-ion bombardment over 5 min at the ion current density of 14 µA/cm² (total Ar⁺ flux is \( \sim 5.3 \times 10^{16} \) ions/cm²) does not change significantly the chemical composition of the CdWO₄(010) surface.
However, such treatment of the CdWO$_4$(010) surface causes partial tungsten ion transformation from W$^{6+}$ to lower valence states (mainly W$^0$). The 3.0 keV Ar$^+$-ion bombardment does not lead to a significant oxygen loss from the CdWO$_4$(010) surface and it causes only an insignificant loss of oxygen atoms which are in the nearest surrounding of tungsten atoms (WO$_6$ octahedra). Further, no partial loss of oxygen atoms belonging to CdO$_6$ octahedra is detected due to 3.0 keV Ar$^+$-ion bombardment of the CdWO$_4$(010) surface. The total and partial densities of states of the CdWO$_4$ tungstate have been calculated in the present work employing the ab initio FP-LAPW method. Our theoretical data indicate that the principal contributors to the CdWO$_4$ valence band are the Cd 4d, W 5d and O 2p states: their contributions occur mainly at the bottom, in the central portion and at the top of the valence band, respectively, with also significant contributions of the mentioned states throughout the whole CdWO$_4$ valence-band region. Further, the FP-LAPW data reveal that the bottom of the CdWO$_4$ conduction band is composed mainly of the unoccupied W 5d states with slightly smaller contributions of the unoccupied O 2p states. Regarding the occupation of the O 2p states, the present FP-LAPW calculation results are confirmed by comparison on a common energy scale of the XPS valence-band spectrum and the XES band representing the energy distribution of the O 2p states in CdWO$_4$. Furthermore, the present FP-LAPW calculations allow us to conclude that CdWO$_4$ tungstate is a non-direct semiconductor.

**Acknowledgements**

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1872-1873.


73. C.J. Bradley, A.P. Cracknell, The Mathematical Theory of Symmetry in Solids, Clarendon Press, Oxford, 1972 (Fig. 3.9, p. 104).
Table 1. Positions of the atoms constituting CdWO$_4$ tungstate used in the present FP-LAPW calculations

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom position</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Cd</td>
<td>0.5</td>
</tr>
<tr>
<td>W</td>
<td>0</td>
</tr>
<tr>
<td>O1</td>
<td>0.242</td>
</tr>
<tr>
<td>O2</td>
<td>0.202</td>
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</table>

Table 2. Atomic orbitals used in the present FP-LAPW calculations of the CdWO$_4$ electronic structure

<table>
<thead>
<tr>
<th>Atom</th>
<th>Core electrons</th>
<th>Semi-core electrons</th>
<th>Valence electrons</th>
<th>Number of electrons involved in the FP-LAPW calculations</th>
</tr>
</thead>
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<tr>
<td>Cd</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 3d$^{10}$</td>
<td>4s$^2$ 4p$^6$</td>
<td>4d$^{10}$ 5s$^2$</td>
<td>20</td>
</tr>
<tr>
<td>W</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 3d$^{10}$ 4s$^2$ 4p$^6$</td>
<td>4f$^{14}$ 5s$^2$ 5p$^6$</td>
<td>5d$^4$ 6s$^2$</td>
<td>28</td>
</tr>
<tr>
<td>O</td>
<td>1s$^2$</td>
<td>2s$^2$</td>
<td>2p$^4$</td>
<td>6</td>
</tr>
</tbody>
</table>
Table 3. Binding energies (±0.05 eV) of the constituent element core levels and Auger lines in the cleaved CdWO₄(010) surface

<table>
<thead>
<tr>
<th>Core level, Auger line</th>
<th>Binding energy (eV) for the pristine Ar⁺-ion bombarded) surface</th>
</tr>
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<tbody>
<tr>
<td>Cd 4d</td>
<td>10.47 (10.57)</td>
</tr>
<tr>
<td>W 4f_1/2</td>
<td>34.83 (34.64)</td>
</tr>
<tr>
<td>W 4f_3/2</td>
<td>36.90 (36.73)</td>
</tr>
<tr>
<td>W 4d_5/2</td>
<td>246.82 (246.64)</td>
</tr>
<tr>
<td>W 4d_3/2</td>
<td>259.40 (259.19)</td>
</tr>
<tr>
<td>C 1s</td>
<td>Fixed at 284.6 eV</td>
</tr>
<tr>
<td>Cd 3d_5/2</td>
<td>404.25 (404.33)</td>
</tr>
<tr>
<td>Cd 3d_3/2</td>
<td>411.01 (411.08)</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.68 (529.76)</td>
</tr>
<tr>
<td>O KL_1L_1</td>
<td>741.3 (741.3)*</td>
</tr>
<tr>
<td>O KL_1L23</td>
<td>761.5 (761.4)*</td>
</tr>
<tr>
<td>Cd M₄N₄₅</td>
<td>871.6 (871.7)*</td>
</tr>
</tbody>
</table>

*Uncertainty of the measurements is ±0.1 eV
Captions

Fig. 1. Crystal structure of CdWO₄. Unit cell is outlined.

Fig. 2. A photo of large CdWO₄ crystals grown by the LTG Cz technique.

Fig. 3. A Kikuchi lines pattern recorded by RHEED for the cleaved CdWO₄(010) surface.

Fig. 4. Survey XPS spectra of the (1) pristine and (2) Ar⁺-ion bombarded CdWO₄(010) cleaved surface.

Fig. 5. Detailed XPS (a) Cd 3d and (b) Cd 3p core-level spectra of the (1) pristine and (2) Ar⁺-ion bombarded CdWO₄(010) cleaved surface.

Fig. 6. Detailed XPS (a) W 4f and (b) W 4d core-level spectra of the (1) pristine and (2) Ar⁺-ion bombarded CdWO₄(010) cleaved surface.

Fig. 7. Detailed XPS O 1s core-level spectra of the (1) pristine and (2) Ar⁺-ion bombarded CdWO₄(010) cleaved surface.

Fig. 8. Detailed XPS valence-band spectra of the (1) pristine and (2) Ar⁺-ion bombarded CdWO₄(010) cleaved surface.

Fig. 9. The total DOS and total densities of states of the atoms constituting CdWO₄.

Fig. 10. Partial densities of states of the atoms constituting CdWO₄: (a) cadmium, (b) tungsten, and (c) oxygen.

Fig. 11. Comparison on a common energy scale of (1) the XPS valence-band spectrum and (2) the X-ray emission O Kα band of the CdWO₄(010) cleaved surface.
Highlights

Large high-quality CdWO₄ crystals, up to 115 mm in diameter and mass up to 20 kg, have been grown.

The high-purity cleaved CdWO₄(010) surface has been studied by the XPS and XES methods.

The principal contributors to the CdWO₄ valence band are the Cd 4d, W 5d and O 2p states.