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Low thermal gradient Czochralski growth of large MWO_4 (M = Zn, Cd) crystals, and microstructural and electronic properties of the (010) cleaved surfaces

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The large optical-quality MWO_4 (M = Zn, Cd) crystals of mass up to 14 ($ZnWO_4$) and 20 ($CdWO_4$) kg were grown by Low Thermal Gradient Czochralski Technique (LTG Cz). Crystallographic properties of MWO_4(010) cleaved surface were evaluated by AFM and RHEED, and electronic structure of the surface was studied using XPS. A system of Kikuchi lines has been observed for cleaved MWO_4(010) by RHEED confirming high crystallographic quality of the surface. The XPS valence-band and core-level spectra of MWO_4(010) have been measured. The XPS measurements reveal that W and M atoms are in the formal valences 6+ and 2+, respectively, on cleaved MWO_4(010) surface.

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1. Introduction

Tungstate crystals are widely used in nanotechnologies, photocatalysis, electronics, laser techniques and as efficient scintillator materials [1-11]. Bivalent metal tungstates with common composition $A^{2+}WO_4$ crystallize in wolframite-type structure with space group $P2/c$ at ionic radii r_{A2+} < 77 pm [12,13]. Such tungstates are chemically stable and they are spread in nature as minerals. A chain-type structure is formed by parallel zigzag chains of distorted AO_6 and WO_6 octahedrons spreading along the c axis. The crystals belonging to the wolframite family are characterized by good cleavage properties of the (010) planes [14,15].The tungstates can be synthesized by different chemical routes and they can be grown as high quality single crystals. Thus, the present study is aimed at the observation of Low Thermal Gradient Czochralski technique (LTG Cz) in application to wolframite-type crystal growth and evaluation of morphological and structural properties of the (010) cleaved surface. One of the essential features of the LTG Cz technique is the low thermoelastic stresses in the crystals. Respectively, the crystals are less susceptible to post-growth cracking and the dislocation density is much lower in the crystals grown by the LTG Cz technique. As it was found in initial experiments, the large area atom-smooth cleaved surface can be formed only using high-quality $A^{2+}WO_4$ crystals.

2. LTG Cz growth

The high-quality inclusion-free $ZnWO_4$ and $CdWO_4$ crystals were grown by LTG Cz using the special purity WO_3 (NIIC SB RAS, Russia) with Si content <50 ppm (parts per million) and transition metals content <1 ppm [16]. High purity ZnO (99.995%, Umicore, Belgium) and CdO (99.995 %, Toho Zinc, Japan) were used without further purification. In the LTG Cz technique, the evaporation and decomposition of the melt is much lower than that in the traditional version of the Cz crystal growth [17,18]. Therefore, the initial charges were prepared in the stoichiometric compositions. The synthesis of $ZnWO_4$ or

$CdWO_4$ compounds was being carried out in the growth platinum crucibles at 1000 °C for 6 h. Then, the melts were kept at temperatures by 10-15 °C higher than the melting points, which are 1200 and 1325 °C in the case of $ZnWO_4$ and $CdWO_4$, respectively, to homogenize the melts. The growth of $CdWO_4$ crystal was performed in platinum crucible with diameter 140 mm. The $CdWO_4$ crystal of weight 20 kg is shown in Fig. 1. The total length of the crystal is about 325 mm, and the average diameter of cylindrical part of the crystal is about 105 mm. Consequently, the ratio of crystal diameter to the crucible diameter is 105:140. This diameter relation significantly decreases the open part of the melt surface and, therefore, reduces volatile components evaporation from the melt. The features of growth of $ZnWO_4$ crystal are similar to $CdWO_4$ along [010] direction. The $ZnWO_4$ crystal of 8 kg weight is shown in Fig. 2. At present time, the $ZnWO_4$ crystal of 14 kg weight has been grown at the enterprise CML Ltd, Novosibirsk. The cooling process after the growth for both crystals was similar, and it was carried out at the rate of 80 °C/h. The (010) substrates with dimensions 12×0.7×12 mm^3 for the surface evaluation were fabricated by accurate cleaving of a single crystal parallelepiped. The cleavage was mechanically produced with a steel knife.

Fig. 1. $CdWO_4$ crystal grown by LTG Cz technique (CML ltd, Novosibirsk)

Fig. 2. $ZnWO_4$ crystal grown by LTG Cz technique (NIIC SIB RAS, Novosibirsk)

3. Cleaved surface characterization

The surface micromorphology was studied by atomic force microscope (AFM) Solver P-47H in the semicontact mode. The top-surface crystallographic properties were evaluated with reflection high-energy electron diffraction (RHEED) using EFZ4 device at the electron energy of 50 keV. The extended discription of AFM and RHEED measurements can be found elsewhere [19-22]. The topographical 10×10 μm^2 AFM image of cleaved $CdWO_4$(010) surface is shown in Fig. 3. Commonly, the cleaved $CdWO_4$(010) surface is formed by a system of wide plane terraces with as low roughness as ~0.2 nm and the typical area of 3-10 mm^2. The set of terrace edges is evident in Fig. 3. The elementary level step between the terraces is very close to cell parameter *b*. Thus, the cleaved $CdWO_4$(010) surface can be considered as the atomically smooth one. The micromorphology of cleaved $ZnWO_4$(010) surface is similar to that of $CdWO_4$(010), and the terrace area and root mean square (rms) parameters are nearly the same for these crystals. The cleaved surface parameter similarity found for the LTG Cz grown MWO_4 (M = Zn, Cd) crystals verifies high reproducibility of the growth technology. The system of Kikuchi lines, as shown in Fig. 4, was observed for the $CdWO_4$(010) substrate by RHEED observation, and that confirms the high crystallographic quality of the cleaved surface. The RHEED pattern recorded from the $ZnWO_4$(010) surface was similar to that of the $CdWO_4$(010) surface.

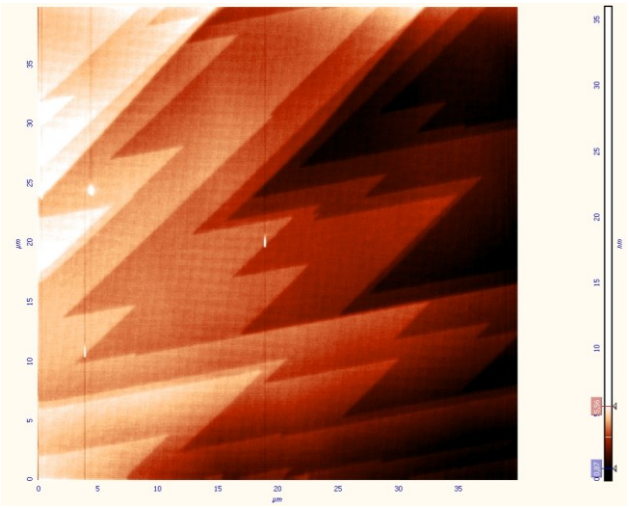

Fig. 3. The flat terrace esheletons at cleaved $CdWO_4$(010) surface

The energy distribution of electronic states of the constituent atoms of the MWO_4 (M = Zn, Cd) crystals was comprehensively evaluated by theoretical and experimental methods. With this purpose, we have employed possibilities of the full potential linearized augmented plane wave (FP-LAPW) method as incorporated in the

WIEN97 code [23] in order to study total density of states (DOS) and partial densities of states of the compounds. Additionally, the core levels and energy distribution of the valence states were recorded for MWO_4 (M = Zn, Cd) by the X-ray photoelectron spectroscopy (XPS) following the technique reported in detail elsewhere [24-30]. As an example, the results obtained for $ZnWO_4$ are shown in Figs. 5 and 6. It is worth mentioning that, in the present band-structure calculations of $ZnWO_4$, the unit-cell parameters (a = 4.69263 Å, b = 5.72129 Å, c = 4.92805 Å, and β = 90.6321°) and atomic positions were used strictly as they were reported for this tungstate in Ref. [31].

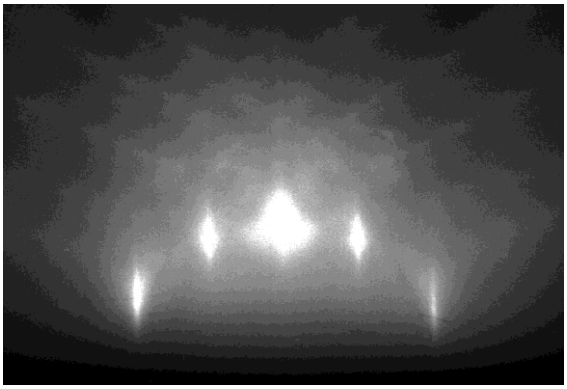

Fig. 4. Kikuchi lines observed by RHEED from the cleaved $CdWO_4$(010) surface

The results of the FP-LAPW calculations of $ZnWO_4$ reveal that main contributors in the valence band of the tungstate are the O 2p-, W 5d- and Zn 3d-like states. In particular, the W 5d- and Zn 3d-like states contribute mainly at the bottom, whilst the O 2p-like states at the top of the valence band of $ZnWO_4$, with also significant portions of contributions of the above states throughout the whole valence-band region. The results are in good relation to the XPS measurements. As can be seen from Fig. 6, the XPS valence-band spectrum of $ZnWO_4$(010) consists of two fine-structure peculiarities, namely A and B (the small feature A′ near the Fermi level is originated from the XPS Zn 3d spectrum excited by the Mg Kα satellites). From comparison of Figs. 5 and 6, one can state that the fine-structure peculiarity B of the XPS valence-band spectrum of $ZnWO_4$(010) is due to contributions of mainly the Zn 3d-like states, while the peculiarity A is formed mainly by the O 2p-like states (its top) and the W 5d-like states (its lower portion). Furthermore, the data of the FP-LAPW calculations indicate that the conduction band of $ZnWO_4$ is dominated by contributions of the W 5d-like states.

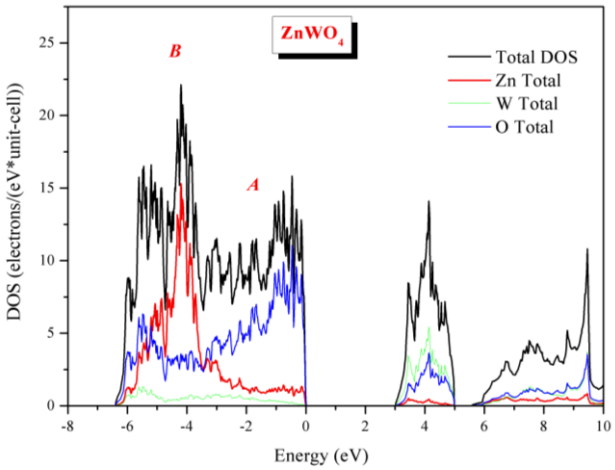

Fig. 5. Total DOS and partial densities of states of the atoms constituting $ZnWO_4$ (within valence and conduction bands)

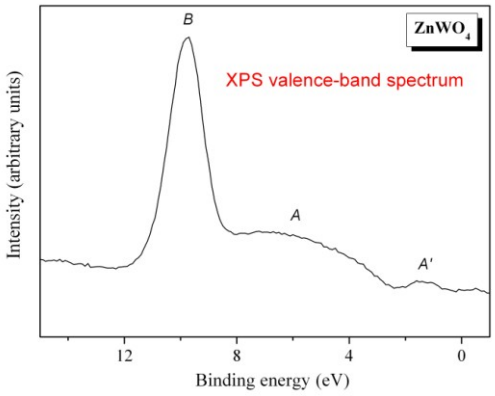

Fig. 6. Valence band of $ZnWO_4$, as measured by XPS

The main contributions of the O 2p- and W 5d-like states at the top and at the bottom of the valence band of $ZnWO_4$, respectively, as the above FP-LAPW calculations indicate, seem to be a general feature of the electronic structure of the $A^{2+}WO_4$ tungstates crystallizing either in the wolframite- or scheelite-type structures. It is worth to mention that previously the main contributions of the O 2p- and W 5d-like states at the top and at the bottom of the valence band were confirmed either theoretically or experimentally for a series of the $A^{2+}WO_4$ tungstates, where A^{2+} = Fe, Co, Cu, Pb, Sr (see, e.g., [32,33] and references therein). However, the predominant contributions of the electronic states associated with the A^{2+} ions into the valence band of the $A^{2+}WO_4$ tungstates look to be significantly dependent on the A position in the Periodic Table.

4. Conclusions

The large optical-quality MWO_4 (M = Zn, Cd) crystals of mass up to 14 ($ZnWO_4$) and 20 ($CdWO_4$) kg were grown by Low Thermal Gradient Czochralski Technique (LTG Cz). Crystallographic properties of MWO_4(010) cleaved surface were evaluated by AFM and RHEED, and electronic structure of the surface was studied using XPS. A system of Kikuchi lines has been observed for cleaved MWO_4(010) by RHEED confirming high crystallographic state of the surface. The XPS valence-band spectra were measured for the low-defect cleaved surface. The total and partial densities of states of the MWO_4 tungstates were calculated employing the *ab initio* FP-LAPW method and the calculated results are in good relation to XPS measurements. Thus, this algorithm of electronic structure observation can be used for other wolframite family crystals and other crystals having cleavage planes. The LTG Cz method can be used for the high-quality crystal growth and this is a key step for the creation of atomically smooth cleaved surface. It can be concluded that large-size wolframite crystals possess specifically high bulk quality needed for high structural quality of the cleaved surfaces.

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